

MOLTEN SALTS

PROCEEDINGS OF THE FOURTH INTERNATIONAL SYMPOSIUM ON

MOLTEN SALTS

Edited by

Milton Blander Chemical Technology Division Argonne National Laboratory Argonne, Illinois

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PHYSICAL ELECTROCHEMISTRY DIVISION

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PREFACE

The Fourth International Symposium on Molten Salts was held in San Francisco, May 8-13, 1983 as part of the 163rd Meeting of the Electrochemical Society under the sponsorship of the Physical Electrochemistry Division. This volume contains about 85% of the papers presented at that symposium. Four of the papers presented were consolidated and two appear under somewhat different titles. Although a broad spectrum of topics is covered, emphasis was placed on research on chloroaluminate melts and batteries. The number of papers presented exceeded that of the three earlier symposia; meeting attendance and the discussions were excellent for a large fraction of the sessions. These symposia thus appear to serve an important function in providing a forum for the exchange of ideas on molten salts. The papers in this volume appear in their order of presentation.

The considerable assistance of Mary C. Burke and Kathleen L. Shields was essential in assembling and editing this volume. I would like to thank the editors who helped not only on this volume but also in the organization of the symposium. Most of all, thanks are due to the participants for their contributions to a successful symposium.

> Milton Blander December 1983

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MOLECULAR DYNAMICS CALCULATIONS OF MAX₄ MELTS

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ABSTRACT

Molecular dynamics calculations for MAX₄ melts are reported for two different sets of cation/anion radius ratios which were chosen so as to emulate melts such as chloroaluminates and fluoroyttriates. The results are expressed as radial distribution functions, the angular distributions of selected triplets and the number of ions which have particular integer values of the coordination numbers. For the small radius ratio, the A⁺³ ion is tetrahedrally coordinated and the structure of this completely ionic melt is consistent with the presence of X⁻, AX₄⁻, A₂X₇⁻ and A₃X₁₀⁻ species which equilibrate by the reactions $2AX_4^- \rightleftharpoons A_2X_7^- + X^-$ and $3AX_4^- \rightleftharpoons A_3X_{10}^- + 2X^-$. For the large radius ratio, the A⁺³ cations are mostly octahedrally coordinated and there is considerable bridging between AX_n^{3-n} moieties which leads to a tendency for long range order.

INTRODUCTION

The concept of complexing in binary molten salt mixtures has been used for structural interpretations of thermodynamic, spectroscopic and kinetic data in a class of strongly interacting melts such as the chloroaluminates.¹⁻⁷ The system NaCl-AlCl₃ is perhaps the most thoroughly studied complexing melt. Consequently, in this paper, we will focus largely on melts in which the interionic separations are similar to those expected in NaAlCl₄ melts. The main purpose is to explore the characteristic structures in this melt for comparison with those deduced from experiment. In addition, we will also examine the structures in a melt with a larger cation/anion radius ratio and a larger average coordination number of the A⁺³ ions.

MOLECULAR DYNAMICS COMPUTATIONS

Calculations were performed on an assemblage of 83 M⁺, 83 A⁺³ and 332 X⁻ ions which interacted according to the potential⁸

$$u_{ij} = Z_i Z_j e^2 / r + Bexp[A(\sigma_i + \sigma_j - r)]$$
(1)

where e is the electronic charge, Z_k is the integral number of charges on the k'th ion and has the same sign as the charge, r is the distance between ions, the constants A=3.155Å⁻¹, B=0.190(10⁻¹²)erg and σ_k is the 'radius' of the k'th ion. Two sets of radii were chosen with different values of σ_A/σ_X while keeping both $\sigma_A + \sigma_X$ and $\sigma_M + \sigma_X$ constant and at values which lead to interionic distances which correspond to those of Al⁺³-Cl⁻ and Na⁺-Cl⁻ respectively.⁹ The two sets of values of ($\sigma_M, \sigma_A, \sigma_X$) chosen (in Å) are potential 1 (1.352, 1.372, 1.578) and potential 2 (1.052, 1.072, 1.878).

The molecular dynamics calculations generated an ensemble of consecutive configurations of the 498 particles at about T=500K. Details of the calculation which are for constant but very low pressure are discussed elsewhere.^{10,11} The time steps were 10^{-15} seconds and typically about 12,000 time steps were run after the temperature was stabilized. The radial distribution functions were averaged over all of these time steps whereas all the other calculated quantities were averaged over 1200 steps.

RESULTS AND DISCUSSION

In what follows we will define $M^+=1$, $A^{+3}=2$ and $X^-=3$ and the charges on these three ions will be understood when not explicitly stated.

A. Radial Distribution Functions (rdfs) and Coordination Numbers

The six calculated rdfs, $g_{ij}(\mathbf{r})$, for MAX₄ are plotted in Fig. 1 for the two potentials. In addition, we have also plotted $N_{ij}(\mathbf{r})$, the number of ions of kind j about an ion of kind i within a radius r. The value of $N_{ij}(\mathbf{r})$ taken at the first minimum in $g_{ij}(\mathbf{r})$ at \mathbf{r}_o is defined as the average coordination number, Z_{ij} . In addition, we define a number $n_{ij}^{(z)}$ which is the number of i ions which have exactly z j ions in their first coordination shell.

It is difficult to draw detailed conclusions based solely on rdfs, which is of course a pair distribution function. It is sometimes possible to infer such detail from a multiplicity of pair correlations (such as e.g. $g_{23}(r)$ and $g_{33}(r)$ to infer the tetrahedrality of AX_4^- moieties). However, as we will show, in order to extract much of the structural information requires a knowledge of higher order (i.e. triplet) correlations. With this limitation in mind we can examine the rdfs.

The values of g_{23} have steep narrow first peaks with maxima near 2Å of about 10 and 18 and drop to very small values between 3.0 and 3.8Å. This characteristic can be expressed in terms of a potential of mean force, $V_{ij}(\mathbf{r})$ which is defined as -kTln $g_{ij}(\mathbf{r})$. A plot of $V_{ij}(\mathbf{r})$ exhibits a potential well of about 6kT. From this, one

would expect that an X anion in the first coordination sphere of an A cation will seldom 'escape' from that sphere without first entering the coordination sphere of another nearby A cation. The coordination number, Z_{23} for potential 1 is 5.8 and for potential 2 it is 4.0 suggesting tetrahedral coordination for the latter case and octahedral coordination for the former case.

With potential 1, the coordination number of 5.8 means that a significant fraction of the X ions must form A-X-A bridges. If the bridges are single and there are no free X anions, then the number of X ions in the first shell around an A which are part of a bridge is $2(Z_{23}-4)$ which is also the coordination number of A about A, Z_{22} . This is consistent with our results. For potential 2 there is very little bridging which is reflected in small first peaks in $g_{22}(r)$ and small values of Z_{22} . Z_{22} is non-zero because of a dissociation reaction we discuss later. The A-A correlations $g_{22}(r)$ are therefore quite different for the two potentials. For potential 1 the first peak is sharp and located at about 4.5Å with 3.6 coordination. For potential 2 the first peak at 4.7Å is very small and there is a larger broad peak at about 6.2Å.

Since the first maximum in $g_{22}(r)$ for potential 1 is at about twice the distance to the first maximum in $g_{23}(r)$ it follows that of the average of 5.8 X neighbors of A, 3.6 form a relatively straight A-X-A bridge from one A to another A under the first peak in $g_{22}(r)$. The near linearity of the bridge suggests that the strongly repelling A cations remain far enough apart so that the A-A repulsions are at least partly shielded by intervening X anions.

One expects that the strong A-X attractions will dominate the tendency for close packing of X ions about A. The decrease in coordination number from 5.8 to 4.0 with an increase in the X-X repulsive core potential demonstrates the fact that the triple charges on A cations lead to the maximum possible packing of X anions in the first coordination shell within the limits set by the combination of anionic coulombic and core repulsions.

The first peaks in $g_{33}(r)$ when compared with the peaks in $g_{23}(r)$ indicate very different local structures for the two potentials. The ratios of the distances are consistent with an approximately octahedral coordination for potential 1 and tetrahedral for potential 2. This point will be amplified below.

B. Structural Implications

Coulombic forces together with steric effects determine the structure of ionic systems in general. In the present study one can show that i) repulsions betweeen A cations should be more significant than between other like charge coulomb repulsions; ii) the A-X attraction will dominate over M-X attractions; and iii) the generated structures of X ions around A anions are sensitive to the core repulsions between X ions.

As discussed above, the analyses of g_{23} and g_{22} suggest an almost linear configuration for A-X-A bridges. To test this possibility, we calculated the distributions of angles of A-X-A triplets which are exhibited in Fig. 2 for the case in which the A-X distance is less than 3.0Å. The results do show a predominance of angles close to 180° but indicate a significant fraction of triplets at much smaller angles (e.g. 30% at less than 150°). In any case, the small angular spread leads to the possibility that the structural correlations among the A cations could be of quite long range.

The tendency toward tight packing of the X anions about A cations appears to be energetically limited by two factors, i) the core repulsions between X ions which makes a positive energetic contribution and ii) the formation of A-X-A bridges and the consequent A-A positive repulsive energy when Z_{23} is greater than 4. When the anion-cation radius ratio increases, the core repulsions between X ions is enhanced and Z_{23} should tend to decrease. The number of bridges decreases as Z_{23} decreases and the repulsions between A cations becomes energetically smaller. As expected, Z_{23} is smaller for potential 2 than for potential 1. In order to determine the structure and symmetry of the X anions about the A cations we computed the angular distribution of X-A-X triplets which are plotted in Fig. 3. For potential 1 the distribution has maxima at angles close to 90° and 180° ($\cos\theta = 0$ and -1 respectively) which is consistent with octahedral symmetry. For potential 2 the maximum in the distribution lies close to the tetrahedral angle of 109°28' ($\cos\theta$ = -1/3) as is expected for four coordination. In both cases, the spread in the distribution of angles is consistent with that expected for thermal motions.¹².

The distribution $n_{23}^{(z)}$ of A cations as a function of the coordination number z has also been calculated and is given in Table I. The results show that there is a broader distribution of coordination numbers for potential 1 than for potential 2 for which essentially all of the A ions are four coordinated. In many real molten salt systems, there is likely to be a distribution of coordination numbers, which in some cases might even be broader than that of potential 1. In such cases, it would be very difficult to interpret structure related measurements in a precise manner. A precise description requires one to specify not only the moieties which are present but also the relative amounts of all moieties.

The observation that most of the A-X-A angles are close to 180° and that the X-A-X angles are concentrated near 90° and 180° leads to the possibility that the long range A-A-A triplets should exhibit some regularity. A suggestion of this regularity can be found in the plots of g_{22} for potential 1 where the second and third maxima are located at 1.4 and 2 times the first peak distance. This suggests that there is a preference for 90° and 180° angles in these triplets. To examine this point, the angular distribution of A-A-A triplets located within a sphere centered on A and having a 5.2Å radius was calculated. The results are plotted in Fig. 4. The peaks at about 90° and 180° ($\cos\theta = 0$ or -1) indicate a tendency for octahedral ordering up to at least the fourth nearest neighbors which are 9-10Å apart. However, there are other significant peaks in this angular distribution at 60°, 80°, and 102-110° which reflects complexities in the long range ordering and structures of these melts.

C. Complexing and Structure

A predominance of coordination numbers $z_{23} = 4$ or 6 is present for the two pair potentials. This result coupled with other studies underway suggest that there is a probable energetic preference for these values relative to 3 or 5. However, this preference is not absolute and other coordination numbers (such as e.g. 3 and 5) can be present for other pair potentials (e.g. for potentials intermediate betweeen potentials 1 and 2). The tendency for a preferential coordination number, often ascribed to covalent or non-ionic bonding, can thus be shown to be a characteristic of purely ionic systems as well.

From earlier considerations, the first peaks in g_{22} (Fig. 1) are shown to be related to the formation of A-X-A bridges between the AX_n moieties. The bridging anions by definition, are those X ions which have a nearest neighbor coordination number of 2. We have calculated the distribution of coordination numbers of the X ions, $n_{32}^{(z)}$, which is given in Table II. For both potentials the expected number of bridging anions is close to the number of A-A nearest neighbor pairs (i.e. $83Z_{22}/2$). The distribution of coordination numbers of X ions, $n_{32}^{(z)}$, given in Table II and of A ions, $n_{22}^{(z)}$ given in Table III for potential 2 indicate that many of the bridging anions are part of configurations which are complex and can be defined as $A_2X_7^$ or $A_3X_{10}^-$. For example, there are 13 bridging X ions and 13 X ions which are 'free' and have no A cations as nearest neighbors. Of the thirteen bridging anions, some belong to the 3 (+1) triplets with one A cation having two others as neighbors as given in Table III. If all A-A-A triplets have one of their three A-A pairs with a distance greater than 5.2Å then there are about 3 $A_3X_{10}^-$ species which have a total of 6 A ions with coordination 1 and 3 with coordination 2. This leaves 17 A cations with coordination 1 which can be part of 8.5 $A_2X_7^-$ moieties. The number of bridges, 14.5 thus calculated is somewhat larger than the value of 13 given in Table II. This discrepancy can be related to the cutoff distance of 5.2Å for the results in Table III. Since there is obvious overlap between the two peaks on either side of this distance (see g_{22} for potential 2 in Fig. 1), this number, 14.5, includes unbridged A-A pairs associated with the broad peak at 6.2Å. These configurations are surprisingly similar to what has been postulated $^{1-5}$ for NaAlCl₄ melts, reactions which involve complex species such as

$$Cl^- + Al_2 Cl_7^- \rightleftharpoons 2AlCl_4^- \tag{2}$$

$$3Cl^{-} + Al_3Cl^{-}_{10} \rightleftharpoons 3AlCl^{-}_4 \tag{3}$$

The structures of the ionic species $A_2X_7^-$ or $A_3X_{10}^-$ are those of two or three AX_4 tetrahedra, respectively, which share one or two corners. (One possibility is that three tetrahedra share 3 corners to form an A_3X_9 species. The uncertainties in some of the data do not permit us to check this possibility at present.)

For potential 1, there is considerably more bridging as evidenced by the distribution of A coordination numbers in table III. The bridging and the tendency for A-X-A angles close to 180° explains the distribution of the angles of the A-A-A triplets exhibited in Fig. 4. However the presence of other peaks indicates that additional factors are also significant. The angular distribution of A-X-A triplets indicates that significant numbers have angles which are substantially different from 180° (i.e. 90% less than 170°, 64% less than 160° and 30% less than 150°). In addition, the spread in the angular distribution of X-A-X triplets indicates that there is significant thermal motion and the concomitant tendency for the octahedra to distort. The presence of peaks other than at 90° and 180° in Fig. 4 is probably related to preferred structures based on small distortions of the angles of the octahedra and the A-X-A bridges. Of particular interest in Fig. 4 is the sharp peak at 60° which represents an equilateral triangle of three A cations connected by bridging anions. When the AX_n octahedra were stiffened to 'resist' distortion in another potential (which is not reported here) the peaks other than those at $\cos\theta = 0,-1$ in Fig. 4 become smaller, which is consistent with our suggestion that these other peaks, at least in part, represent distortions of the basic octahedral structure of AX_n configurations for potential 1. The type of structural ordering indicated by Fig. 4 extends to quite long range (at least to 9-10Å) and appears to be related to bridging. Thus, we expect analogous long range ordering for potential 2 for compositions higher in the AX₃ component. For this case, an expected tendency for local tetrahedral configurations of the $AX_4^$ species would propagate into the longer range distributions of the A-A-A triplets. A more detailed analysis of bridging and structure in such systems is underway. In addition, the constancy of the average nearest neighbor coordination numbers of A (such as 4 for potential 2) with a change of composition is not assured.

CONCLUSIONS

It has been shown that characteristics of binary MAX₄ melts such as chloroaluminates often ascribed to covalency and other non-ionic interactions between ions are present in an ionic solution. For potential 2 the A cations are tetrahedrally coordinated and form $A_2X_7^-$ and $A_3X_{10}^-$ moleties analogous to species postulated to be present in chloroaluminates. For potential 1 there is considerable bridging and a tendency for long range octahedral-like order up to at least 10Å. The nearest neighbor coordination numbers and the symmetry of anions about the polyvalent cations do not completely account for the complexing observed in the present ionic molten salt solutions. From our results, many melts would be expected to have a distribution of coordination numbers for individual ions rather than a single value. This possibility means that it is generally difficult if not impossible to precisely define the structure of melts. Studies are underway of the influence of composition, different charges on the polyvalent ion as well as of radius ratios on the structures and energetics of melts which will include MX-AX₂ mixtures analogous to NaF-BeF₂, KCl-MgCl₂ and CaO-SiO₂ mixtures.

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REFERENCES

- S. J. Cyvin, P. Klæboe, E. Rytter and H. A. Øye, J. Chem. Phys. <u>52</u>, 2776 (1970)
- E. Rytter, H. A. Øye, S. J. Cyvin, B. N. Cyvin, and P. Klæboe, J. Inorg. Nucl. Chem. <u>35</u>, 1185 (1973).
- 3. G. Torsi, G. Mamantov and G. M. Begun, Inorg. Nucl. Chem. Lett, <u>6</u>, 553 (1970).
- L. G. Boxall, H. L. Jones and R. A. Osteryoung, J. Electrochem. Soc. <u>120</u>, 223 (1973).
- H. Linga, K. Motzfeldt and H. A. Øye, Ber. Bunsenges. Phys. Chem. , <u>82</u>, 568 (1978)
- 6. E. W. Dewing, Met. Trans., 12B, 705 (1981).
- M. Blander and M.-L. Saboungi, Proceedings Third International Symposium on Molten Salts, Eds. G. Mamantov <u>et al.</u>, The Electrochemical Society, Pennington, N. J., 212 (1981)
- F. G. Fumi and M. P. Tosi, J. Phys. Chem. Sol. <u>25</u>, 31 (1964); M. P. Tosi and F. G. Fumi, J. Phys. Chem. Sol. <u>25</u>, 45 (1964).
- 9. N. C. Baenziger, Acta Cryst., 4, 216 (1951); K. N. Semenenko, V. N. Surov

and N. S. Kedrova, Russ. J. Inorg. Chem., 14, 481 (1969).

- 10. M. Dixon and M. J. L. Sangster, J. Phys. C 10, 3015 (1977).
- 11. M. Parrinello and A. Rahman, J. Appl. Phys. 52, 7182 (1981).
- 12. S. J. Cyvin, B. N. Cyvin and I. Hargittai, J. Mol. Str. 23, 385 (1974)

Table I.	The Distribution of A ⁺³ ions					
	According to Their Coordination					
	by X ⁻ Ions $(n_{23}^{(z)})$ for $r \leq 3.0$ Å for Different Pair Potentials					

Potential/z	4	5	6	Z_{23}^{\bullet}
1	0	12	71	5.8
2	83	0	0	4.0

* Z_{23} is the weighted average of various $n_{23}^{(z)}$.

Table II. The Distribution of X⁻ Ions According to Their Coordination by A⁺³ Ions $(n_{32}^{(z)})$ for $r \leq 3.0$ Å for Different Pair Potentials

Potential/z	0	1	2	Z^{*}_{32}
1	5	168	159	1.5
2	13	306	13	1.0

* Z_{32} is the weighted average of various $n_{32}^{(z)}$.

Table III. The Distribution of A^{+3} Ions According to Their Coordination by A^{+3} Ions $(n_{22}^{(z)})$ for $r \leq 5.2$ Å for Different Pair Potentials

Potential/z	0	1	2	3	4	5	6	Z_{22}^{*}	
1	0	2	7	22	28	22	2	3.8	
2	58	23	$<\!\!3$	0	0	0	0	0.4	

* Z_{22} is the weighted average of various $n_{22}^{(z)}$.



1. Radial distribution functions, $g_{ij}(r)$ and radius dependence of the average coordination numbers, N_{ij} calculated for MAX₄ using potential 1 (solid line) and potential 2 (dashed line).



Fig. 2.

Angular distribution of the A-X-A triplets in MAX4 for a maximum distance of the A-X pairs of 3.0 Å. Potential 1 (solid line); potential 2 (dashed line).





Fig. 4.

Angular distribution of the A-A-A triplets in MAX4 for a maximum distance of the A-A pairs of 5.2 Å; potential 1 (dashed line), the solid line is for a potential in which the anion-cation radius ratio is somewhat larger than for potential 1. Note that this decreases the peaks at angles other than 90°. The arrows indicate the angles at 90° and 60°.

THE COUPLING BETWEEN TRANSPORT OF ELECTRIC CHARGE AND CHEMICAL REACTION

by

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Abstract

A type of electrochemical cell was investigated where chemical reactions take place in compartments between membranes. A theoretical treatment of the cells is presented whereby the Gibbs energy of reaction is avoided in the basic flux equation and the equation for entropy production. Experimental data and theoretical calculations are presented for a cell of the above type.

Introduction

Many processes in physical chemistry involve coupling of transport and a chemical reaction. A very simple example is the isothermal cell

(Pt) H₂(g) |HCl(aq) |Cl₂(g) (Pt)

where the chemical reaction

$$\frac{1}{2}H_2(g) + \frac{1}{2}Cl_2(g) = HCl(aq)$$
 (1)

causes transport of charge across the cell. When a small charge is transferred under near equilibrium conditions, the emf, $\Delta\phi$, in dimensions JF⁻¹ (the electric work per faraday) is related to the Gibbs energy of reaction by the Nernst equation

$$\Delta G + \Delta \phi = 0 \tag{2}$$

For this cell the electric work and the vectorial ion fluxes are coupled to the scalar function ΔG in a simple way. For more complex cells, where chemical reactions take

place in compartments between membranes, the above kind of correlation between Gibbs energy of reaction and electric work may not be valid. In the cells dealt with in this paper, only part of the Gibbs energy of reaction is converted to electric work.

To calculate local loss of energy, we will use the formalism of irreversible thermodynamics, and derive local flux equations. In these flux equations we avoid the scalar function ΔG of reaction, and thus avoid the problem of scalar - vector coupling.

The following theoretical treatment is based on the assumption of local equilibrium. The number of components is limited to that required by the phase rule. As a consequence the scalar function ΔG of reaction does not enter our flux equations. The components are neutral compounds or elements (see refs. (1) and (2)).

We will first demonstrate the method of calculation for the above simple cell.

Reformulation of the Nernst equation

The system in the above cell has three components in accordance with the phase rule. They are e.g. H_2 , HCl and H_2O . The chemical potential, μ , of each one of these species can be varied independently. The fourth species, Cl_2 , is not a component as its chemical potential is given by the species HCl and H_2 . When there is local equilibrium in the system, we have

$$\frac{1}{2}\mu_{\rm Cl_2} = \mu_{\rm HCl} - \frac{1}{2}\mu_{\rm H_2}$$
(3)

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When a positive charge of one faraday is passed through the cell from left to right, $\frac{1}{2}$ mole of Cl₂ and $\frac{1}{2}$ mole of H₂ are removed from the cell at the left and right hand side electrode respectively. Since Cl₂ is not chosen to be a component, the removal of $\frac{1}{2}$ mole Cl₂ is described as a removal of 1 mole HCl and a simultaneous supply of $\frac{1}{2}$ mole H₂. That is, $\frac{1}{2}$ mole H₂ is transported across the cell from a chemical potential $\mu_{H_2}^{(g)}$ at the right hand side electrode where there is $H_2(g)$ at 1 atm pressure, to a chemical potential of

$$^{\mu}H_{2}(g) = ^{2\mu}HCl(aq) - ^{\mu}Cl_{2}(g)$$

at the left hand side electrode where there is Cl₂(g) at l atm pressure.

The chemical potential of HCl is the same at both electrodes, and thus HCl is transported over a zero gradient in chemical potential. The emf of the cell can be related to the transfer of neutral components by the equation (see ref. (2))

$$\Delta \phi = - \int_{1}^{2} \Sigma t_{i} d\mu_{i}$$
(4)

where t_i is the number of moles of the neutral component i transferred per faraday. The left and right hand side electrode are indicated by 1 and 2 respectively. For the present system with the two components H_2 and HCl, Eqn. (4) gives

$$\Delta \phi = - \int_{1}^{2} (t_{H_2} d\mu_{H_2} + t_{HC1} d\mu_{HC1}) = - \int_{1}^{2} t_{H_2} d\mu_{H_2}$$
(5)

where t_{H_2} is the number of moles of H_2 transferred per faraday. Since $\frac{1}{2}$ mole H_2 is transferred per faraday, $t_{H_2} = \frac{1}{2}$.

Thus

$$\Delta \phi = - \int_{1}^{2} \frac{1}{2} d\mu_{H_{2}} = -\frac{1}{2} (\mu_{H_{2}}(g) - \mu_{H_{2}}^{o}(g))$$
(6)

which is equivalent to Eqn. (2). For the more complex cells, following below, the advantage of the method is revealed.

Cells with cation and anion conducting membranes.

A cell of this type is shown in Fig. 1. It was investigated by Makange (3). The theoretical treatment of this cell is based on the postulates of irreversible thermodynamics. Again, the number of components used to describe the system, is the minimum required by the phase rule.

The cell has a number of compartments separated by cation selective membranes, C, and anion selective membranes, A. The region of the cell denoted "repeating unit", extending from the middle of compartment I to the middle of compartment V, can be repeated several times. The electrodes are Ag/AgCl electrodes. Electric potential gradients, $\nabla \phi$, can be measured introducing small Ag/AgCl test electrodes anywhere in the system (in order to obtain defined electric potentials in compartment III and IV, very small quantities of KCl must be added). In order to increase the conductivity in compartment III, an electrolyte HA (or KCl) is added.

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By the transfer of one faraday, the cell reaction in a "repeating unit" is

 $HCl + KOH = KCl + H_{2}O$ (7)

We choose the following set of components

KCl, HCl, H₂O and HA.

They are given the numbers 1 - 4. KOH is not considered a component. It can be expressed by the others:

 $KOH = KC1 + H_2O - HC1.$

Local entropy production and flux equations.

Transference numbers for neutral components are used (compare ref. (2)). They are defined as

$$t_{i} = \left(\frac{J_{i}}{I}\right)_{\nabla \mu_{j}=0} \qquad j = 1 \dots 4$$
(8)

where J is the flux of the component i in dimensions mol $m^{-2}s^{-1}$, and I is the current density in dimensions $Fm^{-2}s^{-1}$.

The local entropy production per unit volume per unit time, θ , is given by the equation (see ref. (1))

$$\mathbf{T}\boldsymbol{\Theta} = \sum_{i=1}^{4} \mathbf{J}_{i} (-\nabla \boldsymbol{\mu}_{i}) + \mathbf{I} (-\nabla \boldsymbol{\phi})$$
(9)

and the flux of charge, or current density

$$I = -\sum_{i=1}^{4} L_{5i} \nabla \mu_{i} - L_{55} \nabla \phi$$
(10)

Rearrangement gives

$$\nabla \phi = -\frac{4}{\Sigma} \frac{\mathbf{L}_{5i}}{\mathbf{L}_{55}} \nabla \mu_{i} - \frac{\mathbf{I}}{\mathbf{L}_{55}}$$
(11)

where L with subscript is a phenomenological coefficient used in the linear theory of irreversible thermodynamics.

Further

$$\frac{\mathbf{L}_{5i}}{\mathbf{L}_{55}} = \left(\frac{\mathbf{J}_{i}}{\mathbf{I}}\right)_{\nabla \mu_{j}=0} = \mathbf{t}_{i}$$
(12)

The Eqns. (9-12) do not contain the scalar function ${\boldsymbol{\vartriangle}}$ G of reaction.

The emf is obtained by integrating Eqn. (11) for I \approx 0.

$$\Delta \phi = - \int_{I}^{V} (t_{HCl} d\mu_{HCl} + t_{KCl} d\mu_{KCl} + t_{H_2} o^{d\mu}_{H_2} o + t_{HA} d\mu_{HA})$$
(13)

For zero current there will be no gradient in concentration of HA in compartment III. Further, we have $d\mu_{\rm H_2O} \approx 0$ over the whole system since all electrolytes are dilute. This means that the two last terms may be neglected.

The component transference numbers are related to the ionic transference numbers (see ref. (3)). For the cell given in Fig. 1 with perfectly selective cation and anion membranes we will have the following changes when one faraday passes through the cell from left to right. One mole of Cl⁻ ions is produced at the right hand electrode. This is compensated for by a transfer of K^+ through the cation

membrane from compartment IV to V, $t_{K}^{+} = 1$. Further, OH⁻ is transferred from compartment IV to III through the anion membrane, $t_{OH}^{-} = 1$. Again H⁺ is transferred from compartment II to III through the cation membrane, $t_{H}^{+} = 1$. Finally Cl⁻ is transferred from compartment II to I, $t_{Cl}^{-} = 1$, and in compartment I, one mole of Cl⁻ ions is removed.

From stoichiometric relations we have $n_{KC1} = n_{K^+}$ and $n_{HC1} = n_{C1} - n_{K^+}$. The transference number of KCl is equal to the transference number for K^+

$$t_{KCl} = t_{K}^{+}$$
(14)

The transfer of Cl⁻ from left to right is equal to the quantity reacted at the electrodes minus the quantity migrated from right to left through the electrolyte, $l-t_{cl}$. This gives for t_{HCl} :

$$t_{HC1} = (1 - t_{C1}) - t_{K}^{+}$$
(15)

Since the sum of all ionic transference numbers are equal to unity we have

$$t_{HC1} = 1 - t_{C1} - t_{K} + = t_{H+} + t_{OH} - t_{A} -$$
(16)

In the cell we thus have $t_{\rm KCl}$ equal to unity from compartment IV to V and equal to zero elsewhere, while $t_{\rm HCl}$ is equal to unity from compartment II to IV and equal to zero elsewhere. When these relations are introduced in Eqn. (13), one obtains

$$\Delta \phi = - \int_{II}^{IV} d\mu_{HCl} - \int_{IV}^{V} d\mu_{KCl}$$
(17)

$$\Delta \phi = - (\mu_{\text{HCl IV}} - \mu_{\text{HCl II}} + \mu_{\text{KCl V}} - \mu_{\text{KCl IV}})$$
(18)

The chemical potential μ_{HC1} TV can be expressed as

$${}^{\mu}\text{HCl}_{\text{IV}} {}^{=\mu}\text{KCl}_{\text{IV}} {}^{+\mu}\text{H}_{2}\text{O}_{\text{IV}} {}^{-\mu}\text{KOH}_{\text{IV}}$$
(19)

With the choice of components that we made, any transfer of an ion containing oxygen represents a transfer of H_2O since this is the only component containing oxygen, (KOH is not a component). Thus the transfer of OH^- from compartment IV to III corresponds to a transfer of H_2O . This transfer of H_2O may be introduced together with Eqn. (19) in Eqn. (18) (even though transfer of H_2O does not contribute to $\Delta\phi$). Electroosmotic water transfer is neglected. Then eqn. (18) obtains the form

$$\Delta \phi = - (\mu_{\text{KCl}} v + \mu_{\text{H}_20} \text{III}^{-\mu_{\text{HCl}}} \text{III}^{-\mu_{\text{KOH}}} \text{IV})$$
(20)

or

$$\Delta \phi = -\Delta G = - (\Delta G^{O} - RT \ln c_{H} + TT x c_{OH} - TV)$$
(21)

where ΔG^{O} is the standard Gibbs energy of reaction, see Eqn. (7), (activity coefficients have been omitted). Thus, under the conditions of perfectly selective membranes and no impurities in compartment III, we arrive at the Nernst equation through equations that express $\Delta \phi$ by means of <u>gradients</u> in chemical potentials of neutral components only (compare Eqn. (11)). As will be shown below, the method allows us to calculate local energy losses under other conditions.

or

Calculations of loss of energy in the cell.

By the energy loss in an electrochemical cell we understand the difference between the maximum emf obtainable and the actual measured value. The maximum value $\Delta \phi$, calculated from ΔG (omitting activity coefficients) is 0.71 V. The measured value having pure water in compartment III (no HA is added) was 0.52(3). The membranes are not 100% selective (99% for cation selective membranes and 96% for anion selective membranes). The above difference, however, is too large to be explained by membrane imperfection. One may understand the cause of the difference by inspecting Eqns. (13-16). The main cause of loss in $\Delta\phi$ must be small quantities of impurities in compartment III, making $t_{H}^{+} + t_{OH}^{-} < 1$. In order to investigate this loss in electric potential further, two sets of experiments were performed.

In the first set of experiments known quantities of KCl were added to the water in compartment III (no HA is added).

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The main contribution to the emf is the integral $-\int t_{HCl} d\mu_{HCl}$ over compartment III and the two neighboring membranes. The maximum contribution is for $t_{HCl} = 1$. Lower values of t_{HCl} means lower coupling between transfer of HCl and transfer of charge. Contribution to the emf by the integral $\int t_{KCl} d\mu_{KCl}$ over compartment III is very small and is neglected. The loss in emf can be expressed as (compare Eqn. (16)).

Loss =
$$-\int_{II}^{IV} (1-t_{HC1}) d\mu_{HC1} = -\int_{II}^{IV} (t_{K} + t_{C1} -) d\mu_{HC1}$$
 (22)

Since the transference number of an ion, t_i , is proportional to the ion mobility, u_i , and to the ion concentration, c_i ,

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we have

$$t_{i} = \frac{u_{i}c_{i}}{\sum u_{j}c_{j}}$$
(23)

and

$$t_{K}^{+} + t_{C1}^{-} = \frac{u_{K} c_{K}^{+} u_{C1} c_{C1}}{u_{H} c_{H}^{+} u_{OH}^{+} c_{OH}^{+} u_{K}^{+} c_{K}^{+} u_{C1}^{+} c_{C1}^{-}}$$
(24)

With known concentration profiles one can use Eqns. (22, 24) to calculate the loss in emf as a function of the KCl concentration.

When compartment III is filled with a KCl solution of concentration c, there will be an interdiffusion of positive ions across the cation membrane on the left hand side and an interdiffusion of negative ions across the anion membrane on the right hand side. In a short time the H^+ will have replaced most of the K^+ adjacent to the cation membrane while similarly OH⁻ will have replaced Cl⁻ adjacent to the anion membrane. Further, a non-stationary diffusion will take place across the compartment whereby H^+ and $OH^$ will meet and combine.

We will consider two extreme models for the concentration profiles.

- A. Early in the diffusion process, we assume constant concentration of Cl⁻ in the left hand part of the compartment and constant concentration of K⁺ in the right hand part.
- B. We assume that the concentration of Cl^- and of K^+ adjacent to the cation membrane and the anion membrane respectively will keep equal to c until the concentration of each had attained $\frac{1}{2}$ c at the neutral point

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 $(c_{\rm H}^{+} = c_{\rm OH}^{-} = 10^{-7})$. By assuming linear gradients, the loss in emf can be calculated.

The calculated loss for the two cases A and B are shown in Fig. 2 together with observed losses. (Corrections for non-ideal solutions would give slightly better agreement with experiments). Measurements of emf were carried out for concentrations of KCl sufficiently high to predominate over impurities.

From the above calculations and measurements one can see that KCl should not be used to improve conductivity in compartment III, since KCl gives large losses in emf. One can also see how small quantities of impurities in the experiment with water in compartment III give significant reduction of the emf.

In the second set of experiments, different types of organic acid/bases were tested as the component HA. In this case the transference number of HCl is given by Eqn. (16), and A^{-} as well as H^{+} and OH^{-} contribute to t_{HCl} .

With electric current passing through the cell (in positive direction) HA will accumulate on the left hand side of compartment III, and the last term of the integral in Eqn. (13) will be different from zero.

The additional contribution to the emf is

$$-\int t_{HA} d\mu_{HA} = -\int (-t_{A}) d\mu_{HA}$$
(25)

since $t_{HA} = -t_A -$

The contribution is negative, i.e. there is a loss in emf.

For a current density of 100 mA cm⁻², a concentration $c_{HA} = 0.1 \text{ mol } dm^3$ and a length of compartment III of 1 mm, the calculated loss in emf due to this term is only about 0.3 mV.

The effect of different types of HA on the cell emf is shown in Table 1 (see ref. (3) for further details). One of the components in Table 1, aminonapthalene disulfonic acid, is capable of restoring the emf to 94% of the theoretical value. This molecule contributes to $t_{\rm HC1}$ both as a positive and as a negative ion.

This analysis demonstrates the importance of a continuous description of emf in cells with chemical reaction. The method permits us to locate energy losses, and to predict means of minimizing the losses. The addition of HA improves electric conductivity in compartment III without reducing the coupling between electric energy and Gibbs energy of reaction. The coupling is destroyed by additions of KC1.

Cells containing reciprocal salt pairs.

With the present efforts in many laboratories to develop high temperature ion selective membranes for batteries, one may consider a high temperature cell of the type shown in Fig. 3. Here one set of membranes is selective for Li^+ ions, the other set for K⁺ ions. By transfer of one faraday, the cell reaction in a "repeating unit" is

$$LiBr + KCl = LiCl + KBr$$
 (26)

In fused salt chemistry it is common practice to describe this kind of system by three components. We may choose the following components, LiCl, LiBr and KCl. In mixtures of

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fused salts it is unsuitable to use single ion chemical potentials(4), so we continue using chemical potential of neutral salts and transference numbers of neutral salts.

For I = 0 the emf per "repeating unit" is (compare Eqn.(13))

$$\Delta \phi = - \int_{1}^{2} (t_{\text{LiCl}} d\mu_{\text{LiCl}} + t_{\text{LiBr}} d\mu_{\text{LiBr}} + t_{\text{KCl}} d\mu_{\text{KCl}}) \qquad (27)$$

From stoichiometric relations $(n_{KC1} = n_K, n_{LiBr} = n_{Br} - and n_{LiC1} = n_{Li} - n_{Br}$) the transference numbers of neutral salts cen be identified:

$$t_{KC1} = t_{K}^{+}; t_{LiBr} = -t_{Br}^{-} = 0$$

and $t_{LiC1} = t_{Li}^{+} + t_{Br}^{-} = t_{Li}^{+}$ (28)

The transference number $t_{Br}^{-} = 0$ since all membranes are cation selective

Thus
$$\Delta \phi = - \int_{1}^{2} (t_{\text{Li}} + d\mu_{\text{LiCl}} + t_{\text{K}} + d\mu_{\text{KCl}})$$
 (29)

and for perfectly ion selective membranes

$$\Delta \phi = - \int_{II}^{III} d\mu_{LiCl} - \int_{I}^{II} d\mu_{KCl}$$
(30)

or

$$\Delta \phi = - (\mu_{\text{LiCl III}} - \mu_{\text{LiCl II}}) - (\mu_{\text{KCl II}} - \mu_{\text{KCl I}}) (31)$$

In compartment II the chemical potential of KCl may be expressed as
$$\mu_{\text{KCl}} = \mu_{\text{KBr}} + \mu_{\text{LiCl}} - \mu_{\text{LiBr}}$$
(32)

This gives the anticipated result

 $\Delta \phi = - (\mu_{\text{LiCl III}} + \mu_{\text{KBr II}} - \mu_{\text{KCl I}} - \mu_{\text{LiBr II}}) \quad (33)$ The derivation (27-31) shows the validity conditions for eqn. (33).

Thus if the cell unit starts in the state

.... LiBr || KCl || LiBr || KCl

then, through the transfer of charge we will end up with

.... KBr || LiCl || KBr || LiCl

or a complete reaction of the reciprocal salt pair.

Conclusion

The method developed permits calculations of emf for complex galvanic cells, where chemical reactions take place in compartments between membranes. Apart from the condition of local equilibrium, no restrictions are needed in the method of calculation. The method permits analysis of local energy losses.

The present way of treating the coupling between chemical reaction and electric work may be profitable in the search for new types of batteries.

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References

- Førland, T. and Ratkje, S.K., Electrochim. Acta <u>25</u>)1980) 157.
- Førland, K.S., Førland, T. and Ratkje, S.K., Acta Chem. Scand. <u>A31</u> (1977) 47.
- 3. Makange, A., Acta Chem. Scand. A35 (1981) 255.
- 4. Førland, T. and Grjotheim, K., Met. Trans. 9B (1978) 45.

Table l

Variation of cell emf E by addition of components HA $(10^{-2} \text{mol dm}^{-3})$ to compartment III of the cell in Fig. 1. The theoretical maximum value of emf is $E_T = 0.71$ V and n is the efficiency of the cell. The temperature is 25° C.

НА	E VOLT	n = E/E _T	
BENZYLAMINE	0.42	0.59	
N-PHENYLMETHYL NAPHTALENESULFONAMID	0.46	0.65	
NAPHTALENESULFONIC ACID	0.52	0.73	
AMINONAPHTALENE DISULFONIC ACID	0.67	0.94	
$KC1, 10^{-2} mol dm^{-3}$	0.17	0.24	



Fig. 1. Acid-base reaction in an electrochemical cell. A and C are anion and cation selective membranes respectively. HA is an electrolyte which main purpose is to increase conductivity of compartment III. The anion A⁻ is too large to diffuse through the membrane.



<u>Fig. 3</u>. Reciprocal salt pair reaction in an electrochemical cal cell. The cell contains cation conducting membranes, one set selective for K^+ ions and one set selective for Li^+ ions. Electrolytes are fused salts.

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- A: Calculated loss at an early stage of diffusion process.
- B: Calculated loss at an later stage of diffusion process .
- O: Experimental points

CHARACTERISTIC DIFFUSION PHENOMENA OF FLUORINE IN MOLTEN LiF-BeF₂ and NaF-BeF₂ SYSTEMS

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ABSTRACT

Self-diffusion coefficients of fluorine and cations in molten LiF-BeF₂ and NaF-BeF₂ systems were measured by the capillary reservoir technique. The characteristic diffusion phenomena of fluorine in these molten alkali fluoroberyllates are very similar to those of oxygen in molten CaO-SiO₂ and CaO-SiO₂-Al₂O₃ slag. The dynamical behavior of Li and F in molten Li₂BeF₄ was also analyzed by NMR techniques.

INTRODUCTION

It has been reported that the alkali fluoroberyllate melt systems, RF-BeF₂(R=Li,Na,K) are quite similar to the alkaline-earth silicate melt systems, R'O-SiO₂(R'=Mg,Ca,Ba). Especially, the phase diagram of MgO-SiO₂ scaled down by the relation $[(t^{c}+273^{c})/2.88]+273$ fit most of the diagram of LiF-BeF₂, as indicated by Thillo and Lehmann[1]. It was also recently found that the physical properties, such as viscosity, electrical conductivity, and molar volume, depend on simple quantitative relationships between molten alkali fluoroberyllate system and molten alkaline earth silicate system[2]. The results indicate that the statistical and dynamical properties of constituent ions in these molten states also have similar behavior.

Cantor et al.[3] showed in their viscosity study of molten LiF-BeF₂ that the viscosity decreases rapidly with an increase of LiF concentration, due to breaking of the fluorine bridges in a three-dimensional network of Be-F bonds, and estimated that the melt might lose its network character for a BeF₂ content smaller than 65mol%.

We have already reported the self-diffusion coefficients and their temperature dependence for F and Li in molten Li₂BeF₄ and LiBeF₃ and for F and Na in molten NaBeF₃ by the capillary reservoir technique[4-8],X-ray diffraction analysis of molten Na₂BeF₄ and NaBeF₃[9] and nuclear spin relaxation of 7 Li and 19 F in solid and molten Li $_{2}$ BeF4[10]. In this report, all these data are summarized and compared with those in molten alkaline-earth silicates.

EXPERIMENTALS

The method of measurements of self-diffusion coefficients was described in detail elsewhere[4-8]. The procedure of the experiment was carried out by the capillary reservoir technique.

PREPARATION OF RADIOACTIVE OR STABLE TRACER

The fluorine radioactive F-18 was prepared using JRR-3 (Japan Research Reactor-3). Highly purified Li₂CO₃ was used as a target material and the following reactions occurred to produce ¹⁸F.

$$^{\circ}_{3}\text{Li}(n,\alpha)^{3}_{1}\text{T} \text{ and } ^{1\circ}_{8}O(\text{T},n)^{1\circ}_{9}\text{F}$$
 (1)

After irradiation, Li_2CO_3 powder was treated with aqueous hydrogen fluoride in a platinum crucible to produce the labelled $Li^{18}F$ deposit. On the other hand, the lithium stable ⁶Li was prepared using Li_2CO_3 powder which a ⁶Li/⁷Li abundance ratio of 19 and then Li_2CO_3 was treated with aqueous hydrogen fluorine in the same way as above mentioned. ²⁴Na was made from NaF powder irradiated by thermal neutron for 1 min. in JRR-2.

PREPARATION OF Li2BeF4, LiBeF3 and NaBeF3

For the preparation of Li₂BeF₄,LiBeF₃ and NaBeF₃ in the diffusion cell, a mixture of BeF₂ and LiF or NaF was melted in a platinum container, treated with a HF+H₂ mixture at 600°C and then purged with He. The chemicals used were as follows:LiF and NaF prepared by Merck Co.(Germany), granulation of single crystal(l-4mm); BeF₂ prepared by Rare Metallic Co.(Japan)[known impurities(in ppm):K+Na,600;Ca,10; Al,20;Cr,30;Fe,10;Ni,10].

APPARATUS AND PROCEDURE

A schematic diagram of the apparatus is shown in Fig.l. In this work some devices were adopted to avoid solidification of the melted tracer mixture in the capillaries before each diffusion run. After the tracer salt(C) in the Pt crucible(D) and non-tracer salt(E) in the Ni crucible(F) were melted under He atmosphere, the movable Ni rod with the capillaries was lowered into the Pt crucible. The capillaries were filled with the molten tracer salt by dipping their mouths into the salt under a vacuum and then feeding He gas slowly back in the apparatus. The capillaries were raised out of the molten tracer salt by means of the Ni rod and then submerged in the molten non-tracer salt after

turning the stainless steel flange(I).

The capillaries which were 1mm inner diameter and 30-40mm length were made of Ni. The duration of diffusion run was in the range of 20-120 minutes. The maximum difference in temperature between the top and the bottom of the capillary was about 0.5°C

After the diffusion run, the capillaries were lifted from the molten non-tracer salt and then removed. After cleaning the capillaries, they were cut by a saw at intervals of about 2mm. The concentration profiles of tracer $^{18}\mathrm{F}$ and $^{24}\mathrm{Na}$ or $^{6}\mathrm{Li}$ in the capillaries were measured with y-ray spectrometer or ion micro mass analyser(HITA-CHI IMA-SS), respectively.

NUCLEAR MAGNETIC RESONANCE

Spin-lattice relaxation time T₁ was measured by pulse



Fig.1 Apparatus for Diffusion Measurement

A:Ni capillary, B:Ni rod, C: Tracer salt, D:Pt crucible,E: Non-tracer salt, F:Ni crucible, H:Heater, I:Stainless steel flange, T:C.A. thermocouple.

spectrometer controlled by a micro-processer. For T1 values less than 0.1sec "180°- τ -90°" pulse technique was applied and the longer T_1 was measured by "(n.90°)- τ -90°" pulse The 90° pulse length was about 15µs. For magnetechnique. tization $M_z(\tau)$ the intensity of free induction decay(FID) signal following second 90° pulse were measured as a func-The absolute $M_{Z}(\tau)$ decay obeyed exponential law tion of τ . in all samples. In order to improve signal to noise ratio a digitalized signal averager Was utilized. In all experiments a frequency of 10MHz or 20MHz was employed. Each sample was sealed in quartz sample tube with a length a length of a diameter of lcm. Temperature of the specimens 4cm and was controlled up to 630°C with accuracy of ± 2 °C in an electrical furnace which was mounted between pole pieces of magnet. Temperature was measured by an Pt-Pt(13%Rh) thermocouple attached to the sample tube.

 T_1 for ⁷Li and ¹⁹F has been determined using the relations $\overline{I}=I_0[1-\exp(-\tau/T_1)]$ for relatively long $T_1(T_1>0.1sec)$

or $I=I_0[1-2exp(-\tau/T_1)]$ for relatively short $T_1(T_1<0.1sec)$.

RESULTS AND DISCUSSION

Typical concentration profiles of 18 F and 6 Li in capillaries are shown in Figs.2 and 3. The salt was not contained within a few mm from the capillary mouth due to the volume contraction of the salt.

The diffusion coefficient D was calculated by applying the following equation to the observed concentration profiles,

$$C_x = C_0 erf[x/(Dt)^{1/2}],$$
 (2)

where C_0 is the initial concentration of the tracer and C_x the concentration of the tracer at distance x from the boundary after diffusion time t.

The diffusion coefficients are written in the form

 $D=D_0 \exp[-E/RT], \qquad (3)$

where E is the activation energy, R the gas constant and T the absolute temperature. The results as shown in Table 1 and Fig.4 were obtained by a least squares analysis from all experimental data.

Table 1 Summary of self-diffusion coefficients D=D0exp[-E/RT] in molten Li2BeF4,LiBeF3 and NaBeF3

	D ₀ (m2s ⁻¹)	E (KJ·mol ^{~1})	Observed tempera- ture range(°C)
Li ₂ BeF ₄	· _		
Li	9.27×10^{-7}	32.5 <u>+</u> 8.4	470-640
F	6.61x10 ⁻¹	128.1 <u>+</u> 14.2	510-650
LiBeF3			
Li	1.12×10^{-6}	38.7±12.5	440-560
F	3.16x10 ⁰	144.0±16.3	450-670
NaBeF3			
Na	7.80×10^{-7}	40.2-5.6	420-560
F	4.93×10^{-4}	79.6 <u>+</u> 6.5	440-600



Fig. 2 The distribution of ¹⁸F in a capillary after a diffusion run.



Fig. 3 Distribution of ⁶Li in a capillary after a diffusion run.



Fig.4 Summary of the diffusion coefficients of fluorine and lithium or sodium in molten Li₂BeF₄,LiBeF₃ and NaBeF₃.



- Fig.5 Comparison of self-diffusion coefficient of various cations in molten salts and molten silicates under the reduced temperature scale T/T_m (a) KF(K); (b) NaCl(Na); (c) NaF(Na); (d) NaF-AlF₃(Na); (e) NaI(Na), (f) KCl(K); (g) RbCl(Rb); (h) CsCl(Cs); (i) LiCl(Li); (j) FLINAK(Na); (k) FLINAK(K); (l) FLINAK(Li);
- (m) Na₂O-SiO₂ (23-77mol%) (Na);
- (n) $CaO-SiO_2-Al_2O_3$ (42-45-12mol%) (Ca);
- (o)CaO-SiO₂-Al₂O₃(42-45-12mol%) (Ca);
- $(p)CaO-SiO_2(56-44mol_{8})(Ca)$.





(a) KCl(Cl); (b) NaCl(Cl); (c) RbCl(Cl); (d) NaI(I); (e)CsCl(Cl); (f)TlCl(Cl); (g)FLINAK(F); $(h)CaO-SiO_2(56-44mol_{\ })(0);$ $(i)CaO-SiO_2^-Al_2O_3(42-45-12)$ mol (0);

(j)CaO-SiO₂(40-60mol%)(O).

Figs.5 and 6 show the results of self-diffusion coefficients in these molten alkali fluoroberyllates compared with those of cations and anions in molten alkali halides and molten silicates under the reduced temperature scale, $T/T_m,$ where T_m is the melting point. The diffusion coefficients and the activation energies of cations in molten Li2BeF4,LiBeF3 and NaBeF3 follow a similar pattern to those of cations in molten alkali halides. On the other hand, self-diffusion of fluorine in these molten alkali fluoroberyllates have unusually high diffusion coefficients and activation energies. The activation energies for self-diffusion coefficients of fluorine were larger than those for electrical conductivities[11] and viscosity coefficients [3].

It was reported from the analysis of X-ray diffraction [9,12] and the Raman spectrum measurements[13] that complex anions exist, such as BeF_4^{2-} and $Be_2F_7^{3-}$ in molten Li2BeF4, LiBeF3 and NaBeF3. The fact that the magnitude of the diffusion coefficient measured in this work is un usually large can not be explained solely by mass transfer due to migration of the large fluoroberyllate anions.

Possible explanations for the large value of the fluorine diffusion coefficient could be the exchange of fluorine atoms between neighbouring beryllate units including the rotation of beryllate anions, or the fluorine diffusion by means of neutral ion pair, such as LiF, diffusion mechanism. The exchange mechanism involves the breaking of Be-F bonds and some steric difficulties with anion rotation, which can account for a high energy of activation for fluorine diffusion. In ion-pair diffusion, on the other hand, the movement of fluorine with lithium involves breaking of Be-F bonds, because the content of free fluorine atoms in the melt seems small. This mechanism can also have a high activation energy.

Fig.7 shows the temperature dependence of spin-lattice relaxation time T_1 of ¹⁹F and ⁷Li in molten Li₂BeF₄[10]. T_1 of ¹⁹F had minimum and T_1 at frequency of 20MHz was longer than that at frequency of 10MHz at temperatures below T_1 minimum. However, both values of T_1 approached to the same at temperatures above T_1 minimum. T_1 of ⁷Li had also minimum and the minimum temperature of ⁷Li was a little higher than that of ¹⁹F.

The magnetic impurities such as Ni^{2+} and Fe^{2+} in the sample will have important effect upon the relaxation time and resonance absorption spectra. The concentration of magnetic impurity was estimated by the analysis of magnetic susceptibility measured at temperatures below 4.2°K. The concentration of magnetic impurity used in the measurements of NMR was about 2.9ppm calculated in terms of Fe²⁺ ion.

Fig.8 shows the resonance absorption spectra of 19 F and ⁷Li in solid and molten Li₂BeF₄[10]. The frequency was 10MHz. The remarkable result was the line width of resonance absorption spectrum of 19 F at 435°C(solid) is nearly equal to that at 550°C(liquid).



Fig.7 Temperature dependence of T_1 of ⁷Li and 19_F in molten Li₂BeF₄.





As there is mainly BeF_4^{2-} and Li⁺ ions in molten Li₂BeF₄, the following relaxation mechanisms will be considered as the relaxation of ¹⁹F.

- (1) Rotation of BeF_4^2 ion.
- (2) Migration of BeF_4^{2-} ion. (3) Interaction between F^- and Li⁺ jons.
- (4) Dissociation of F atom from BeF_{4}^{2-} ion and diffusion of fluorine.

The contribution of these four mechanisms to T1 are shown precisely in Ref.[10] and the essential equations and results will be presented in this paper.

(1) Relaxation due to the rotation of BeF_2^2 ion.

There are two models, diffusion model and kinetic model. In diffusion model, the relaxation time of rotation τ_2 is much shorter than periodic time of rotation $T_0(\tau_2 < T_0)$ and T_1 is expressed by the following equation,

$$(1/T_{1})_{\text{rot.diff}} = (2/5) (\gamma - 1) \gamma_{F}^{4} \hbar^{2} r_{F-F} I_{F} (I_{F} + 1) x [\tau_{2}/(1 + \omega^{2} \tau_{2}^{2}) + 4\tau_{2}/(1 + 4\omega^{2} \tau_{2}^{2})].$$
(4)

On the other hand, \mathtt{T}_1 in kinetic model($\tau_2{>}\mathtt{T}_0)$ is expressed by the following equation,

 $(1/T_1)_{rot.kin} = (1/5) (1/T_1)_{rot.diff.}$ (5) In these equations, I_F is the quantum number of F nuclear spin(=1/2), γ the number of F atoms in BeF $_2^{4-}$ ion(=4), γ_F the gyromagnetic ratio of F nuclei and r_{F-F} the atomic distance of F-F pair.

The diffusion coefficient D' of rotation of complex ion is expressed by Stokes relation with a viscosity n.

 $D'=kT/8\pi a^3\eta$. (6) The relaxation time τ_2 will be calculated using the relation τ_2 =(6D')⁻¹ and the observed viscosity η =5.94x10⁻⁴exp(38.4/ $R\tilde{T}$) poise[3]. τ_2 at 530°C was roughly estimated to be $1.7 \times 10^{-10} s.$

On the other hand, eq.(4) is expressed using parameter $r_{\rm F-F}{=}2.56{\rm \AA}$ as follows.

 $(1/T_1)_{rot} = 1.7 \times 10^9 [\tau_2/(1+\omega^2 \tau_2^2) + 4\tau_2/(1+4\omega^2 \tau_2^2)] s^{-1}$. (7) This equation has maximum at $\omega\tau_2{=}0.64$. The estimated relaxation time by Stokes relation $\tau_2{=}1.7 {\rm x} 10^{-10} {\rm s}$ show $\omega\tau_2{=}1.02 {\rm x} 10^{-2}$ which is much smaller than unity and can not explain the observed T1 minimum at 530°C.

The contribution of rotation of BeF_4^{2-} ion to T_1^{-1} will be estimated to be 1.4s⁻¹ by eq.(7) and $\omega \tau_2 = 1.07 \times 10^{-2}$, which is much smaller than the observed value $(1/\text{T}_1) \exp = 200\text{s}^{-1}$. Then the contribution of rotation to T_1 will be small small.

(2) Relaxation due to the migration of BeF_4^{2-} ion.

 T_1 due to the migration of complex ion will be expressed by $(1/T_1)_{diff} = 3/2 \gamma^4 \hbar^2 I(I+1) [8\pi/15 J(\omega) + 32\pi/15 J(2\omega)]$

(8)

and

 $J(\omega) = (N/dD) \int_{0}^{\infty} [J_{3/2}(u)]^2 udu/(u^4 + \omega^2 \tau^2)$, (9)

where D is the diffusion coefficient of migration of complex ion, N the spin density, d the diameter of complex ion and $J_{3/2}$ Bessel function. The integration in eq.(9) has maximum value 0.133 at $\omega\tau=0$ and decreases monotoically. Then (1/T1) diff has no maximum.

The diffusion coefficient D of migration of complex ion is roughly estimated by Stokes relation $D=kT/6\pi an$ and D is $1\times10^{-10}m^2/s$ at 530°C. Then using $N=7\times10^{30}/m^3$ and $D=1\times10^{-10}m^2/s(530°C)$, the contribution of migration of BeF 4^- ion to T_1 is estimated to be $(1/T_1)_{diff}=0.3$, which is also much smaller than the observed value.

(3) Relaxation due to interaction between Li⁺ and F⁻

T₁ will be expressed essentially by eq.(8) with different parameters such as I=3/2, $D=a^2/6\tau$, $d=r_{Li-F}$, N=spin density of Li and $\gamma^4=\gamma_F^2\cdot\gamma_{Li}^2$. Using $r_{Li-F}=1.85A$, $N=3.5 \times 10^{30}/m^3$ and $D_{Li}=9.27 \times 10^{-7} \exp(-32.5/RT)$, we get $(1/T_1)_{F-Li}=1.5 \times 10^{-3}$, which is also much smaller than the observed value.

(4) Dissociation of F atom from BeF_4^{2-} ion and diffusion of fluorine

The behavior of T_1 is attributed to the dissociation of F from complex ions and the long distance diffusion of F ions in the liquid by the following mechanisms.

In exchange model of fluorine atoms between neighbouring beryllate units including rotation of beryllate anions, the diffusion distance with one step will be at most 6Å. Using the relation $D = \langle a^2 \rangle / 6\tau$ and the observed diffusion co-efficient $D = 2 \times 10^{-9} m^2 / s$ at 530°C, the estimated correlation time τ is $2 \times 10^{-11} s$ which is much smaller than the observed $\tau = 3 \times 10^{-9} s$ and is comparable with that of the rotation of the molecule. This is not reasonable.

On the other hand, in dissociation and long distance diffusion model of fluorine, the relaxation time will be expressed by the following equation.

$$L/T_1 = 8\pi/15 \cdot \gamma^4 \hbar I (I+1) N/a^3 [\tau/[2(1+(\omega\tau/2)^2] + \tau/(1+\omega^2\tau^2)]$$

---(10) Equation (10) has maximum at $\omega\tau=1.41(\tau=2.25\times10^{-8}s$ at $\omega=$ $6.28 \times 10^7 \text{ s}^{-1}$) and we get $(1/T_1)_{\text{max}}=50$, which is much larger than the former three relaxation mechanisms. Then root mean square(RMS) distance $\sqrt{\langle \ell^2 \rangle}$ of one step of fluorine diffusion, which is the distance between dissociation of F from a complex ion, diffusion in the liquid and trap at F vacancy of another complex ion, is roughly estimated by relation $\langle \ell^2 \rangle = 6\tau D$. At 530°C, the observed value of τ and D were 2.25x10⁻⁸s and 2x10⁻⁹m²/s, respectively and $\sqrt{\langle \ell^2 \rangle} \simeq$ 100Å was obtained.

The results of NMR indicate that the dissociation of F from complex ions and the long distance diffusion of F ions has largest contribution to the diffusion in molten Li_2BeF_4 and T_1 of this mechanism is in good agreement with the experimental value. The solid curves in Fig.9 are the theoretical ones with $1/\tau = 2 \times 10^{15} \exp(-103.7/\text{RT})$,

and

 $1/T_1 = S[\tau/(1+\omega^2\tau^2) + 4\tau/(1+4\omega^2\tau^2)].$ (12)

(11)

S was determined to fit the theoretical curve to the observed one at 640°C and $\omega{=}2\pi{x}10^7{s}{-}1$. The theoretical equation indicates good agreement with temperature and frequency dependency of the observed T_1 . The activation energy 103.7KJ/mol is also in good agreement with that of selfdiffusion of fluorine with tracer method, 128KJ/mol, as shown in Table 1.



Fig.9 Temperature dependence of $(1/T_1)$ of ^{19}F in molten Li₂BeF₄. The solid curves are the theoretical one with $1/\gamma = 2 \times 10^{15}$ exp(-103.7/RT).

CONCLUSION

- (1) Characteristic diffusion of fluorine in molten alkali fluoroberyllates could be explained by the diffusion mechanism with dissociation of F from complex anion and long distance diffusion.
- (2) The results of self-diffusion of fluorine in molten Li₂BeF₄,LiBeF₃ and NaBeF₃ are qualitatively similar to those of oxygen in molten CaO-SiO₂ and CaO-SiO₂-Al₂O₃ slag[14,15]. X-ray diffraction analysis of molten NaBeF₃ [9] and CaSiO₃[16] also indicates the similarity of the structures, Thus, the research on molten alkali fluoroberyllates will contribute to the analysis of statistical and dynamical behaviors of constituent ions in molten alkaline-earth silicates which is relatively difficult because of high temperature.

REFERENCES

- E.Thillo and H.A.Lehmann, Z.Anorg.Chem., 258, 332(1949).
- [2] K.Furukawa and H.Ohno, Trans. Japan Inst. Metal, 19, 553 (1978).
- [3] S.Cantor, W.T.Ward and T.Moyniham, J.Chem.Phys., <u>50</u>, 2874 (1969).

- [4] H.Ohno,Y.Tsunawaki,N.Umesaki,K.Furukawa and N.Iwamoto, J.Japan Inst.Metals,41,391(1977) (in Japanese).
- [5] T.Ohmichi, H.Ohno and K.Furukawa, J.Phys.Chem., <u>80</u>, 1628 (1976).
- [6] H.Ohno, K.Furukawa, Y.Tsunawaki, N.Umesaki and N.Iwamoto, J.Chem.Res. (S), 1978, 158.
- [7] N.Iwamoto,Y.Tsunawaki,N.Umesaki,H.Ohno and K.Furukawa, J.Chem.Soc.,Faraday Trans.II, 75, 1277 (1979).
- [8] Y.Tsunawaki, H.Ohno, H.Katsuta and K.Furukawa, Chem.Soc. Japan, 1982, (6), 956 (in Japanese).
- [9] N.Umesaki, N.Iwamoto, H.Ohno and K.Furukawa, J.Chem.Soc., Faraday Trans.1, 78, 2051 (1982).
- [10] T.Matsuo, H.Suzuki, H.Ohno and K.Furukawa, Chem.Soc. Japan, 1982, (6), 892 (in Japanese).
- [11] G.D.Robbins and J.Braunstein in "Molten Salts:Characterization and Analysis", G.Mamantov, Ed., Marcel Dekker, New York, N.Y., 1969, p. 443.
- [12] F.Vaslow and A.H.Narten, J.Chem. Phys., 59, 4949 (1973).
- [13] A.S.Quist, J.B.Bates and G.E.Boyd, J.Phys.Chem., <u>76</u>, 78 (1972).
- [14] T.Saito,Y.Shiraishi,N.Nishiyama,K.Sorimachi and Y.Sawada, Proc. 4th Japan-USSR Joint Symp.Phys.Chem. Metallurg.Processes, 1973, p.53.
- [15] P.J.Koros and T.B.King, Trans.AIME, 224, 299(1962).
- [16] Y.Waseda, H.Suito and Y.Shiraishi, J.Japan Inst.Metals, 41,1068(1977) (in Japanese).

NEUTRON DIFFRACTION STUDIES OF MOLTEN SALTS

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Abstract

Neutron diffraction, exploiting the isotope effect, a now well established technique, is unique in that it enables <u>partial</u> structure factors and radial distribution functions (rdf's) to be extracted. This review of the structures of molten chlorides will include a comparison with X-ray work on similar salts; complementing of the two techniques; description of all aspects of structural data which can be determined from partial structure factors and rdf's; results on chloride melts so far examined, in particular alkali halides, alkaline-earth halides, and solid-state layer lattice melts; and finally details of binary experiments proposed to investigate thermodynamic properties of mixing. Preliminary results on magnesium and manganese chlorides will be given.

1. Introduction

For many years, molten salt chemists and electrochemists have been interested in molten salt structures, in particular in the existence of species in a melt. Industrially such information can be the key to the design of a process; for example, metal extraction success depends on lack of corrosion, among other things, this being linked to the existence of species, and ion mobility, for example, in the chloride ternary or higher melts used.

Apart from applied interest, there is obviously the desire to know and understand melt structures, since then, from systematic studies, behaviour predictions can be made and theoretical models can be tested. This is the case since ultimately models such as the hypernetted chain (HNC) method, with use of various interionic potentials, must be tested against structures derived experimentally.

Until the 1970's very little information on full, unambiguous molten salt structures existed. The simple reason was that only X-ray experiments were feasible before neutron diffraction became a routine technique,following the availability of neutron beam research facilities and isotopes.

Unfortunately, from an X-ray spectrum, only certain aspects of a melt structure can be deduced, with set limits on values, rather than absolute values themselves which can be extracted from neutron diffraction through partial structure factors and radial distribution functions (rdf's), see §3. It will be seen how vital a knowledge of these partial rdf's is in understanding the shortcomings of theoretical

models.

First then, in §§2-4 neutron and X-ray work will be compared and areas where they can complement each other will be defined. In particular, the isotopic substitution neutron diffraction method will be outlined. Then concentrating on mainly neutron work, the remaining sections will consist of: §5 an outline of materials which can be examined; §6 features of melts and melt structure values extractable from partial structure factors and radial distribution functions; §7 specific chloride melts; §8 binary melts.

X-ray diffraction

X-ray diffraction has been widely used to study simple molten salts, an especially extensive range having been examined by Ohno and Furakawa(e.g.,l) where the technique is explained in full. In X-ray diffraction a sample is irradiated with a beam of wavelength about $l^{\rm A}$ and the scattered beam over a momentum transfer (k) range of about $O-12 {\rm \AA}^{-1}$ is analysed, corrected for background, sample container, etc.

The coherent X-ray intensity (in electron units), $I_{eu}^{coh}(k)$ is then given in terms of partial structure factors $S_{\alpha\beta}(k)$:

$$I_{eu}^{coh}(k) = \sum_{\alpha} \sum_{\beta} c_{\alpha} f_{\alpha}(k) f_{\beta}(k) S_{\alpha\beta}(k)$$

where f_{α} , f_{β} are the k-dependent atomic form factors, c_{α} is the concentration of particle α . The total rdf, G(r) - the Fourier transform of F(k) in the neutron case - is given for X-rays by

$$G(r) = 1 + \frac{\sum (\bar{K}_{m})^{2}}{(\sum \bar{K}_{m})^{2} 2\pi^{2} \rho r} \int_{0}^{\infty} ki(k) \sin kr \, dk$$

where the normalised reduced intensity is

$$i(k) = \frac{I_{eu}^{coh}(k)}{\sum_{m} f_{m}^{2}(k)} - 1,$$

where K_m is the effective number of electrons in atom m.

Thus we obtain G(r) which gives the probabilities of locating an ion in an elemental volume, given an ion at the origin. The first peak in G(r) is reasonably assumed to be at the distance of cationanion in the melt.

This peak position is actually an <u>upper</u> limit value, since if a second peak (gaussian) would overlap with the first, then it obviously pulls out the position of the first peak. This overlapping of gaussians is due to penetration of like ions in the first coordination shell, and arises in particular for larger cation melts, see §6(ii).

Integration under the first peak in G(r) gives a value for average coordination number of anions around a cation. Attributing other peaks in G(r) to other ion pairs is somewhat perilous since spurious peaks can be difficult to identify, and usually reference has to be made to a solid-state structure. As an example, in Fig. 1 is shown ki(k) for MnCl₂ due to Ohno and Furukawa (1).

3. Neutron diffraction

As with X-ray diffraction, a sample is irradiated with approximately 1Å wavelength neutrons and the scattered beam analysed. After corrections have been made, a k-space intensity is obtained. In contrast with X-ray work, neutron diffraction can be carried out exploiting the isotope effect (i.e. non-systematic variation of scattering length of a nucleus with atomic weight). Using three separate isotopic substitutions eg. $Zn^{35}Cl_2$, $Zn^{37}Cl_2$, and, say, $Zn^{-1}Cl_2$, we can derive more than the total structure factor, F(k). That is, the partial structure factors, S(k), can be determined, leading to unambiguous information about ion-ion correlation functions. The technique is well documented (2).

Let me briefly clarify use of the technique mathematically. For a simple melt, say ZnCl₂,

$$F(k) = 2c_{Zn}c_{C1}b_{Zn}b_{C1}[s_{ZnC1}(k)-1] + c_{Zn}^2b_{Zn}^2[s_{ZnZn}(k)-1] + c_{C1}^2b_{C1}^2[s_{C1C1}(k)-1]$$

where c is ion concentration, b is ion scattering length. Clearly, three different F(K)'s relating to three different scattering lengths, $b(^{35}\text{Cl})$, $b(^{37}\text{Cl})$, $b(^{natural}\text{Cl})$, will yield the three partial structure factors S(k). Transform of S(k) gives the <u>partial</u> radial distribution, $g_{\alpha\beta}(\mathbf{r})$ through

$$S_{\alpha\beta}(k) = 1 + \frac{4\pi\rho}{k} \int [g_{\alpha\beta}(r) - 1]r \sin kr dr,$$

where ρ is number density (Å⁻³), k represents angular momentum transfer (Å⁻¹). As an example, the F(k), S(k) and g(r) for MgCl₂ due to Biggin, Gay and Enderby (3) are shown in Figs. 2-4 (preliminary results).

4. Neutron and X-ray diffraction

To check that neutron and X-ray experiments are producing consistent results, three molten salts on which both neutron and X-ray data existed were chosen. In order to make a comparison, the S(k)'s from the neutron experiments were combined using X-ray form factors to reproduce an X-ray spectrum. This is compared in Fig. 5 for NaCl with the normalised reduced intensity due to Ohno and Furukawa (4). Another test, on MnCl₂, was performed by taking partial structure factors S(k) from MgCl₂ melt. The S(k) from MgCl₂ combined impressively to reproduce the neutron total structure factor F(k) and so it is valid

to make this combination and assume MgCl₂ and MnCl₂ to be isomorphous in the melt. The reproduced X-ray reduced scattering intensity i(k) plotted as ki(k) against k in Fig. 1 along with the ki(k) due to Ohno and Furukawa (1) is only scaled along k (ion size requirement). Again the agreement is satisfactory. A similar combination of neutron structure factors for zinc chloride provided excellent agreement above $3 Å^{-1}$ with the ki(k) due to Takagi and Nakamura (6).

From this it follows that the neutron and X-ray data can be combined in determining partial structure factors, any differences pointing to areas which need further investigation (artifacts) in one or other of the experiments.

5. Melts amenable to study

There are limitations to use of the isotope substitution method. We know that scattering length b varies with atomic weight. It is obvious that (at least) two isotopes with sufficiently different values for b are required to obtain the three different samples described in §3. Chlorine is a good example : $b(^{35}Cl) = 1.17$, $b(^{37}Cl) = 0.308 (10^{-12} \text{ cm}, \text{values due to Koester et al.} (7))$. Bromine offers no possibilities since $b(^{79}\text{Br}) \sim b(^{81}\text{Br})$. Only ¹²⁹I occurs naturally, but ¹²⁷I is only weakly radioactive and may be exploitable (Welland and Enderby, private communication). Anions which can be studied are nitrate and nitrite complexes (Neilson in particular has examined a range of aqueous solutions where ¹⁴N and ¹⁵N have provided the required scattering variation between samples (eg.8)), and sulphates, sulphites, and more easily selenates, selenites.

As regards cations, both lithium and nickel provide an interesting opportunity for simplifying study. Since both have negative scattering-length isotopes, zero-scattering (null) samples can be made by mixing. Thus study of a single sample of, say, $^{0}NiCl_{2}$, can yield S_{ClCl}(k) directly. Other cations which have suitable scattering length variations are K⁺, Cu , Mg²⁺, Ca²⁺, Fe³⁺ (see Enderby and Biggin (9) for more detail).

A final point to note is that (i) <u>absorption</u> cross sections must be taken into account: lithium 6 (⁶Li) has an extremely high σ_{a} (945 barns for 2200 ms⁻¹ neutrons); and (ii) incoherent scattering cross sections which are high, e.g.,for H (σ_{nc} = 79.7 barns), will have the result that the coherent scattering signal will be swamped; deuteration is essential, for example, in ammonium salts.

The salts are usually held in quartz or vanadium containers, the choice depending on attack by the molten salt. Non-standard techniques for salt drying often have to be invoked, since drying with HCl or Cl gas can lead to undesirable chlorine exchange.

6. General features of S(k) and g(r)

From S(k) and g(r), information on the following can be extracted:

(i) coordination number, n; (ii) ion-ion separation, \bar{r} ; (iii) penetration of like ions into first coordination shell; (iv) charge cancellation; (v) existence of species, pseudo-species; (vi) peak heights in g(r); (vii) coulomb peak positions; (viii) site type. Let us consider these features individually.

(i) As described elsewhere, Biggin and Enderby (9,10), values for coordination number depend on definition. There is no significance to the coordination number n from the statistical mechanical viewpoint, since themodynamic properties relate to integrals of $g_{\alpha\beta}(\mathbf{r})$ over all r. Clearly, comparisons require that definitions be made. Waseda defined and discussed (11) four standard methods (i) integration to the first minimum in $r^2g(\mathbf{r})$; (ii) integration under the first peak in symmetrical $r^2g(\mathbf{r})$.

As pointed out by Biggin and Enderby (9,10), for salts with large cations, eg. BaCl₂, SrCl₂, there is considerable penetration of like ions into the first coordination shell, the first peak in G(r) is not symmetrical, and integration using any method to find n₁ is not reliable. Only integration in g₁ yields reliable values. However, for small cation melts, eg. NaCl, use of either G(r) or g₁ (r) is satisfactory. We have shown (9) that for a small cation, n₁ varies only a little between the four methods used applied to g₁ (r) and G(r) (3.9-5.3 for NaCl) whereas for a large cation the variation is large (6.4-26 for BaCl₂).

Now, method (iii), $rg(r)_{symm}$, is valid if solid-like local order is assumed. This follows from work by Coulson and Rushbrooke (12), who demonstrated simply that for a liquid approximated by an Einstein model (ions moving in a restricted region independent of their neighbours), then rg(r) is symmetrical (this follows from taking spherically symmetric distributions and counting number of ions in a shell between r and r+dr). On this basis, use of method (iii) should yield coordination numbers in good agreement with the semi-empirical formula of Ohno and Furukawa (4):

 $n_{+-}(\text{liquid}) = n_{+-}(\text{solid}) \frac{v_s}{v_1} \left[\frac{r_{+-}(\text{liquid})}{r_{+-}(\text{solid})} \right]^3$

where V and V are liquid and solid-state molar volumes. Enderby and Biggin (9) have shown that n_{\pm} values calculated using this equation agree well with those from method (iii).

(ii) The first peak position in $g_{+}(r)$ and G(r) indicates the cation-anion average separation and is an upper limit when taken from G(r), the deviation from the true value (ie. that found from the partial rdf) being largest for large cations because of gaussian overlap. For a most physical interpretation, cation-anion separation should be read from $r^2g_{+}(r)$ curves, because $r^2g_{+}(r)$ relates to number of ions at r, whereas $g_{-}(r)$ relates to density of ions at r. X-ray results for r_{+-} are usually quoted in D(r) (equivalent of $r^2G(r)$).

(iii) As mentioned in (i) the amount of penetration of like ions into the first coordination shell increases with ion size. Compare the g(r) for $ZnCl_2$ and $BaCl_2$ in Fig. 9. For $ZnCl_2$, there are no chloride ions in the zinc ion positions, but for $BaCl_2$, chloride and barium ions exist at the same r.

Also noted by McGreevy and Mitchell (13), with large cations shielding by the anions is increased, so that although penetration does occur, on average the cation-cation distance is larger such that for SrCl₂ and BaCl₂, it is proposed that second not first interstitial sites are filled.

(iv) The phenomenon of charge cancellation is a signal of a 1:1 salt where beyond about 4\AA , the g(r) are phased so that the $g_{++}(r)$ and $g_{-}(r)$ together are π out of phase with $g_{+-}(r)$. This can be seen clearly in the $g_{\alpha\beta}(r)$ curves for CuCl, see Fig. 6.

(v) How would the existence of a species be manifest in $g_{\alpha\beta}(r)$? The radial distribution functions, g(r), determined using neutron diffraction are "snap-shots", t=0 and so structural parameters evaluated are time-average values. Now for example, if ZnCl existed predominantly in ZnCl₂ melt, then this would be a pseudo l:l melt, with ZnCl and Cl, and charge cancellation would be expected in g(r).

Second, if the r in the species differed from the average cationanion distance of the host melt, then a separate peak in g_(r) must be observed. If r_is the same for melt and species, then the existence of a species depends on its lifetime. We need somehow to show that the complex ions are not exchanging at normal ion exchange times ($\sim 10^{-15}$ s) in order to prove they are "bound". The molecular dynamics (MD) studies of de Leeuw (15) are relevant here. He finds that groups of ions like SrCl do indeed exist for times long compared with the collision time. Even so, these results cannot be regarded as evidence for stable entities, since the prospective species SrCl must retain its identity for a time several orders of magnitude longer than the lifetime of any other group eg. SrCl₃.

It seems justifiable then to stipulate that for a species, MX, the diffusion coefficient of M in the species must be equatable to that of X in the species. It has been shown that for this to be the case, the binding time of M and X in the species must be $\sim 10^{-11}$ s. Such a long-lived arrangement would be seen in g(r), in that the first peak in $g_{\perp}(r)$ would be extremely well coordinated, provided the species was a major constituent (but see (vi)).

(vi) Peak heights in g(r) give an indication of how well coordinated a melt is. For example, the first peak in $g_{\perp}(r)$ for ZnCl₂, see Fig. 7, is much higher and narrower than, say, that for BaCl₂. From this we deduce that the ions are very specifically sited in a well defined network (not necessarily evidence of species existence). The fact that g(r) falls to zero beyond the first peak, as is also the case for MgCl₂, supports this deduction. (vii) The coulomb peaks (in k-space) in 1:1 salts, see for example Fig. 8 for NaCl, are the main peaks which occur at one position in k-space, the peak being negative in $S_{\perp}(k)$. This is related to the regular real-space charge distribution in 1:1 salts.

(viii) The ratio $r_{r_{+}}/r_{+}$ gives an immediate indication of coordination. For example, $r_{-}/r_{+} = \sqrt{8/3}$ for a tetrahedrally coordinated cation. For an octahedral site, $r_{-}/r_{+} = \sqrt{2}$. An example of each type is given by $r_{-}/r_{+} = 1.65$ for CuCl (Eisenberg, et al, (14)), and 1.41 for NaCl (BiggIn and Enderby (5)). Of the melts studied, only ZnCl₂ and CuCl are tetrahedrally coordinated, as they are in the solid.

The fact that other small-cation melts are not tetrahedrally coordinated, eg. MgCl₂, indicates that ion size alone does not control the melt structure. According to its size, 0.74Å, it would be expected that the zinc ion would occupy an octahedral site (radius 0.20 x chloride ion diameter = 0.72Å), instead of the smaller tetrahedral site (radius 0.11 x chloride ion diameter = 0.40Å). The strong polarizing power of the zinc ion (and the cuprous ion in CuCl) enables it to occupy the site.

I have discussed the melt features in general. Now let us consider specific melts.

7. Specific melt structures

Above, we have considered the main points of information extractable from partial $S_{\alpha\beta}(k)$ and $g_{\alpha\beta}(r)$. Now let us consider the structures of specific melts which have been examined. If we then compare these structures with those predicted by theoretical methods or models, eg. Monte Carlo, Molecular Dynamics, Hypernetted Chain (HNC), then we can pinpoint shortcomings of the models in their occasional failure to make accurate predictions.

It will be instructive to categorize the salts into three groups: (i) 1:1 salts; (ii) 2:1 salts; (iii) solid-state layer lattice salts.

(i) Of 1:1 chlorides, a large number have the NaCl structure in the pre-melting solid phase: Li, Na, K, Rb, Cs and Ag. Only cuprous chloride has a four-coordinated (zinc blende) structure. In all cases, except CuCl, the melts show 1:1 characteristic charge cancellation, increasing penetration with ion size, a slight reduction of r_{\perp} on melting and $r_{\perp} \sim r_{\perp} + r$ where r_{\perp} and r_{\perp} are the cation and anion radii. Now, cuprous chloride is tetrahedrally coordinated in both melt and solid with $r_{\perp}/r_{\perp} \sim \sqrt{8/3}$. The $g_{\perp+}(r)$ for CuCl shows unusually little structure, see (14,17) and Fig. 6, compared with that from other salts and although such high penetration of like ions into the first coordination shell together with r_{\perp} being considerably less than $r_{\perp} + r_{\perp}$ (2.38 cf. 2.77Å) indicates a degree of covalency (an octupole moment is set up, see Mahan (18)), there is contrary experimental evidence, see Boyce and Mikkelson (19), from NMR work.

Another problem area lies in some of the results for AgCl, CsCl and KCl. Some of the fine structure in the S(k)'s (20) is thought to

result from the method used to obtain g $_{qR}(r)$, as was reported to be the case for CsCl, now re-examined by Mitchell et al. (private communication).

For all the NaCl-type melts, coordination number according to the rg(r) method falls from 6, to about 4 on melting. For the larger cation melts, higher values are quoted for n , but usually through methods such as integrating to the first minimum in r g(r). Ohno and Furukawa (4) have shown that there is excellent agreement between their semi-empirical formula used to calculate n_{+-} for l:l salts, and results obtained.

In recent work by Ohno et al.(21), KBr is examined using X-ray diffraction, and a comprehensive table of 1:1 salt parameters is given. Again $\bar{r}_{+} \circ r_{+} + r_{+}$ the coordination number by any method is close to 4, and $\bar{r}_{-}/r_{+} \circ \sqrt{2}$, indicative of octahedral siting. It would be interesting to extract partial $g_{\alpha\beta}(r)$'s for KBr using a neutron experiment, because since the values for n_{+} by any method are close to 4, little penetration can be present, and -K must be considered "small" relative to Br (the results for NaCl from X-ray diffraction using methods ii-iv listed in the section on coordination number vary by about the same amount 4.0 - 4.1 for NaCl, 3.5 - 3.7 for KBr).

The difference between $g_{++}(r)$ and $g_{--}(r)$ is thought to be due to polarisation (5), this difference being very slight. Within the error of an experiment carried out on the Dido reactor, Harwell, these g(r) are barely distinguishable, but results in general indicate that $g_{++}(r)$ falls slightly lower than $g_{++}(r)$.

Theorists can obtain <u>all</u> features of these 1:1 salts using models such as the HNC (where direct and indirect correlation functions are summed iteratively to give the total correlation function), i.e. peak positions, amount of penetration, peak heights, coulomb peaks.

(ii) McGreevy and Mitchell have reviewed the 2:1 salts $ZnCl_2$ (16), $CaCl_2$ (10), $BaCl_2$ (22), $SrCl_2$ (23). Increased coordination number follows ion size, as does penetration. Zinc behaves like Cu in CuCl, in that it occupies a tetrahedral site which changes very little on melting. Both $BaCl_2$ and $SrCl_2$ have the fluorite structure in the premelting phase, with close-packed cations. Their coordination number falls from 12 to about 8 on melting. In all cases, the $g_{-}(r)$ lies at about 3.7 - 3.8Å, its width increasing and height decreasing with increase of penetration with ion size for these salts.

The only non-characteristic feature of these melts is the high ordering of ZnCl₂, see Fig. 7, but this follows from its "covalent" nature shown in the solid resulting from its electronic structure.

There is another feature, the first peak position in $g_{++}(r)$ for both $ZnCl_2$ and $CaCl_2$, which is <u>not</u> predicted correctly by HNC calculations using a purely <u>ionic model</u>. All other features of this 2:1 series, including the $g_{++}(r)$ for $SrCl_2$ and $BaCl_2$ are correctly predicted (A. Copestake, private communication). For $ZnCl_2$, $\bar{r}_{+} = 3.8$ Å, vthe solid-state value. For $CaCl_2$ however, the Ca-Ca distance 3.6Å is less than the solid values : two Ca^{2^+} ions at 4.2Å and 8 at 4.95Å from an origin Ca^{2^+} ion. X-ray work by Iwamoto et al.(24) has given a Ca-Ca distance of 6.4Å.

Whether the difference is due to a specific plus-plus interaction or results from polarisation of the anion is an area for further investigation.

(iii) Solid-state layer lattices of the CdCl₂ type include MgCl₂, NiCl₂, FeCl₂, MnCl₂ which therefore consist of octahedrally coordinated cations in a ccp anion array. Zinc chloride was reported as being CdCl₂ type, but is clearly tetrahedrally coordinated (16). The results for S_{$\alpha\beta$}(k) and g_{$\alpha\beta$}(k) for MgCl₂ are shown in Figs. 3-4. The Mg-Cl separation is 2.45Å just under the solid state value. Similar to other salts the Cl-Cl separation is 3.64±0.05Å with a coordination number n = 6.85±1. For magnesium ions, \bar{r}_{++} is 3.62±0.08Å, with n_{++} = 5.2±1.5. The coordination number n₊₋ ranges from 3.7 for method rg(r) to 3.5 for integration to the first minimum in g(r). The ion is very small, so the method has little influence on n₊₋. Also note there is little penetration of like ions into the first coordination shell.

It was shown in §4 that MnCl₂ is isomorphous with MgCl₂ with n₊₋ \sim 4 again. Also for NiCl₂, n₊₋ \sim 4 (A. Howe, private communication).

8. Binary melts

For a binary melt AX .BY, ten isotopic substitution experiments are required to extract all ten partial structure factors, although for any <u>one</u> structure factor only four experiments are required, three if the ion-ion pair is of <u>like</u> ions. If, however, one of the ions is a null scattering ion, eg. 0 Li , 0 Ni , then the binary melt becomes effectively a single melt again and only three experiments will completely define the structure.

One such experiment currently in progress (Biggin and Blander , private communication) is the study of $AlCl_3$.⁰LiCl, which will be of interest for several technologies.

Another binary melt about to be investigated (Biggin) is MgCl₂. BaCl₂, in order to provide structural evidence for the inference by Lumsden (25) that the melt changes structure at equimolar composition, giving rise to discontinuities in the enthalpy of mixing curves.

If we are interested in thermodynamic properties of mixing, eg. AG AG, AH, then neutron diffraction provides a route: only three partial structure factors, evaluated at k=0 are needed. This follows from an extension of the formulation given by Enderby and Neilson (26) based on work by Kirkwood and Buff (27): from a knowledge of (S AA (0)+ BB (0)-2S AB (0), these thermodynamic functions can be derived (they are linked through activity coefficient). Given knowledge of isothermal compressibility and number density, only one partial structure factor from the above three is needed to access excess functions.

A preliminary study carried out by Biggin has shown that ΔG^{excess} can be evaluated to the correct order of magnitude for salt mixtures

such as (Na,K)Cl using S(0) values taken from MSA (mean spherical approximation) calculations. Thus we expect good agreement with calorimetry when this work is extended to neutron scattering examination of binary melts at zero wave-vector.

9. Discussion

It is clear from the melt structures considered, that ion size plays an important role in determining melt parameters. However, the $ZnCl_2$ structure, for example, emphasizes that electronic configuration also has an influence and can bring about a degree of covalency. Neutron diffraction alone is not sufficient to give specific results on existence of species (being a "t=0" experiment), but can indicate from average ion positions whether their existence is likely.

There are still aspects of structure which cannot be modelled correctly, such as the Zn-Zn separation predicted on an ionic basis. The value of separating out <u>partial</u> structure factors and radial distribution functions is seen when comparisons are made with theoretical predictions, since only in this way can <u>specific</u> shortcomings in the theory be identified.

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REFERENCES

1	H. Ohno and K. Furukawa, J. Chem. Soc. Faraday Trans. I, 74 (1978) 804.
2	F.G. Edwards, J.E. Enderby and D.I. Page, J. Phys. C., 8 (1975) 3483.
3	S. Biggin, M. Gay and J.E. Enderby, J. Phys. C., to be submitted.
4	H. Ohno and K. Furukawa, J. Chem. Soc. Faraday Trans. I, 77 (1981) 1981.
5	S. Biggin and J.E. Enderby, J. Phys. C., 15 (1982) L305.
6	Y. Takagi and T. Nakamura, J. Chem. Soc. Japan, Chem. Ind. Chem., 6 (1982) 928.
7	L. Koester, K. Knopf and W. Waschowski, Z. Phys., A 282 (1977) 371.
8	G.W. Neilson and J.E. Enderby, J. Phys. C., 15 (1982) 2437.
9	J.E. Enderby and S. Biggin, Advances in Molten Salt Chemistry,
	Vol. 5, Ch.1, Elsevier Scientific Publishing Co., 1983.
10	S. Biggin and J.E. Enderby, J. Phys. C., 14 (1981) 3577.
11	Y. Waseda, Structure of Non-Crystalline Materials: Liquids and
	Amorphous Solids, McGraw-Hill, Maidenhead, UK, 1980.
12	C.A. Coulson and G.S. Rushbrooke, Phys. Rev., 56 (1939) 1216.
13	R.L. McGreevy and E.W.J. Mitchell, J. Phys. C., 15 (1982) 5537.
14	S. Eisenberg, JF. Jal, J. Dupuy, P. Chieux and W. Knoll, Phil.
	Mag., 46A (1982) 195.
15	S.W. de Leeuw, Mol. Phys., 36 (1978) 103.
16	S. Biggin and J.E. Enderby, J. Phys. C., 14 (1981) 3129.
10	D.1. Page and K. Mika, J. Phys. C., $4(19/1)$ 3034.
10	G.D. Manan, Chem. Phys. Lett., 76 (1980) 183.
70	J.B. Boyce and J.C. Mikkelson, J. Phys. C., 10 (1977) L41.
20	U.I. Derriell and J. Dupuy, J. de. Phys., 36 (1975) 191.
21	Chem Son Earaday Trang 2 70 (1092) 462
22	E C Edwards J E Endorby P A Hove and D J Dago J Dhug C
22	11. (1978) 1053
23	$R_{\rm L}$ McGreevy and $E_{\rm L}W_{\rm L}$ Mitchell, T Phys. C 15 (1982) 5537
24	N. Iwamoto, N. Umesaki, T. Asahina and M. Kosaka, J. Chem. Soc.
	Japan, Chem. Ind. Chem., 6 (1982) 920.
25	J. Lumsden in Ionic Liquids. (eds. D. Inman and D.G. Lovering).
	Plenum Press, 1981.
26	J.E. Enderby and G.W. Neilson, Rep. Prog. Phys., 44 (1981) 593.
27	J.G. Kirkwood and F.P. Buff, J. Chem. Phys., 19 (1951) 774.

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Figure 1. Reduced intensity function ki(k) for $MnCl_2$: \circ X-ray data due to Ohno and Furukawa [1]; \cdot neutron data due to Biggin et al.[3].



Figure 3. S $_{\alpha\beta}^{\beta}(k)$ due to Biggin et al.[3] for MgCl₂.



Figure 2. F(k) for MgCl due to Biggin et al.[3]. A: raw data; B: reconstructed F(k)using S(k) in Fig. 3.



Figure 4. $g_{\alpha\beta}(\mathbf{r})$ due to Biggin et al. [3] for MgCl₂. ---Mg-Cl; \cdots Cl-Cl; ----Mg-Mg.



Figure 5. Reduced intensity for NaCl: ··· X-ray data due to Ohno and Furukawa [4]; _____ neutron data due to Biggin and Enderby [5].



Figure 7. $g_{\alpha\beta}$ for ZnCl₂, due to Biggin and Enderby [16]. A:ZnZn; B:ClCl; C:ZnCl.



Figure 8. S (k) for NaCl due to Biggin and Enderby [5]. A:NaNa; B:ClCl; C:NaCl.



Figure 9. Increased penetration with ion size _____ cation-anion; +++ anion-anion.

THERMODYNAMIC PROPERTIES OF A1C13-CONTAINING MELTS

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ABSTRACT

A model of the vapor pressure of the ternary liquid LiCl-NaCl-AlCl₃ system has been developed based on available thermodynamic data. This model covers the entire ternary miscibility range and has been programmed on a digital computer.

INTRODUCTION

Melts of NaCl-LiCl-AlCl₃ occur in many processes. Previous thermodynamic models of the vaporization behavior of these melts have dealt with only binary systems (1) or the ternary system with very low AlCl₃ concentrations (2). In some instances, higher concentrations of AlCl₃ are expected to be encountered and systems where $X_{AlCl_3} \simeq 0.50$ are especially interesting. The model described in this paper makes use of available published data to treat the ternary system between 0 and 80% AlCl₃ (80% AlCl₃ is the approximate point at which a miscibility gap is encountered). This model has been translated into a digital computer program.

The data on which this model is based are not considered final and model revisions are expected as more data emerge. However, the present model is believed to give a reasonably realistic description of the NaCl-LiCl-AlCl₃ system.

PHYSICAL BASIS OF THE MODEL

A 19-parameter model is developed for the ternary system LiCl-NaCl-AlCl₃ based on equilibrium constants and activity coefficients. The description of the basic range $(X^{O}_{AlCl_{3}} < 0.5)$ hardly needs to be improved, while further refinements are recommended for the acid range as more accurate data become available. The model can be used for calculation of (a) activities, (b) vapor pressure and composition above

liquid, (c) composition of liquid and vapor when temperature and pressure are given, (d) condensation temperatures of gas and composition of condensing liquid.

The model will, as far as possible, be based on established structural data and thermodynamic principles. An important feature of the present model is that it will contain previously developed models as limiting cases (*i.e.*, the systems LiCl-AlCl₃: $X^{O}_{AlCl_3} < 0.50$, NaCl-AlCl₃: $X^{O}_{AlCl_3} < 0.50$, LiCl-NaCl-AlCl₃: $X^{O}_{AlCl_3} < 0.64$). Emphasis will be put on making a simple model, even if at first glance it may not seem so to the reader. It is, however, to be remembered that it is a very complex system which is to be described over a wide temperature range. It is believed that the developed 19-parameter model indeed represents a minimum number of parameters needed for a meaningful description.

The systems MeCl-AlCl₃ are characterized by a liquidus temperature of about $600-800^{\circ}C$ in the basic range which then drops sharply to 150- $200^{\circ}C$ around $X^{\circ}_{AlCl_3} = 0.50$. An isothermal study of the system over the entire concentration range of interest ($0 < X^{\circ}_{AlCl_3} < 0.80$) has not been carried out due to the high vapor pressure of the acid mixtures at elevated temperatures. Based on Raman and infrared spectroscopy (3-6), the structural entities in these melts can nevertheless be summarized as follows:

X ^o AlCl ₃	0	0.50	0.667	0.80
Stoichiometric Composition	MeC1	MeA1C14	MeAl ₂ Cl ₇	
Melt species	Li ⁺ , Na ⁺ Cl ⁻ , AlCl ₄	Li ⁺ , Na ⁺ AlCl ₄ Al ₂ Cl ₇ , Al ₂ Cl ₆ (Al ₃ Cl ₁₀)		

The present model will be based on the presence of the major species given above. For simplification the species Al_3Cl_{10} is neglected although it probably exists (4-6).

With reference to earlier work on the vapor above basic melts (1,2) the gas is considered to consist of the following molecules:

LiAlCl₄, NaAlCl₄, AlCl₃, Al₂Cl₆

The gas is assumed to behave ideally and no corrections are performed due to nonideality even at high pressures. Such a correction would, however, be easy to perform but it is not considered necessary at the present stage.

The melt is considered to be a modified Temkin mixture (7) by considering Li⁺ and Na⁺ as a cationic mixture and Cl⁻, $Alcl_{4}$, Al_2Cl_{7} , and Al_2Cl_6 as a modified anion mixture. Temkin activity coefficients will be introduced when justified by experimental data.

The following eight independent equilibria will be considered:

$LiAlCl_4(\ell) =$	LiA1Cl ₄ (g)	(1)	I
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 $NaA1Cl_{4}(\ell) = NaA1Cl_{4}(g)$ (2)

$$A1C1_3(\ell) = A1C1_3(g) \tag{3}$$

 $LiAlCl_{4}(\ell) = LiCl(\ell) + AlCl_{3}(\ell)$ (4)

 $NaAlCl_{4}(\ell) = NaCl(\ell) + AlCl_{3}(\ell)$ (5)

$$2\text{LiAlCl}_{4}(\ell) = \text{LiCl}(\ell) + \text{LiAl}_{2}\text{Cl}_{7}(\ell)$$
(6)

 $2NaAlCl_{4}(\ell) = NaCl(\ell) + NaAl_{2}Cl_{7}(\ell)$ (7)

$$2A1C1_3(g) = A1_2C1_6(g)$$
 (8)

Equilibria in a mixed Li^{\downarrow} , Na⁺ system will be described by the Flood-Muan or by a first-approximation of the Flood, Førland, and Grjotheim model (8).

$$\ln K_{\text{Li,Na}} = X_{\text{Li}} \ln K_{\text{Li}} + X_{\text{Na}} \ln K_{\text{Na}}$$
(9)

where

$$X_{Li} = \frac{n_{Li}^{+}}{n_{Li}^{+} + n_{Na}^{+}}$$
 and $X_{Na} = \frac{n_{Na}^{+}}{n_{Li}^{+} + n_{Na}^{+}}$ (10)

This simplified equation may be elaborated further if more data become available.

The avoidance of thermodynamic inconsistencies is emphasized in the model. The primary quantities calculated are the vapor pressure and activity of AlCl₃. The AlCl₃ activity has a straightforward meaning as:

$$a_{A1C1_3} = P_{A1C1_3}/P^{O}_{A1C1_3}$$
, where

 ${\rm P^O}_{\rm A1C1_3}$ denotes pressure over pure A1C1_3. This activity is also common

to all chloroaluminate melts and no standard state confusion is likely to occur.

The quantity pCl(-log c_{Cl} -) is often used as a primary quantity of chloroaluminate melts but it has an inherent weakness. Used properly, in the meaning a_{MCl_y} , it is well defined, but very often pCl is used loosely as an undefined single ion activity. This may lead to confusion, especially in connection with interpretation of concentration cells (9). In addition, the standard state will vary according to which MCl_y chlorides are present. However, if one wishes to calculate pCl it may be obtained through a Gibbs-Duhem integration from a_{AlCl_3} .

DEVELOPMENT OF MODEL

Notation

In order to treat the present system in an efficient way, it is necessary to use a simple and easily understandable notation. The following definitions are introduced:

Main Symbols

	Х	:	Modified Temkin ion fraction (see below)
	Р	:	Pressure in atm
	n	:	Number of moles
	а	:	Activity
	γ	:	Temkin activity coefficient
	К	:	Thermodynamic equilibrium constant
	к'	:	Ion fraction stoichiometric coefficient
	x _A o	:	Bulk composition of AlCl ₃ in mole fraction.
Subsci	ipt	<u>s</u> to	ο X, P, n, a, and γ:
	г:	Li	h^+ , N : Na ⁺ , 1 : Cl ⁻ , 4 : AlCl ₄
	3:	Al	Cl_3 , 6 : Al_2Cl_6 , 7 : Al_2Cl_7
	t:	to	otal .
Subscr	<u>ipt</u>	<u>s</u> t	co K and K':
	Acc	ordi	ng to Equations (1-8).

Examples

$$X_{N} = \frac{n_{Na}^{+}}{n_{Li}^{+} + n_{Na}^{+}}$$
$$X_{4} = \frac{n_{A1C1_{4}}}{n_{C1}^{-} + n_{A1C1_{4}}^{-} + n_{A1_{2}C1_{7}}^{-} + n_{A1_{2}C1_{6}}^{-}}$$
$$a_{N4} = a_{NaA1C1_{4}}^{-} = X_{N}^{X_{4}} \gamma_{N4}^{-} \cdot$$

Model for the Binary Systems LiCl-AlCl₃ and NaCl-AlCl₃

The strategy of the present model construction is first to obtain models for the two binary systems $LiCl-AlCl_3$ and $NaCl-AlCl_3$ and then obtain a model for the ternary system $LiCl-NaCl-AlCl_3$ as an extension of the binary model.

The work by Linga *et al.* (1) is the most complete vapor pressure study of basic chloroaluminate melts and the models developed from that study will be included in the present model. Their models do, however, only treat compositions where $\chi_A^{O} < 0.50$ and the presence of Al₂Cl₇ and Al₂Cl₆ (or AlCl₃) in the liquid phase was ignored. Therefore Equations (6) and (7) were not considered.

With reference to the physical model given, the following stoichiometric relations are valid using LiCl-AlCl₃ as an example:

Base 1 mole of mixture: $n_{A1C1_3}^{o} + n_{LiC1}^{o} = X_A^{o} + X_L^{o} = 1$

$$X_{A}^{0} = n_{4} + 2n_{6} + 2n_{7}$$
 (11)

$$1 - X_A^0 = n_1 + n_4 + n_7$$
 (12)

$$\Sigma n = n_1 + n_4 + n_6 + n_7 = 1 - X_A^O + n_6$$
(13)

$$X_1 = \frac{n_1}{1 - X_A^0 + n_6}, \quad X_4 = \frac{n_4}{1 - X_A^0 + n_6}$$
 (14)

$$X_6 = \frac{n_6}{1 - X_A^0 + n_6}, \quad X_7 = \frac{n_7}{1 - X_A^0 + n_6}$$
 (15)

$$2\text{LiAlCl}_{4}(\ell) = \text{LiCl}(\ell) + \text{LiAl}_{2}\text{Cl}_{7}(\ell) : K_{6}^{\prime} = \frac{X_{1}X_{7}}{X_{4}^{2}}$$
(16)

$$LiAlCl_{4}(\ell) = LiCl(\ell) + 0.5Al_{2}Cl_{6}(\ell) : K_{4}^{\prime} = \frac{X_{1}X_{6}^{0.5}}{X_{4}}$$
(17)

Equations (11-17) give expressions for X_1 , X_4 , X_6 , X_7 in terms of K_6' and K_4' . The same expressions will be valid for the NaCl-AlCl₃ system when K_7' and K_5' are substituted for K_6' and K_4' . The solutions of the equations will not be given here, but will be part of the complete model for the ternary system given in the next section.

Following the model of Linga $et \ al.$ (1), the activity coefficients of LiCl and LiAlCl, are given as:

$$\gamma_{L1} = \exp\left\{\frac{\alpha_L \beta_L}{RT} \left(\frac{X_{4}}{X_1 + \beta_L X_{4}}\right)^2\right\}$$
(18)

$$\gamma_{L4} = \exp\left\{\frac{\alpha_L}{RT}\left(\frac{X_1}{X_1 + \beta_L X_4}\right)^2\right\}$$
(19)

In the present model where high precision is not attempted in the acid region, we set

and

$$\gamma_{L7} = 1$$

As $X_1 \simeq 0$ in the acid region, we obtain the following simplified expression for the thermodynamic equilibrium constants K_4 and K_6 in this region using Equations (18) and (19).

$$K_{4} = K_{4}^{\prime}\sqrt{2} \exp\left\{\frac{\alpha_{L}}{\beta_{L}RT}\right\}$$
(20)

$$K_{6} = K_{6}^{*} \exp \left\{ \frac{\alpha_{L}}{\beta_{L} RT} \right\}$$
(21)

Similar expressions are valid for the NaCl-AlCl₃ system.

Model for Ternary LiCl-NaCl-AlCl₃ Melts

The previous model for ternary $LiCl-NaCl-AlCl_3$ melts with low content of $AlCl_3$ was semiempirical with basis in measured total pressure.

The formation of AlCl₃(g) can be written in a general way as follows:

$$MA1Cl_4(\ell) = MCl(\ell) + A1Cl_3(g)$$
(22)

*)
$$a_{A1_2C1_6} = a_{A1C1_3}^2 = 2X_{A1_2C1_6}$$

This means that $\gamma_6 = 2$ is introduced. The basis for this is the knowledge that a liquid-liquid immiscibility gap appears for NaCl-AlCl₃ at $X^O_A \simeq 0.80$ where $X_{Al_2Cl_6} \simeq 0.50$. The pressure of $AlCl_3(g)$ can be represented by a Flood-Muan (8) model as follows:

$$P_{3} = K_{3}(K_{4})^{X_{L}}(K_{5})^{X_{N}} \left(\frac{X_{4}}{X_{1}}\right) \left(\frac{\gamma_{L4}}{\gamma_{L1}}\right)^{X_{L}} \left(\frac{\gamma_{N4}}{\gamma_{N1}}\right)^{X_{N}}$$
(23)

The other vapor pressures are then given in terms of P3 as:

$$P_{L4} = K_1 (K_3 K_4)^{-1} X_L X_1 \gamma_{L1} P_3$$
(24)

$$P_{N4} = K_2 (K_3 K_5)^{-1} X_N X_1 \gamma_{N1} P_3$$
(25)

$$P_6 = K_8 P_3^2$$
 (26)

$$P_{t} = P_{3} + P_{L4} + P_{N4} + P_{6}$$
(27)

As the model now stands, only binary data are needed for the calculation of the pressures above the ternary melts.

A minor ternary term used successfully for ternary melts dilute in $AlCl_3(2)$ will, however, be introduced. This implies introducing regular solution activity coefficients due to the mixing of Li⁺ and Na⁺ ions. We hence get:

$$\gamma_{L1} = \exp\left\{\frac{bX_N^2}{T}\right\} \exp\left\{\frac{\alpha_L \beta_L}{RT} \left(\frac{X_4}{X_1 + \beta_L X_4}\right)^2\right\}$$
(28)

$$\gamma_{L4} = \exp\left\{\frac{bX_{N}^{2}}{T}\right\} \exp\left\{\frac{\alpha_{L}}{RT} \left(\frac{X_{1}}{X_{1} + \beta_{L}X_{4}}\right)^{2}\right\}$$
(29)

RESULTS

The final model was arrived at through an extensive trial-and-error process proceeding partly from a simpler model than the final and partly from a more complex model. The trial-and-error procedure will not be discussed, but we will here present the final model in a closed form with parameters.

(a) Fractions $X_1,\;X_4,\;(X_6),$ and (X_7) are given as functions of $K_{\rm A}'$ and $K_{\rm B}'$ by solution of two quadratic equations:*)

$$\frac{K_{A}^{\dagger} n_{4}^{2} + n_{1} n_{4} + n_{1}^{2} - n_{1} + X_{A}^{0} n_{1} = 0}{(30)}$$
*) $K_{A}^{\dagger} = \frac{X_{1} \cdot X_{7}}{X_{4}^{2}} \qquad K_{B}^{\dagger} = \frac{X_{7}}{X_{1} \cdot X_{6}}$

$$n_{4}^{2} + n_{4} (2X_{A}^{0} - 1 + K_{B}^{i} n_{1} + 3n_{1}) + n_{1}^{2} (2K_{B}^{i} + 2) + n_{1} (-2K_{B}^{i} + 3K_{B}^{i} X_{A}^{0} + 3X_{A}^{0} - 2) + X_{A}^{0^{2}} - X_{A}^{0} = 0$$
(31)

$$n_6 = n_1 + 0.5n_4 - 1 + 1.5X_A^0$$
 (32)

$$X_1 = \frac{n_1}{1 - X_A^0 + n_6}$$
 $X_4 = \frac{n_4}{1 - X_A^0 + n_6}$ (33)

$$X_6 = \frac{n_6}{1 - X_A^0 + n_6}$$
 $X_7 = 1 - X_1 - X_4 - X_6$ (34)

$$K_{A}' = \left(K_{6} / \exp \left\{ \frac{\alpha_{L}}{\beta_{L} RT} \right\} \right)^{X_{L}} \left(K_{7} / \exp \left\{ \frac{\alpha_{N}}{\beta_{N} RT} \right\} \right)^{X_{N}}$$
(35)

$$K_{B}' = \frac{\frac{X_{L}}{K_{6}} \frac{X_{N}}{K_{7}}}{K_{4} \frac{2X_{L}}{K_{5}} \frac{2X_{N}}{K_{5}}} \left(\exp \left\{ \frac{\alpha_{L}}{\beta_{L} RT} \right\} \right)^{X_{L}} \left(\exp \left\{ \frac{\alpha_{N}}{\beta_{N} RT} \right\} \right)^{X_{N}}$$
(36)

(b) Equations for cation fractions:

$$X_{\rm L} = \frac{X_{\rm L}^{\rm o}}{1 - X_{\rm A}^{\rm o}}$$
 (37)

$$x_{N} = \frac{x_{N}^{o}}{1 - x_{A}^{o}}$$
(38)

(c) Pressure equations:

$$P_{3} = K_{3} K_{4}^{X} K_{5}^{X} \left(\frac{X_{4}}{X_{1}}\right) \left(\frac{\gamma_{L4}}{\gamma_{L1}}\right)^{X} \left(\frac{\gamma_{N4}}{\gamma_{N1}}\right)^{X} N$$
(39)

$$P_{L4} = K_1 (K_3 K_4)^{-1} X_L X_1 \gamma_{L1} P_3$$
(40)

$$P_{N4} = K_2 (K_3 K_5)^{-1} X_N X_1 \gamma_{N1} P_3$$
(41)

$$P_{6} = K_{8} P_{3}^{2}$$
 (42)

$$P_{t} = P_{3} + P_{L4} + P_{N4} + P_{6}$$
(43)

fitting
the
from
obtained
parameters
constant
Equilibrium
(P)

	K473	K973	∆H ⁰ 973	^S ⁰ 973	^C ⁰
	(atm,stands	ırd state)	J/mol	J/mol degree	J/mol degree
(1) $LiAlCl_4(\ell) = LiAlCl_4(g)$	4.80.10 ⁻⁶	0.348	85720	79.31	-68
(2) NaAlCl ₄ (\mathcal{K}) = NaAlCl ₄ (g)	$1.42 \cdot 10^{-8}$	$6.12 \cdot 10^{-2}$	116900	96.91	-68
(3) A1Cl ₃ (χ) = A1Cl ₃ (g)	$1.48 \cdot 10^{-3}$	19.88	58950	85.44	0≠
(4) $LiAlCl_4(\ell) = LiCl(\ell) + AlCl_3(\ell)$	5.11.10 ⁻⁷	$1.03 \cdot 10^{-2}$	75840	39.88	0
(5) NaAlCl ₄ (λ) = NaCl(λ) + AlCl ₃ (λ)	1.55.10 ⁻⁹	4.22.10 ⁴	95780	33.82	0
(6) $2LiAlCl_4(\ell) = LiCl(\ell) + LiAl_2Cl_7(\ell)$	$1.32 \cdot 10^{-6}$	$5.13 \cdot 10^{-3}$	63258	21.18	0
(7) $2NaAlCl_4(\ell) = NaCl(\ell) + NaAl_2Cl_7(\ell)$	6.66.10 ⁻⁹	3.06.10 ⁻⁴	84058	21.18	0
(8) $2AIC1_3(g) = A1_2C1_6(g)$	1.11.10 ⁶	0.156	-115725	-134.40	0≠

 $K_3 = \exp \left[-\frac{1}{T} (7089.6 - 9.474T + 0.00793T^2 - 7.797.10^{-6}T^3 + 3.9.10^{-9}T^4 - 7.716.10^{-13}T^5 + 6070) \right]$ + 10.276 - 9.474 lnT + 0.01586T - 1.17.10⁻⁵T² - 5.2.10⁻⁹T³ - 9.645.10⁻¹³T⁴ + 56.9]

 $K_8 = \exp \left[-\frac{1}{T} \left(-13918.1 + 0.5482T + 3.319\cdot 10^{-3}T^2 - 3.92\cdot 10^{-6}T^3 + 2.324\cdot 10^{-9}T^4 - 5.482\cdot 10^{-13}T^5 \right) \right]$ ۳ ۲ -6 2 ĩ

- 6.852.10⁻¹³T⁴ - 6.904],

66

 ΔC_p^o is set equal to zero for all reactions involving only liquid phases. This is, however, not justified when gaseous phases appear in the equilibrium. For Equations (3) and (8), K is known as a function of temperature from the JANAF Thermochemical Tables (10). For Equations (1) and (2), the approximation formula given by Kubaschewski and Alcock (11) is used.

$$A_x B_y(\ell) = A_x B_y(g)$$
 $\Delta C_p^o = -2.7 (x + y) cal/mol degree$

This gives ΔC_p^0 = -68 J/mol degree for Equations (1) and (2). The equations for K then have the form:

$$K_{\rm T} = \exp \left\{ \frac{1}{R} \left[\frac{-\Delta H_{973}^{\rm o}}{T} + \Delta S_{973}^{\rm o} + \Delta C_{\rm P}^{\rm o} \left[\frac{973 - T}{T} + \ln \left(\frac{T}{973} \right) \right] \right\}$$
(44)

(e) Activities of liquid mixtures:

$$\gamma_{L1} = \exp\left\{\frac{b X_{N}^{2}}{T}\right\} \exp\left\{\frac{\alpha_{L} \beta_{L}}{RT} \left(\frac{X_{4}}{X_{1} + \beta_{L} X_{4}}\right)^{2}\right\}$$
(45)

$$\gamma_{L4} = \exp\left\{\frac{\mathbf{b} \ \mathbf{X}_{N}^{2}}{T}\right\} \exp\left\{\frac{\alpha_{L}}{\mathbf{R}T} \left(\frac{\mathbf{X}_{1}}{\mathbf{X}_{1} + \beta_{L}\mathbf{X}_{4}}\right)^{2}\right\}$$
(46)

$$\gamma_{N1} = \exp\left\{\frac{b X_L^2}{T}\right\} \exp\left\{\frac{\alpha_N^2 \beta_N}{RT} \left(\frac{X_4}{X_1 + \beta_N X_4}\right)^2\right\}$$
(47)

$$\gamma_{N4} = \exp\left\{\frac{b X_{L}^{2}}{T}\right\} \exp\left\{\frac{\alpha_{N}}{RT} \left(\frac{X_{1}}{X_{1} + \beta_{N} X_{4}}\right)^{2}\right\}$$
(48)

The following activity coefficient parameters are introduced:

$$\frac{\alpha_L}{R} = 2150 \qquad \frac{\alpha_N}{R} = 1843$$

$$\beta_L = 3.115 \qquad \beta_N = 3.051$$

$$b = -564$$

$$\gamma_6 = 2$$

$$\gamma_7 = 1 (i.e., deviation from ideality is ignored)$$

(f) Variables

 X_A^o , X_L^o and T X_N^o = 1 - X_A^o - X_L^o

The present model is a 19-parameter model with 12 equilibrium parameters (ΔH^{o} and ΔS^{o}) and six activity coefficient parameters and one assumption concerning ΔC_{p}^{o} for Equations (1) and (2). The data for Equations (3) and (8) are taken from JANAF Thermochemical Tables (10).

The 12 parameters ΔH_1^0 , ΔS_1^0 , ΔH_2^0 , ΔS_2^0 , ΔH_4^0 , ΔS_4^0 , ΔH_5^0 , ΔS_5^0 , α_L/R , β_L , α_N/R , and β_N are all taken from a refitting of the data for the two binary systems LiCl-AlCl₃ and NaCl-AlCl₃ (1). This fit is based on determinations of total pressure as well as vapor composition (1,2). The relevance of the parameters has been discussed earlier.

The parameter b was estimated from data by Hersh and Kleppa (12) on LiCl-NaCl mixtures but could, of course, have been made an adjustable parameter.

The parameter $\gamma_6 = 2$ was introduced in order to obtain liquid-liquid immiscibility at $X_A^O = 0.80$. The last five parameters were used for bridging the high-temperature data for basic melts and low-temperature data for acidic melts. ΔH_7^O and ΔS_7^O were given values so that $P_t = 0.382$ atm for $X_{A}^O = 0.50$ and t = 700°C Linga *et al.* (1) and $P_t = 0.0946$ atm at $X_{A}^O = 0.60$ and t = 200°C Viola *et al.* (13). This is a somewhat bold procedure and would have had to be abandoned if unreasonable values of ΔH_7^O and ΔS_7^O had resulted. Rather probable values are, however, obtained.

Then ΔS_6^o was set equal to ΔS_7^o and ΔH_6^o was determined by the requirement that

 P_t (LiC1-A1C1₃) = $2P_t$ (NaC1-A1C1₃)

for x_A^o = 0.60 and t = 200°C. This last condition is a rough guesstimate, but better values may be inserted.

Chloride Activity

The chloride activity in binary $LiCl-AlCl_3$ and $NaCl-AlCl_3$ or ternary $LiCl-NaCl-AlCl_3$ melts may be obtained straightforwardly by modification of Equations (45) and (47).

$$a_{MC1} = X_1 \left(\exp \left\{ \frac{\alpha_L \beta_L}{RT} \left(\frac{X_{i_k}}{X_1 + \beta_L X_{i_k}} \right)^2 \right\} \right)^{X_L} \left(\exp \left\{ \frac{\alpha_N \beta_N}{RT} \left(\frac{X_{i_k}}{X_1 + \beta_N X_{i_k}} \right)^2 \right\} \right)^{X_N}$$
(49)

or by integration of the Gibbs-Duhem equation:

$$\int_{X_{1}=1}^{X_{1}} d\ln a_{MC1} = -\int_{X_{1}=1}^{X_{1}} \frac{X_{A}^{o}}{1 - X_{A}^{o}} d\ln P_{A1C1_{3}}$$
(50)

where the ratio $X_{T_{i}}/X_{N}$ is kept constant. *)

Equation (49) is the easiest to use, but calculations according to (50) were also carried out for the binary as well as a ternary system to perform the consistency check that they indeed give identical results.

As an illustration, Table I gives the drop in chloride activity around 50 mol% AlCl $_3$ for 1073 K and 473 K.

A typical feature of the chloride activity is that the drop around $X^{O}_{AlCl_{3}} = 0.50$ is much less pronounced at 1073 K than at 473 K for the binary NaCl-AlCl₃ system. The ratio

$$a_{MC1}(X_{A1C1_3}^{o} = 0.48) / a_{MC1}(X_{A1C1_3}^{o} = 0.52)$$
 is

 $3.8\cdot10^6$ at 473 K but only 13 at 1073 K. The activity drop for the LiCl-AlCl₃ is less than for the NaCl-AlCl₃ system while the Li_{0.5}Na_{0.5}Cl-AlCl₃ shows an intermediate behavior.

DISCUSSION

Comparison with Experimental Data

In certain concentration areas, the developed model must still be

*)A direct use of Equations (45) and (47) with the Temkin activity definition gives:

$$\mathbf{a}_{MC1}' = \mathbf{a}_{LiC1}^{X} \cdot \mathbf{a}_{NaC1}^{N} = (\mathbf{X}_{L} \mathbf{X}_{1})^{X} \cdot \mathbf{y}_{L1}^{X} (\mathbf{X}_{N} \mathbf{X}_{1})^{N} \mathbf{y}_{N1}^{X}$$

$$= X_{L}^{X_{L}} X_{N}^{X} \left(\exp \left\{ \frac{b X_{L}^{2}}{T} \right\} \right)^{X_{L}} \left(\exp \left\{ \frac{b X_{N}^{2}}{T} \right\} \right)^{X_{N}} \cdot a_{MC1}$$

where a_{MC1} is the activity given by Equation (49). It is seen that the first four terms are constant when X_L/X_N and T are constant. They disappear due to the requirement that the chloride activity is set equal to unity for a pure chloride mixture as well as for pure LiCl or NaCl.

considered as crude, and it has some deficiencies which will be discussed later. Let us, however, first examine the model for temperatures and concentrations where fairly reliable data are available and see how it performs. Table II gives some comparisons with experimental data for the binary systems and Table III for available ternary data.

Table II shows that the good agreement between model and data for the binary systems LiCl-AlCl₃ and NaCl-AlCl₃ for $0 < X_A^0 \le 0.50$ and T = 973 K is retained by the expansion of the model. It is encouraging to note that the expansion to also cover the data for 50 mol% NaCl - 50 mol% AlCl₃ at 973K did not have any adverse effect on the lower range.

The representation of the data for NaCl-AlCl₃, $0.50 < X_A^0 \le 0.80$ at 473 K are quite good when it is realized that the data is extrapolated 500K. It is not considered complicated to expand the model to give better agreement by introduction of $\Delta C_P^0(AlCl_3(\ell))$ (14) and variable activity coefficients for Al₂Cl₇ and Al₂Cl₆. The species Al₃Cl₁₀ may also be introduced. This procedure is, however, not considered justified at the present stage as the experimental data are under revision.

Table III shows that the model gives a very good description of available ternary data for mixtures with low AlCl₃ content. The content of AlCl₃ in the vapor is slightly underestimated, P_{LiAlCl_4} coming out exact and P_{NaAlCl_4} slightly overestimated so that the total pressure is equal to the experimental pressure.

A Qualitative Description of the System

(a) Binary Systems

On the basic side the gaseous molecule MAlCl₄ is the main gaseous species until near 50 mol% AlCl₃ when AlCl₃ becomes the major gas species.

Table IV gives the composition $X^{O}_{\mbox{A}}$ when AlCl3 or Al2Cl6 becomes the major gas species.

In the temperature range $473 \leq T \leq 773K \text{ AlCl}_3$ or Al_2Cl_6 becomes the major gas species between $0.48 < X_0^A < 0.5$. At low temperatures Al_2Cl_6 becomes the major gas species at lower AlCl_3 content for the NaCl-AlCl}3 than for the LiCl-AlCl}3 system, while the opposite is the case at higher temperatures due to dissociation of the LiAlCl}4.

The total pressure increases rapidly with addition of small amounts of AlCl₃, then there is a moderate increase (at one part nearly no increase) till near 50 mol% AlCl₃. Around this concentration a strong increase is seen and then the pressure increases until 80 mol% AlCl₃ where the pressure becomes equal to the pressure of pure AlCl₃(ℓ) as it should. The model is, of course, only valid above the liquidus line of the system. This means that the pressure in the range $0 < X^{O}_{AlCl_{3}} < 0.40$ and 473 K does not have any meaning. It is, however, interesting to note that if the liquid could be super-cooled to this temperature, a liquid-liquid immiscibility on the basic side should be observed.

The total pressure of the LiCl-AlCl₃ system is higher than the corresponding NaCl-AlCl₃ system, except near 80 mol% AlCl₃ when they have to become approximately equal. The difference is up to a factor of 10 on the basic side and a factor of 2 on the acid side.

(b) The LiCl-NaCl-AlCl₃ Ternary System

The model bears out the same feature that were observed for binary mixtures dilute in AlCl₃ (2), NaAlCl₄ is more abundant in the gas phase than LiAlCl₄ for $X_{Li} = X_{Na}$; in spite of that, the total pressure above the LiCl-containing system is up to ten times higher than for the corresponding NaCl-containing system. The pressure of AlCl₃ and the total pressure are satisfactory predicted by the Flood-Muan model (8) as far as it can be checked.

REFERENCES

- H. Linga, K. Motzfeldt and H.A. Øye, Ber. Bunsenges. Phys. Chem. <u>82</u>, 568 (1978).
- B. Knapstad, H. Linga and H.A. Øye, Ber. Bunsenges. Phys. Chem. <u>85</u>, 1132 (1981).
- S.J. Cyvin, P. Klæboe, E. Rytter and H.A. Øye, J. Chem. Phys. <u>52</u>, 2776 (1970).
- 4. G. Torsi, G. Mamantov and G.M. Begun, Inorg. Nucl. Chem. Lett. <u>6</u>, 553 (1970).
- E. Rytter, H.A. Øye, S.J. Cyvin, B.N. Cyvin and P. Klæboe, J. Inorg. Nucl. Chem. <u>35</u>, 1185 (1973).
- J. Hvistendahl, P. Klæboe, E. Rytter and H.A. Øye, Inorg. Chem. <u>22</u>, 000 (1983).
- 7. H.A. Øye, E. Rytter, P. Klæboe and S.J. Cyvin, Acta Chem. Scand. <u>25</u>, 559 (1971).
- T. Førland, "Fused Salts", B.R. Sundheim, Ed., McGraw-Hill, New York (1965).
- 9. H.A. Øye and L.A. King, Inorg. Nucl. Chem. Lett. 16, 547 (1980).
- 10. "JANAF Thermochemical Tables", Natl. Stand. Ref. Data Serv., National Bureau of Standards No. 37 (1971).
- Kubaschewski and C.B. Alcock, "Metallurgical Thermochemistry", 5 ed., Pergamon, New York (1979).
- 12. L.S. Hersh and O.J. Kleppa, J. Chem. Phys. 42, 1309 (1965).
- J.T. Viola, L.A. King, A.A. Fannin, Jr., and D.W. Seegmiller, J. Chem. Eng. Data <u>23</u>, 122 (1978).
- 14. A.A. Fannin, L.A. King, D.W. Seegmiller and H.A. Øye, J. Chem. Eng. Data 27, 114 (1982).

Sustan	Т		^a MC1	
System	К	X _A ^O =0.48	$X_{A}^{O} = 0.50$	$X_{A}^{o}=0.52$
NaC1-A1C13	473	0.258	1.55×10^{-4}	6.76×10^{-8}
LiC1-A1C1 ₃	473	0.307	2.38×10^{-3}	1.35×10^{-5}
$Li_{0.5}Na_{0.5}C1-A1C1_3$	473	0.281	6.07×10^{-4}	9.55×10^{-7}
NaCl-AlCl ₃	1073	0.141	4.10×10^{-2}	1.06×10^{-2}
LiC1-A1C1 ₃	1073	0.214	0.139	9.15×10^{-2}
Li0.5 ^{Na} 0.5 ^{C1-A1C1} 3	1073	0.164	7.46×10^{-2}	3.33×10^{-2}

Table I. Some Calculated Chloride Activities at 473 and 1073 K.

Table II. Total Pressure Calculated from Model Compared with Experimental Data.

Reference	Temp. K	x _A	x ^o L	x _N ^o	P (mod) atm	P _t (exp) atm
Linga et al. (1)	973	0.10 - 0.20 - 0.30 - 0.40 -	0.90 0.80 0.70 0.60	- 0 - 0 - 0 - 0	0.198 0.245 0.315 0.496	0.191 0.242 0.315 0.575
Linga <i>et al</i> . (1)	1073 973	0.10 - 0.20 - 0.30 - 0.40 - 0.50 -	0 0 0 0	- 0.90 - 0.80 - 0.70 - 0.60 - 0.50	0.076 0.108 0.146 0.222 0.3831*	0.075 0.117 0.150 0.240 0.382
Viola et al. (13)	473	0.52 - 0.56 - 0.60 - 0.64 - 0.68 - 0.72 -	0 0 0 0 0	- 0.48 - 0.44 - 0.40 - 0.36 - 0.32 - 0.28	0.001 0.017 0.096* 0.354 0.828 1.398	0.007 0.027 0.095 0.279 0.703 1.51
Fannin <i>et al</i> . (14) JANAF Tables (10)	473	0.80 -	0	- 0.20	2.54	2.53

*Constraints

Composition:	$x_A^o = 0.02, x_L^o = 0.4$	9 $X_{N}^{O} = 0.49, T = 973 K$
Vapor	P(model), atm	P(exp), atm
LiAlC14	0.00380	0.00378
NaAlCl ₄	0.01630	0.01538
AlCl ₃	0.00526	0.00623
Total	0.02537	0.02539

Table III. Partial Vapor Pressure Calculated from Model Compared with Experimental Pressures (2).

Table IV. Composition in Mole Fraction AlCl $_3$ when AlCl $_3$ or Al $_2$ Cl $_6$ Becomes the Major Gas Species.

Temp., K	LiC1-A1C1 ₃	Li0.5 ^{Na} 0.5 ^{C1-A1C1} 3	NaCl-AlCl ₃
473	0.500	0.492	0.493
575	0.496	0.491	0.492
673	0.492	0.487	0.489
773	0.484	0.483	0.488
873	0.464	0.472	0.486
973	0.400	0.447	0.479
1073	<0.02	0.403	0.466

THERMODYNAMICS OF EVAPORATION OF ALKALI-TETRACHLORO-ALUMINATES AlkAlC1

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ABSTRACTS

Low temperature-investigations (200 ° to 560 °C) on vapour pressures (vapour transference, Knudsen-effusiondeposition and Knudsen-effusion mass-spectrometry, double oven mass-spectrometry) and vapour composition reveal relatively complicated vapour-phase equilibria of the complex-salts LiAlCl₄, NaAlCl₄ and KAlCl₄. Over alkalichloride saturated melts starting from KAlCl₄ passing to NaAlCl₄ and to LiAlCl₄ the vapour pressures (or dissociation pressure) of AlCl₃ strongly increases. Therefore Al₂Cl₆-partial pressure is 'comparable to the AlCl₃pressure. above LiAlCl₄-melts at 300 °C whereas Al₂Cl₆- and AlCl₃pressures are negligable above KAlCl₄-melts. Partial pressures of Alkalitetrachloroalanate (AlkAlCl₄) increase strongly from KAlCl₄ to LiAlCl₄. (7.5 '10⁻¹ torf and 90 torr at 560 °C).⁴ The mass-spectrometric investigations show that evaporated alkalitetrachloro-alanates form dimers (Alk₂Al₂Cl₈) in the vapour-phase but only to an appreacable extent in the vapour of LiAlCl₄. Because the apparent vaporization enthalpy of the dimers equals nearly that of the monomer, the dimer content of saturated vapours does not depend on temperature. In vapours of LiAlCl₄ additionally Li₂AlCl₅ may be presumed.

INTRODUCTION

As fundamental basic data for process-development and engineering of aluminium electrowinning from melts of alkali-tetrachloro-alanates especially for the process of aluminiumchloride-preparation and purification and for the electrolysis proper the volatility of solid and molten alkali-chloro-alanates must be available. Different authors (e.g. L.A. King and collaborators /1/ and Øye and the Trondheim school /2/3/) have worked on this field. From the data of these authors it was already known that the volatility of the alkali-chloro-alanate increases from KAlCl₄ via NaAlCl₄ to LiAlCl₄ and that dissociation pressure ⁴ of AlCl₃ increases likewise above alkali-chloroalanates from ⁵ potassium via sodium towards lithium.Nome of these investigations, however, tried to identify different species in the vapour-phase and to solve the question whether - for instance - increased AlCl₂-volatility was due to formation of complex species with Al to alkali ratio of higher than one (e.g. AlkAl₂Cl₂).

EXPERIMENTAL

Investigation into vaporization equilibria and massspectra of salt vapours confined to temperature range 200° to 560 °C as the maximal temperature in order to be still close to the Knudsen-effusion condition for Knudsen-effusion mass-spectrometry and effusion-deposition-experiments. (For pressures being less than one and half an order of magnitude above the upper limit for Knudsen-effusion, experimental corrections and calibrations of MS-signal/partial pressure correlation were applied to take into account of non-Knudsen-behaviour). Within this temperaturerange Knudsen-effusion and vapour-transference were used to determined formal vapour-pressures and chemical composition of the vapours and parallel to these measurements Knudsen-effusion mass-spectrometry was applied in order to get some insight into the stoichiometry of different molecular species in the vapour-phase. However, only a limited number of species could be observed and identified as (relatively unstable) radical cations of the mothermolecules whereas especially the more massive mother-molecules were missing as cationic peaks mostly and could only be supposed to exist because of some unexpected ions (so Alk_2Cl^+ and $Alk_2AlCl_4^+$ were indicative of the existence of $Alk_2Al_2Cl_8$ or Alk_2AlCl_5 resp.). Only by application of the double-furnace-technique which used constant temperature in the upper furnace and variable temperature in the lower furnace and vice versa) clear identification of decomposition-paths and of the original molecule could be made and estimates of the relative amounts of different species could be given. (Below this method will be examplified for vapours above NaAlCl, and LiAlCl,).

RESULTS

a) Vapour transference and Knudsen-effusion-deposition. Apparent vapour pressures and their temperature dependence and vapour composition (e.g. Alk/Al/Cl-ratio) were investigated in temperature range 300 ° to 560 °C for KCl-saturated KAlCl₄, 400 ° to 560 °C for NaCl-saturated NaAlCl₄ and 150 ° to 250 °C for LiCl-saturated LiAlCl₄. The K/Al/Cl-ratio for KAlCl₄-vapours equals very closely /1/1/4/ over the total temperature range investigated; therefore KAlCl₄ (or its polymers) seems to be the only species of significance in the vapour-phase above KAlCl₄. In fig. 1a the apparent KAlCl₄-vapour-pressures (calculated with the assumption that only monomeric species are present in the vapour-phase) is plotted vs 1/T together with data which were extrapolated to lower temperatures from Linga's and Motzfeldt's /3/ paper. The vaporization enthalpy is determined to be 114[±] 14 kJ/mole from our data. ExtraCpolated pressures and vaporization enthalpy (113 [±] 11 kJ/mole) of Linga's and Motzfeldt's agree with our data to a satisfactory extent. Total vapour pressure at 500 °C above KAIC1, comes close to 1 torr. The stoichio-metry of NaC1-saturated NaAIC1,-vapours and of LiC1-LiAIC1,vapours deviates remarkably from the Alk/Al/Cl-ratio of 1/1/4 as always more AlCl₃ is found in the respective vapours: The AlkCl/AlCl₃ ratio in NaAlCl₄-vapours comes close to 0.5 (but is ³slightly decreasing ⁴ from 400 ° to 500 °C) whereas the AlkCl/AlCl -ratio above LiAlCl is around 1/3 for the temperature range 150 ° to 250° 4 C and is nearly independent of the temperature.

In fig. 1b the "apparent vepour pressures of sodium" and of aluminium calculated on the assumption that all sodium is present in form of one species only, namely NaAlCl₄, and aluminium-containing-species are NaAlCl₄ and AlCl 'only) are plotted vs 1/T. An apparent vaporization enthalpy for sodium of 103 kJ/mole and of aluminium of 109 - 10 kJ/mole is determined. Again the value for Na agrees quite well with the value estimated by Linga and Motzfeldt (117 $\stackrel{+}{-}$ 10 kJ/mole). It must be stressed that the observed AlkCl/AlCl, of close to 0.5 is by no means significant for the stoichiometry of some majority species in the vapour (e.g. NaAl₂Cl₇). The same holds for LiAlCl₄-va-pours. Apparent vaporization-enthalpies for Li of 118 $\frac{1}{2}$ 5 kJ/mole and for Al of 108 kJ/mole are determined from similiar plots for vapours of LiCl saturated LiAlCl₄. b) Knudsen-effusion mass-spectrometry.

Qualitative comparison. Knudsen-effusion mass-spectrometry of KAlCl₄-vapours generates signals of the ions K', KCl⁺, K₂Cl, KAlCl₃, K₂AlCl₄, AlCl₂ and AlCl₃. Appearance potentials of K₂Cl⁺ (and the effective very low Appearance potentials of K_2Cl^+ (and the effective very low vapour pressure of KCl above KAlCl₄) show very clearly, that K_2Cl^+ cannot be generated from K_2Cl_2 . Likewise the generation of AlCl⁺ and AlCl⁺ from AlCl₃ can be ex-cluded. K_2Cl^+ and K_2AlCl_4 can be traced back to be gen-erated from the dimer K_AlCl₄ can be traced back to be gen-erated from the dimer K_AlCl₄, which is present in KAlCl₄-vapours in much lower quantities than is guessed from the signal intensities and AlCl₂ and AlCl₃ can be shown to be generated mainly from KAlCl₄-molecules and their dimers. From NaAlCl₄-vapours the respective cations as given for KAlCl₄ are generated by mass-spectrometry but

additionally NaAlCl⁺₄, Al⁺, AlCl⁺ and Al₂Cl⁺₅ are detected, whereas in mass-spectra of LiAlCl₄-vapours⁵ additionally the cations LiAl₂Cl⁺₆ and Li₂Al₂Cl⁺₈ are observed. Table 1 summarizes the relative peak intensities of different ions in order to show that presumed mother-cations (e.g. AlkAlCl⁺₄, Al₂Cl⁺₆ and even AlCl⁺₃) are by far the relative least intensive (AlCl⁺₃ is always weaker than AlCl⁺₂) and that the cation of the assumed dimer is only observed in mass-spectra of LiAlCl₄-vapours.

c) Temperature dependence and double-furnace-technique. Determination of apparent vaporization enthalpies (fig.2: plot of lg I⁺ vs 1/T for cations of the mass-spectrum of NaAlCl₄) demonstrates that Alk₂AlCl₄ and Alk₂Cl⁺ certainly are generated from the same mother-molecule where-as $A\Sigma l_2$, AlkAlCl₃ and Alk⁺ seem to originate from another common mother-molecule. Appearance-potentials for the different cations reveal that Alk₂Cl and Alk₂AlCl as well as Alk₂AlCl₄, AlkAl₂Cl and Alk₂Cl are the from the dimer $Alk_2Al_2Cl_8$.

Fig. ³a shows for the m.s. of NaAlCl₄-vapours the results of a double-furnace experiment (lower furnace, containing NaAlCl₄ is kept at constant temperature, T_1 =250 °C, upper temperature T_u is variable:250 °C to 400 °C). The steep decrease of the signals of Na₂AlCl₄ and Na₂Cl with increasing upper temperature occurs without a corresponding increase in the signal-intensity of NaAlCl₄. This different and independent temperature dependence of fragment-cation intensities for monomer- and dimer-fragments reveals the relative low degree of dimerization of NaAlCl₄ in equilibria-vapours (T_u = T_1). Very similar are the results of the double-furnace measurements for KAlCl₄-vapours.

Quite different, however, are the observation made with double furnace-spectrometry for LiAlCl₄ as shown in fig. 3b. A pronounced decrease of the signal intensities of the cations $\text{Li}_2\text{AlCl}_4^+$ and Li_2Cl^+ which stem from dimeric $\text{Li}_2\text{Al}_2\text{Cl}_8$ is accompanied by an initial increase (with increasing temperature) of the fragment cations LiAlCl⁺ and LiAlCl⁺ which originate from the monomer-species. By semiquantitative evaluation a degree of dimerization of more than 60 % is obtained for LiAlCl₄-equilibrium-vapours whereas for NaAlCl₄-vapours the degree of dimerization is less than 10 % and dimerization in KAlCl₄-equilibriumvapours is much lower than 10 %.

Since effective vaporization enthalpies for alkalitetrachloroalanate-monomers and dimers are nearly equal

(because the dimerization enthalpy in the gas phase per mole of dimer nearly equals the molar vaporization enthalpy for the monomers) the degree of dimerization in AlkAlCl₄equilibrium-vapours changes but little with temperature. Table 1 collects partial pressure data for LiAlCl, -vapours. FINAL REMARK

This investigation clearly shows that the relative intensities of different fragment-ions of comparable com-position (e.g. NaAlCl⁺ and Na₂AlCl⁺ or NaCl⁺ and Na₂Cl⁺) is by no means an immediate indication for the relative concentrations of the respective mother-molecules (e.g. NaAlCl₁ and Na₂Al₂Cl₂). It is certainly the possibility to redistribute the energy of the ionizing electron (40 eV) over a larger number of vibration modes which gives rise for a higher yield in more massive fragment-ions originating from the dimer, whereas the surplus in ionizationenergy is consumed to produce numerous smaller fragments which escape detection in case of the some of complex molecule because they either carry monomeric negative charge or are not charged.

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REFERENCES

- /1/ J.T. Viola, D.W. Seegmiller, A.A. Fannin jr., L.A. King
- J. Chem. and Eng. Data 22, 367 (1977) B. Knapstad, H. Linga, H.A. Øye /2/
- Ber. Bunsenges. physik. Chem. 85, 1132 (1981) H. Linga, K. Motzfeldt, H.A. $\phi_{\overline{ye}}$ /3/
- Ber. Bunsenges. physik. Chem. $\underline{82}$, 568 (1978)
- J. Berkowitz, H.A. Tasman, W.A. Chupka /4/ J. Chem. Phys. 36, 2170 (1962)

Table 1:	LiAlC	Mass-spectr 1_{d} (at 460	a of alkal K), NaAlCl	lichloride-sa L _a (at 560 K)	turrated melts and KAlCl ₄	s of (at 560 K)	
	Relat for The most	ive intensi SEM-gain an intensive	ties of di d mass-der peak in ea reference	ifferent frag pendence of g ach mass-spec	ment-ions are nuadrupole tra strum is used XO)	e corrected unsmission as internal	
	Alk ⁺	AlkCl ⁺	Alk ₂ C1 ⁺	Alkalc1 ⁺ 3	Alkalcı4	Alk2AlC14 ⁺	Alk2Al2Cl6
LiAlCl ₄ NaAlCl ₄ KALCl ₄	183 420 1000	7.4 77 29	244 168 4.1	113 70 35	10 0.7	977 107 8.5	15.5 - -
ť	A1 ⁺	Alc1 ⁺	Alc1 ⁺ 2	Alc1 ⁺ 3	Al ₂ Cl ⁺ 5	Alk ₂ ^p	1 ₂ c1 ⁺ 8
Lialcl4 Naalcl4 Kalcl4	2	83	652 1000 65	333 418 10 . 7	1000 1.9 		5.3
ħ	The total 1.2 ^{-10⁻³}	pressures torr (Ma) a	above the nd 7.4°10	melts amount - ³ torr (K).	to ca. 3.10	⁻³ torr (Li),	
Table 2:	Partial p v	ressures of apour-press	different ures of Li	: species in [Cl-saturated	equilibrium-v l LiAlCl _A (160	rapours and to -200 °C)	tal
t / °C	p(LiAlCl4) p(Li ₂ A	1 ₂ c1 ₈)	p(AlCl ₃)	p(Al ₂ Cl ₆)	p(total)	-
205	3.6.10 ⁻⁴	4.2.10	4- -4	8.4°10 ⁻⁴	5.7.10 ⁻⁴	ווטמו 2.19י10 ⁻³	
190 175 160	1.3.10 ⁻⁵ 4.9.10 ⁻⁵ 1.7.10 ⁻⁵	1.6.10 5.8.10 1.9.10	4" N" N"	3.5.10 ⁻⁴ 1.4.10 ⁻⁴ 4.9.10 ⁻⁵	2.810 ⁻⁴ 1.210 ⁻⁴ 5.010 ⁻⁵	9.2 .10 ⁻⁴ 3.6 .10 ⁻⁴ 1.4 .10 ⁻⁴	



Fig. 1 a



Fig. 1 b



Fig. 2



Fig. 3 a



Fig. 3 b

THE USE OF LITHIUM ALUMINUM CHLORIDE MOLTEN SALT AS AN ELECTROLYTE IN LITHIUM CELLS

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<u>Abstract</u> Although lithium aluminum chloride, either as a molten salt or as a solid, is unstable to reduction by lithium at high activities, it is stable to elemental aluminum. It is therefore possible to construct cells with an aluminum negative electrode and a positive electrode reversible to lithium. The thermodynamics of such a system have been examined, and the kinetic behavior of the aluminum electrode investigated in melts of two different compositions. In addition, two lithium vanadium oxides have been tested as possible positive electrode materials.

INTRODUCTION

Molten salts of compositions near LiAlCl, are potentially attractive intermediate temperature electrolytes for lithium cells. The eutectic composition (close to 60 m/o AlCl₃) melts at 103° C and the compound LiAlCl, itself melts at 143.5° C [1]. The free energy of formation of solid LiAlCl, has been determined by Weppner and Huggins [2], allowing the phase diagram for the Li-Al-Cl system to be calculated. This is shown in Figure 1. The voltages are related to the equilibrium activity of lithium present in each of the three-phase regions through the Nernst equation. Although the salt is resistant to oxidation up to high potentials (4.2 V with respect to lithium at 100° C), it is unstable to reduction by lithium at high activities. The reaction:

3 Li + LiAlcl = Al + 4 Licl

(1)

occurs at potentials more negative than 1.7 V with respect to lithium at 100°C.

Neither the molten salt nor the solid can therefore be used as lithium electrolytes in contact with the negative electrode materials used in other lithium cells, such as elemental lithium itself, A1/B-LiA1 or various Li-Si phases. One solution to this problem would therefore be to combine a very low lithium activity negative electrode

with a very high potential positive electrode material. The additional weight of the negative electrode material, however, leads to a considerable loss in specific energy. Another possibility is to use a second electrolyte, probably a solid, between the negative electrode and the LiAlCl₄. This ancillary electrolyte should be stable to high lithium activities, and chemically compatible with the chloroaluminate. This would be analogous to the use of sodium beta-alumina in sodium aluminum chloride based cells [3]. Few lithium electrolytes, however, have been found which are stable in contact with elemental lithium, and little is known of their compatibility with chloroalumunate melts.

A second alternative, proposed here, is the use of aluminum as the negative electrode material. As may be seen from the phase diagram, aluminum metal is stable in contact with the electrolyte. The overall cell reaction would therefore involve displacement of lithium from the electrolyte:

$$(y/3) Al + y LiAlCl_{b} + P = Li_{v}P + (4y/3) AlCl_{3}$$
 (2)

Here P is a positive electrode material which may react with lithium such that the overall cell reaction is spontaneous.

THERMODYNAMIC CONSIDERATIONS

Detailed thermodynamic data are available only for solid LiAlCl₄. In this section the thermodynamic properties concerned with the use of an aluminum electrode are therefore presented, based on data for the solid. Expected modifications for the case of the molten salt will then be compared with some experimental results.

The EMF of the cell:

is given by the free energy change of the reaction shown in equation (2) above. If we subtract from this quantity the free energy of the reaction of lithium with the positive electrode material:

$$y Li + P = Li_y P \tag{3}$$

we obtain the free energy of the reaction:

 $(y/3) Al + yLiAlCl_b = yLi + (4y/3)AlCl_3$ (4)

Thus the EMF of the cell with aluminum as the negative electrode can be calculated if the EMF of the cell:

 $Li(m) | Li^{+} | Li_{\nu}P$ (II)

is known. In fact, the free energy of reaction (4) above is no more than the EMF of the three phase region in which Al, AlCl3 and LiAlCl4 are in equilibrium, measured with respect to lithium. This quantity was determined by Weppner & Huggins [2], and found to be:

2.367 - 6.233*10-4T(K)

Therefore at 100° C, the EMF of the aluminum cell, E(I), is given by the expression:

$$E(I) = E(II) - 2.1 (V)$$
 (6)

Further, the oxidation limit of LiAlCl, with respect to aluminum may also be calculated. This quantity is equal to the free energy of formation of AlCl₃, which is:

$$2.436 - 8.667 \times 10^{-4} T(K) \quad (V) \tag{7}$$

The equilibrium aluminum activity may be calculated in each of the three-phase regions, and these values, expressed as voltages with respect to aluminum, are also shown, in brackets, in Fig. 1.

Above the melting point of the eutectic a liquid is present in the phase diagram (Fig. 2), and the thermodynamic properties of the system will vary across this single phase region. In order to calculate either the variation of the EMF of cell (I) or the variation of oxidation limit of the melt with composition, activity coefficient data must be known across the composition range of the melt. For an ideal solution the variation would be quite small. For an acidic melt, saturated with solid AlCl₃, the oxidation limit will remain the same as that shown in Fig. 1, and this also represents the minimum oxidation limit in the system.

The operational limit of the melt to oxidation was measured using a platinum working electrode, and an aluminum reference electrode (Figure 3). The experimentally determined limit appeared at somewhat lower voltages than predicted by equation 7. This may be due to oxidation of platinum at the high chlorine activities present at these positive potentials. Some evidence of platinum passivation was seen, and the two small reduction peaks close to 1.6 and 1.9 V may be associated with the reduction of platinum chloride layers. In addition, a red layer was seen on the metal after it had been held at high potentials, suggesting the presence of either $PtCl_2$ or $PtCl_4$, both of which are stable under these conditions.

There is, however, an appreciable range of potentials over which the melt can be used.

(5)

KINETICS OF THE ALUMINUM ELECTRODE

The kinetics of aluminum deposition and stripping were first examined in the basic (i.e. LiCl-rich) melt, close to LiAlCl, in composition. Roughly symmetrical steady-state current-voltage plots were obtained, but the morphology of the plated aluminum was very poor: dark in color and poorly adherent. Sweep rate-dependent currents were obtained in cyclic voltammogram experiments (sweep rates of 20 - 0.2 mV/sec were employed). Complex impedance spectroscopy (Figure 4), using a 10mV applied signal and a frequency range of $500 - 5 \times 10^{-3}$ Hz, showed that 0. 0 V with respect to aluminum, the reaction was diffusion at controlled, although charge transfer kinetics were also important at short times. The exchange current density was estimated to be 10 mA/cm² at 160°C. At potentials away from 0.0 V, the interface kinetics become unimportant, and the reaction is completely diffusion limited. This result is not unexpected, since the principal charge carrier in the melt is Li⁺, and the aluminum-containing species must arrive at, or leave the electrode, by diffusion.

In acidic melts (close to the eutectic composition) the kinetics of the aluminum electrode appear to be completely different. Complex impedance spectroscopy was unable to resolve any features beyond a pure resistance, and cyclic voltammograms were independent of sweep rate (Figure 5). It may therefore be supposed that the aluminum electrode is quite reversible in acidic melts, and diffusion is unimportant at low current densities. At much higher current densities (approximately 100 mA/cm²) currents do become limited by some mass-transport process, and a passivation phenomenon is seen. This has been ascribed to the formation of a poorly conducting $AlCl_3$ -rich layer near the electrode surface, due to migration of lithium ions away from the interface [4]. Steady-state current-voltage plots for plating and stripping are shown in Figure 6.

POSITIVE ELECTRODE MATERIALS

In recent years a number of new positive electrode materials for ambient temperature lithium cells have been developed, which are of the insertion type. Lithium (and in some cases other alkali metals) enter the lattice of a host material to form wide range solid-solution phases. Often the capacity of these electrodes is high, and if the voltage of the electrode with respect to lithium is sufficiently great, systems with attractive energy storage capability can be designed. Part of the motivation for this study was to assess the possibility of using some newly developed materials of this type in the lithium aluminum chloride salt.

Most insertion reaction phases do not have sufficiently high voltages with respect to lithium, to allow them to be used with an aluminum negative electrode. As has been seen above, approximately 2.1V is sacrificed in choosing to use the aluminum electrode, rather than elemental lithium. It has been found recently, however, that some lithium vanadium bronzes can accomodate significant amounts of lithium near 3.5V, with respect to lithium: they are therefore candidate materials for use with the aluminum negative electrode.

Two materials are considered here. First, the beta-lithium vanadium bronze, $Li_yV_2O_5$, which has a tunnel structure [5], has been shown at room temperature to be capable of accepting a total of almost 2 equivalents of lithium reversibly. Details of this work will be published elsewhere. The solid state diffusion of lithium in this material is very rapid, even at ambient temperature, and a system operating at molten salt temperatures might be capable of operating at very high rates. The second material tested in this me,t is $Li_{1+y}V_{3}O_8$ which has a layer structure [6] and which has an extensive ion-exchange chemistry [7], as well as the capability of accepting lithium up to y =2 from organic solvent-based electrolytes at room temperature.

Initial experiments were performed in basic melts, and it appears that the vanadium oxides are soluble in this medium. After discharging the electrodes, cyclic voltammetry revealed the presence of redox reactions in the discolored melts, which were not present before the experiments.

In acidic melts however, these materials appear to be stable, and discharge curves obtained at 0.8 mA/cm^2 are shown in Figs. 7 and 8. Some open circuit voltage measurements, made after allowing partially discharged electrodes to equilibrate, are also shown. In the case of the beta lithium bronze phase, the open circuit measurements were made in a melt of slightly different composition from that in which the discharge curve was obtained.

Equilibration times, on interrupting current flow, were short for both materials, indicating rapid diffusion of lithium in these oxides. The principal source of overvoltage was the internal resistance of the electrodes themselves. These materials are semiconductors, and their electronic resistance varies with the alkali metal content. Attempts to add carbon to them in order to improve their electronic conductivities were not successful; the carbon apparently facilitates reaction between the oxide and the melt.

In the beta lithium bronze case, some ambient temperature open circuit voltage data are included in the Figure 7. These data have been approximately corrected for the difference between the lithium and aluminum electrodes (equation 6), since the ambient temperature data were obtained using a lithium reference eelctrode.

CONCLUSIONS

It has been shown that cells using lithium aluminum chloride molten salt as an electrolyte can be constructed using aluminum as the negative electrode, and lithium insertion compounds as the positive electrode. The passage of current through the cell results in changes in composition, and therefore in chemical and physical properties of the salt. The expected open circuit voltage of a cell using lithium as the negative electrode must be reduced by approximately 2.1 V, if aluminum is to be used. Oxidation of a melt, saturated with aluminum chloride should occur at about 2.1 V with respect to aluminum.

The kinetics of the aluminum electrode are quite rapid; however, the morphology of the plated aluminum is unsatisfactory in both basic and acidic melts. In basic melts, diffusion appears to limit the electrode kinetics.

It has been shown that some lithium vanadium bronzes can function as positive electrodes in this cell; however their cycling capability has not been investigated. The materials investigated so far do not have sufficient capacity or high enough voltages versus aluminum to appear attractive for further investigation. A further materials problem is the questionable stability of positive electrode current collector materials at the high chlorine activities encountered in this system.

In view of these problems, it may well be advantageous to consider using an all-lithium system, and with a second electrolyte in series with the molten salt, if such an electrolyte can be found. In addition to completely avoiding the aluminum electrode problems, this would allow somewhat lower voltage positive electrode materials to be used, perhaps eliminating some difficulties associated with working at too high a chlorine activity.

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REFERENCES

[1] J. Kendall, E. D. Crittenden & H. K. Miller, J. Am. Chem. Soc. <u>45</u>, 976 (1923).
[2] W. Weppner & R.A. Huggins. Solid State Ionics <u>1</u>, 3 (1980).
[3] G. Mamantov, R. Marassi, M. Matsunaga, Y. Ogata, J. P. Wiaux, & E. J. Frazer, J. Electrochem. Soc. <u>127</u>, 2913 (1980).
[4] B. Gilbert, D. L. Brotherton, & G. Mamantov, J. Electrochem. Soc. <u>121</u>, 773 (1974).
[5] A. D. Wadsley, Acta Cryst. <u>8</u>, 695 (1955).
[6] A. D. Wadsley, Acta Cryst. <u>10</u>, 261 (1957).
[7] R. Schollhorn, F. Klein-Reesink, & R. Reimold, J. C. S. Chem. Comm. 398 (1979).





Figure 1. Isothermal section of the Li-Al-Cl phase diagram. Voltages within brackets are calculated with respect to Al, those without are with respect to lithium at 100°C.

Figure 2. Isothermal section of the Li-Al-Cl phase diagram at temperatures above the melting point of the eutectic, but below the melting point of LiAlCly.



Figure 3. Cyclic Voltammogram of LiAlCl, (approximately equimolar melt). Sweep Rate: 20mV/s, platinum electrode, surface area: 0.36 cm².







Figure 5. Cyclic Voltammograms of an aluminum electrode in acidic melt (eutectic composition), 0.00V with respect to Al³⁺/Al (area = 0.22 cm²).

Figure 6. Steady-state current-voltage plots for an aluminum electrode in acidic melt (area = 0.22 cm²).



Figure 7. Discharge Curve for $Li_yV_2O_5$ at 0.8 mA/cm² (solid line). The symbol * denotes open circuit voltages.

Figure 8. Discharge Curve for $Li_{1+y}V_3O_8$ at 0.8 mA/cm². (solid line). The symbol * denotes open circuit voltages.

THE FISCHER-TROPSCH REACTION IN CHLOROALUMINATE MELTS

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ABSTRACT

Metallic dispersions in molten acidic AlCl₃-NaCl, prepared by an AC arc between wire electrodes, have been examined as Fischer-Tropsch catalysts at low pressures of carbon monoxide and hydrogen. Low molecular weight alkanes (C_1 to C_4) were produced using cobalt, iron, nickel, platinum, palladium and rhodium dispersions. Addition of aluminum powder increases significantly the conversion of carbon monoxide and the percentage of methane in the mixture.

INTRODUCTION

Metallic dispersions in molten salts have been prepared by Piontelli and coworkers (1) using electric discharge. We decided to explore possible catalytic activity of metallic dispersions in molten chloroaluminates (AlCl₃-NaCl mixtures), with emphasis on the Fischer-Tropsch (F-T) synthesis. The F-T reaction involves the reduction of carbon monoxide with hydrogen (2). Heterogeneous catalysts, principally cobalt, iron, nickel, and ruthenium, yield saturated and unsaturated hydrocarbons, as well as oxygen-containing molecules, with a broad range of carbon numbers (typically C₁ to C_{>20}). This lack of selectivity is the major disadvantage in applying the F-T process to chemical feedstock production.

Promoters have played an important role in the development of F-T catalysts (3-7). The activity of cobalt and nickel catalysts has been increased by presence of small amounts of an oxide which is difficult to reduce, such as thoria or magnesia. These oxides act as structural promoters by increasing the surface area of the catalyst. Supports, present in much larger amounts, also act as structural promoters and increase the surface area, and, therefore, activity. Supports have also been shown to be chemical promoters, that is, they can alter the chemical characteristics of the surface. Supports can possess acidic or basic sites on their surfaces (8), and have been shown to be useful in manipulating selectivity for rhodium catalysts (9). Methane formation is favored on acidic supports such as alumina or titania, whereas alcohol formation is favored on more basic supports, such as magnesia. The most important promoter for iron catalysts is an alkali oxide or salt (10). Such a promoter, for example potassium oxide,

produces three key effects: a) the activity of the catalyst is enhanced; b) the average molecular weight of the products is increased; c) the fraction of alkenes in the hydrocarbon products is also increased.

Reaction conditions cause major changes in product selectivity (3). Increasing the temperature decreases the average molecular weight of the products, as well as the yield of oxygen-containing molecules. As the pressure is increased, the average molecular weight and total yield increase, while the olefin content can decrease or remain the same depending on the catalyst. High hydrogen to carbon monoxide ratios favor alkane formation, while decreasing this ratio increases both the average molecular weight of the products and the ratio of alkenes to alkanes.

In the past few years there has been considerable interest in developing homogeneous F-T catalysts (11-19). High pressure reactions (>100 bar) have produced alcohols and other oxygenated molecules using transition metal complexes, primarily the carbonyls, as catalysts. Hydrocarbons were absent in the products. This absence is significant, since it has been suggested that formation of significant amounts of hydrocarbons is evidence of a heterogeneous process, even when the precatalyst is soluble (20,21). Apparent exceptions have been found by Muetterties and coworkers (22,23). They have shown that osmium and iridium carbonyls are active methanation catalysts in organic solvents at low pressures (22,23). Iridium, rhodium and ruthenium carbonyls in acidic (AlCl3-rich) chloroaluminate melts also are active catalysts and produce low molecular weight alkanes at <2 bar (24,25). An advantage of homogeneous catalysts over heterogeneous ones is that catalyst selectivity may be adjusted by changing ligands as well as solvents (11,26).

Molten salts have several advantages as media for catalysis (27). Because of their high thermal conductivity, the heat of reaction is easily dissipated, thereby avoiding local overheating and possible decomposition that can occur on local supports. It may be possible to work at temperatures at which the products have high vapor pressures and can be removed by volatilization. Catalytic material can remain active over an extended period and is not easily removed with the reaction products. Acidic chloroaluminates have an additional advantage over other solvents for F-T synthesis, since both the Lewis acid (AlCl₃) and the alkali cation (Na⁺) present in these melts may act as promoters.

In this paper we report on the use of metallic dispersions in molten chloroaluminates for the studies of the F-T synthesis at relatively low pressures (1-4 bar).

EXPERIMENTAL

AlCl₃-NaCl (63-37 mole %) melts were prepared from anhydrous, iron-free AlCl₃(Fluka), which was further purified by sublimation, and reagent grade NaCl, which had been dried under vacuum at 400°C. Ir₄(CO)₁₂ (Strem) and Al powder (99.999% from Alfa) were used without further purification. Reagent grade CoCl₂ and NiCl₂ were dried under vacuum at 400°C. The melts and their precursors were handled in a dry box (moisture level <5 ppm) under a nitrogen atmosphere.

Metallic dispersions were prepared by creating an AC arc between two electrodes (of the metal to be dispersed) submerged in the melt (1). These arcs usually involved currents in the range of 10-30 A; however, arcs in excess of 50 A were also sometimes produced. The voltage at which arcing occurred varied with the gap size between the electrodes, as well as with the electrode material. Typically, a voltage of 30-60 V(AC) was required for arcing to occur between electrodes with a 1 mm gap. Particle sizes were in the range \ll 0.1-100µm (28).

Catalytic activity for the various systems was determined by studies of stirred, 24 hour batch reactions in sealed Pyrex vessels. The initial pressure of synthesis gas ($H_2:CO$, 3:1 mixture by volume from Linde or 1:1 mixed from H_2 and CO, obtained from MG Scientific Gases) was 2.3 bar (3.2 to 4.1 bar during reaction); molar ratios of AlCl₃:CO of 32:1 ($H_2:CO=3:1$) or 16:1 ($H_2:CO=1:1$) were used. Products were determined using a Hewlett-Packard Model 5710A gas chromatograph, with cryogenic capabilities and a thermal conductivity detector, equipped with a 15 ft x 1/8 in. Porapak Q column.

RESULTS

The percentage of CO reacted and the C_1 to C_4 product distribution for several of the dispersed metal catalysts are listed in Table I. At 175°C and H2/CO molar ratio of 3, Fe, Pd, Pt and Rh dispersions produced mainly methane. Fe dispersions at 250°C yielded a significant amount of C2H6, but also produced a large amount of CH4, and no higher alkanes. Since methane production is relatively easy (2), it is, therefore, desirable to select catalysts which produce less CH4 and more higher hydrocarbons. Cobalt and nickel catalysts gave lower amounts of CH4 and produced higher gaseous alkanes, however, very little CO reacted (4% for Co, 2% for Ni). No products were formed using either the chloroaluminate melt without the metallic dispersion, or dispersions of Ta and W. Aluminum powder has been shown to be an effective enhancer for F-T catalysis by metal carbonyls in molten haloaluminates (29). The effect of Al powder on the metallic dispersion systems is shown in Table II. Consumption of CO was greatly increased for Co, Fe and Ni in the presence of Al powder.

TABLE I

Product Distribution Using Dispersed Metal Catalysts

Dispersed	Temp.	Δ CO	Dist	ribution o	f the C ₁	to C ₄ alka	nes (%)
Catalyst	(°C)	(%)	Cl	C2	C3	n-C4	i−C ₄
Co	175	4	59	19	14	2	6
Fe	175	4	100				
Fe	250	13	75	25			
Ni	175	2	41	27	20		12
Pd	175	11	97	3			
Pt	175	19	93	6	1		
Rh	175	2	100				

H₂:CO=3:1 by volume

TABLE II

Product Distribution Using Dispersed Metal Catalysts in the Presence of Aluminum

H2	:0	20=3	3:1	by	volume
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Dispersed	A1C13:A1	Temp.	Δ C0	Dist	ribution	of the	C ₁ -C ₄ alka	nes (%)
Catalyst	mole ratio	(C°)	(%)	c_1	C2	C ₃	n-C4	i−C4
Со	65:1	175	12	73	12	5	1	8
Со	3:1	175	61	75	19	4	1	1
Fe	65:1	250	19	81	6	9	1	4
Fe	3:1	250	100	91	6	2	<1	1
Ni	65:1	175	20	79	13	5	1	2
Ni	3:1	175	100	67	19	6	1	7
Pd	3:1	175	14	88	7	2	1	2

The product distribution was modified as follows: a) all C_1 to C_4 alkanes were produced; b) the percentage of CH_4 increased significantly. The Pd dispersion system behaved somewhat differently, in that only a slight increase in the amount of CO consumed was observed, and the amount of CH_4 decreased slightly with the added aluminum.

Since the chloride salt of the metal being dispersed may be produced, along with metal particles, during the discharge, $CoCl_2$ and NiCl₂ (AlCl₃:M=275:1 molar ratio, M=Co,Ni) were checked for catalytic activity, and found to be inactive. Addition of aluminum, however, resulted in quite active systems, presumably due to reduction of Co^{2+} and Ni²⁺ to the metals by aluminum. The product distributions, listed in Table III, are similar to those found for the discharge-produced dispersions in Table II. Evidently the product distributions for these catalysts are independent of the method of preparation of metallic dispersions.

Attempts to increase the average carbon number by decreasing the reaction temperature proved fruitless. The relative amount of CH_4 produced increased, as shown in Table IV for Co and Ni dispersions, and in Table I for an Fe dispersion.

Preliminary experiments using a H_2 :CO ratio of one instead of three, with an Fe dispersion at 250°C in the presence of Al(AlCl₃:Al = 3:1 mole ratio), produced the following results: a) the consumption of CO decreased to 19%; b) the product distribution shifted towards a higher average molecular weight (C₁ to C₄ distribution: CH₄ = 67%, C₂H₆ = 4%, C₃H₈ = 9%, n-C₄H₁₀ = 3%, i-C₄H₁₀ = 17%); c) no alkenes were observed. The complete absence of olefinic products is somewhat unexpected, since iron catalysts are known to produce significant amounts of olefins (3). Apparently the hydrogenation ability of the chloroaluminate-aluminum-iron system is greater than that of conventional iron catalytic systems.

The $Ir_4(CO)_{12}$ system was also studied for comparison with the heterogeneous dispersions; the results are given in Table V. Demitras and Muetterties (24) obtained similar results with respect to the amounts of CH₄ and C_{2H_6} after 24 hours (at shorter reaction times they obtained C_{2H_6} as the major product). Our results showed more C_{3H_8} than observed previously (24), however, $i-C_{4H_{10}}$ was absent. Addition of aluminum produced the same trends as observed with Co, Fe and Ni dispersions, namely, increased CO consumption and a higher percentage of CH₄ in the products, as well as the formation of all C_1 to C_4 alkanes.

Flow reaction systems have been shown to produce significantly different product distributions than those obtained by batch processes (25,30); higher alkanes, such as $i-C_{4}H_{10}$, can become major products. A recycle-flow reactor is currently under construction. Conversion of

TABLE III

Product Distribution Using Metal Chlorides in the Presence of Aluminum As Catalyst Precursors

H₂:CO =3:1 by volume. A1Cl₃:A1 mole ratio 3:1. Temp. 175°C.

Catalyst	Δ CO	Distri	bution of	the Cl	to C ₄ alka	ines (%)
precursor	(%)	Cl	C ₂	Сз	n-C4	i-C4
CoCl ₂	39	74	17	5	1	3
NiCl ₂	100	71	23	4	<1	2

TABLE IV

Methane Production at Different Temperatures Using Dispersed Metal Catalysts

 $H_2:CO = 3:1$ by volume.

Dispersed	A1C13:A1	Temp.	СН4
Catalyst	mole ratio	(°C)	(% of the Cl to C4 alkanes)
Co	3:1	140	85
Co	3:1	175	75
Ni	3:1	140	72
Ni	3:1	175	67

TABLE V

Product Distribution Using $Ir_4(CO)_{12}$ As the Precatalyst

H₂:CO=3:1 by volume. Temp. 175°C

A1C13:A1	ΔCO	Distribution of the C_1 to C_4 alkanes (nes (%)
mole ratio	(%)	C_1	C2	C ₃	n-C4	i-C4
_	11	45	40	15		
65:1	57	74	12	9	1	3
3:1	91	86	8	2	<1	2

CO and product distribution as a function of time will be studied using this system.

CONCLUSIONS

We have demonstrated F-T activity of some metallic dispersions in molten chloroaluminates. Alkanes were produced at relatively low pressures. Alkenes and alcohols, common products of heterogeneous F-T reactions, were not detected.

Compared to $Ir_4(CO)_{12}$, the metallic dispersions without the addition of Al have less favorable conversion of CO and/or product distribution. For most catalysts, the addition of Al has both positive effects (more CO reacts and larger amounts of C₁ to C₄ alkanes are produced), as well as a negative one (a higher percent of CH₄ is produced compared to the C₂ to C₄ alkanes). Aluminum behaves as a reagent and not as a catalyst, since CO consumption increases with the amount of Al.

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REFERENCES

- 1. R. Piontelli, G. L. Coccia and U. Ducati, <u>Electrochim</u>. <u>Metall</u>. III, 343 (1968).
- C. D. Frohning, in "New Synthesis with Carbon Monoxide", J. Falbe, Editor, pp. 309-371, Springer-Verlag, New York (1980), and references within.
- 3. R. B. Anderson, in "Catalysis", Vol. 4, P.H. Emmett, Editor, pp. 29-371, Reinhold Publishing Corp., New York (1956), and references within.
- H. H. Storch, N. Golumbic and R. B. Anderson, "The Fischer-Tropsch and Related Synthesis", John Wiley & Sons, Inc., New York (1951), and references within.
- R. B. Anderson, J. T. McCartney, W. K. Hall and L. J. E. Hoffer, <u>Ind. Eng. Chem.</u>, <u>39</u>, 1618 (1947).
 M. E. Dry, J. A. K. du Plessis and G. M. Leuteritz, <u>J. Catalysis</u>,
- M. E. Dry, J. A. K. du Plessis and G. M. Leuteritz, <u>J. Catalysis</u>, 6, 194 (1966).
- J. A. Cusumano, R. A. Dalla Betta and R. B. Levy, Catalysis in Coal Conversion", pp. 245-266, Academic Press, New York (1978), and references within.

- K. Tanabe, "Solid Acids and Bases", pp. 1-33, Academic Press, New 8. York (1970).
- J. R. Katzer, A. W. Sleight, P. Gajardo, J. B. Michel, E. F. 9. Gleason and S. McMillan, <u>Disc. Faraday</u> Soc., <u>72</u>, 121 (1981). G. Henrici-Olive and S. Olive, <u>J. Mol. Catal.</u>, <u>16</u>, 187 (1982). W. Keim, M. Berger and J. Schlupp, <u>J. Catal.</u>, <u>61</u>, 359 (1980). R. B. King, A. D. King Jr., and K. Tanaka, <u>J. Mol. Catal.</u>, <u>10</u>,
- 10.
- 11.
- 12. 75 (1981).
- R. J. Daroda, J. R. Blackboro, and G. Wilkinson, Chem. Commun., 13. 1098 (1980).
- R. J. Daroda, J. R. Blackboro, and G. Wilkinson, ibid., 1101 14. (1980).
- 15. J. W. Rathke and H. M. Feder, J. Am. Chem. Soc., 100, 3623 (1978).
- Y. Kikuzomo, S. Kagami, S. Naito, T. Onishi, and K. Tamuru, 16. Chem. Lett., 1249 (1981).
- 17. B. D. Dombek, J. Am. Chem. Soc., 102, 6855 (1980).
- B. D. Dombek, ibid., 103, 6508 (1981). 18.
- 19. J. F. Knifton, ibid., 103, 3959 (1981).
- J. P. Collman and L. S. Hegedus, "Principles and Applications of 20. Organotransition Metal Chemistry", p. 450, University Science Books, Mill Valley, CA (1980).
- 21.
- J. S. Brady, J. Am. Chem. Soc., 101, 7419 (1979). M. G. Thomas, B. F. Beier and E. L. Muetterties, <u>ibid.</u>, <u>98</u>, 1296 22. (1976).
- 23. R. A. Schunn, G. C. Demitras, H. W. Choi, and E. L. Muetterties, Inorg. Chem., 20, 4023 (1981).
- 24. G. C. Demitras and E. L. Muetterties, J. Am. Chem. Soc., 99, 2796 (1977).
- H. Wang, H. W. Choi, and E. L. Muetterties, Inorg. Chem., 20, 25. 2661 (1981).
- 26. A. Deluzarche, R. Fonseca, G. Jenner and A. Kiennemann, Erdöl, Kohle, Erdgas, Petrochem., 32, 313 (1979). C. N. Kenney, Catal. Rev., 11, 197 (1975). R. Piontelli, G. L. Coccia, U. Ducati, and C. Annovazzi,
- 27.
- 28.
- Electrochim. Metall. IV, 121 (1969). A. L. Lapidus, M. M. Savel'ev, L. T. Kondrat'ev, and E. V. Yastrebova, <u>Izv. Akad. Nauk SSSR</u>, <u>Ser. Khim.</u>, 1564 (1981). 29.
- 30. J. P. Collman, private communication.
THE ROLE OF COUPLED-TRANSPORT REACTIONS IN THE PREPARATION OF METAL HALIDES AND CHALCIDES USING MOLTEN ALUMINUM HALIDE SOLVENTS

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ABSTRACT

The usefulness of MX_4/Al_2X_6 melts (X = Cl, Br or I) for the synthesis of certain anhydrous group IV transition metal halides and chalcides depends not only on the high melt vapor pressure, which allows separation of the solvent and volatile excess reactants from nonmolecular products, but on the growth of the products at the shallow hot end of the solvent lip, where they are free of contamination by any non-volatile by-products and reagents. These systems have proven to be particularly useful as a route to the syntheses of zirconium(III) halides by the reduction of dissolved ZrX4 with zirconium or aluminum at modest temperatures (200°-300°C). It is postulated that this growth process is the result of a coupled-transport reaction in which the favorable physical transport of the volatile solvent, via the gas phase, using the naturally occurring thermal gradient of the tube furnace, is used to drive the chemical transport of the product, via the liquid phase, against its preferred thermal gradient, thus leading to deposition of the products at the hotter shallow end of the melt. This proposition is supported by approximate thermodynamic calculations which qualitatively reproduce the experimentally observed trends for the aluminum halide melts and suggest that the boiling point of the solvent plays a key role in establishing the optimal average transport temperature.

INTRODUCTION

The molten aluminum halides have certain properties which make them of interest as solvents for the synthesis of anhydrous metal halide and chalcide compounds:

- 1. Large solubilities for the higher oxidation state halides of many elements, as well as for those elements with molecular structures, such as Se_8 , S_8 and I_2 .
- The formation of low melting solute-solvent eutectic systems with convenient liquid temperature ranges that allow the use of Pyrex reaction containers.
- 3. Stability with respect to oxidation-reduction reactions.
- 4. High volatility, allowing easy separation from nonvolatile reaction products.
- 5. Low viscosity, colorlessness and optical transparency throughout the near IR and visible, allowing visual observation of reaction colors and spectral characterization.

6. Provision of an oxygen-free, anhydrous synthesis environment.

It was our desire to find a better method of synthesizing the zirconium(III) halides which first drew our attention to the potential solvent properties of the aluminum halides. Direct preparation of these species via reduction of the zirconium(IV) halides with Zr metal is difficult, due largely to the fact that the tetrahalides all melt above 430°C (ZrCl4 at 435.5°C, ZrBr4 at 450°C, and ZrI4 at 500°C) and then only under pressures of 20 atmospheres or more (2). Consequently, high temperature (480-700°C), high pressure (40-60 atm) bomb reactions are required with reaction times as long as eight weeks, and the resulting trihalides are generally contaminated with unreacted Zr metal (3-6). In contrast, synthesis using the corresponding ZrX_4/Al_2X_6 melts, with Zr metal as the reducing agent, can be conducted in simple Pyrex ampoules at temperatures ranging from 200-300°C, depending on the halide, with the melts yielding macrocrystals of the stoichiometric zirconium(III) halides in about a week (7). More recent work has shown that reduction of $Y_8/A1_2C1_6$ melts (Y = Seg or Sg) with group IVB metals, such as Ti, results in convenient low temperature syntheses of the corresponding dichalcides, and that reduction of the ternary ZrCl4/Yg/Al2Cl6 melts with Zr metal gives novel mixed zirconium chalcochloride species (1,8).

Part of the success of the aluminum halide melts depends on the deposition of the desired reaction products at the shallow hot lip of the melt, where they are free of contamination by any nonvolatile byproducts or unreacted metal reducing agent, a phenomena which appears to involve a transport process of some sort. The use of physical transport processes based on the temperature dependence of phase changes, such as distillation or sublimation, for the purification of substances has been used since the dawn of chemistry. In contrast, the recognition that thermally-reversible chemical reactions may also be used in conjunction with spatially maintained thermal gradients to generate generalized "chemical-transport" processes is much more recent and due largely to the pioneering work of Schäfer in the 1950's (9). Since that time the importance of chemical-transport processes for the preparation and purification of inorganic compounds, particularly those with nonmolecular structures, has grown exponentially (10-14). Though the vast majority of systems studied have involved gas phase transport, examples of liquid phase transport have also been observed (15,16).

From our empirical observation of our synthetic systems, there is little doubt that both physical and chemical transport processes are implicated. Indeed, we would like to call attention to the probable operation of a more complex "coupled-transport" process in which the favorable vapor-phase physical transport of the aluminum halide solvent is used to drive the liquid phase chemical transport of our reaction products against its prefered thermal gradient, leading to the observed deposition of the products at the hot shallow end of the melts (17). Although, such transport is implicated in all of our syntheses systems, our remarks will be focused on the zirconium trihalide systems, for which the greatest body of experience and empirical data are available.

DETAILS OF THE SYNTHESIS TECHNIQUE

All of the reaction systems are run in 75 ml sealed, evacuated Pyrex ampoules (35 mm o.d.) heated in standard 13" laboratory tube furnaces. The basic experimental setup is shown in Figure 1. The furnaces are tilted at angles ranging from $10-45^{\circ}$ and the ampoules positioned so that the lip of the shallow end of the melt is roughly at the center of the furnace cavity. The products are deposited at the shallow lip of the melt as shown in the figure. After a few days the angle of the furnace is increased and the bottom of the reaction ampoule projected from the bottom of the furnace in order to sublime away the Al_2X_6 solvent and any unreacted ZrX4. This experimental procedure was developed by trial and error with appropriate consideration given to avoiding temperatures at which the internal pressure within the ampoule would be excessive. The net chemical change in the system is represented by equation (1) and typical melt compositions

 $2r_{(s)} + 32rX_{4(so1)} + 42rX_{3(s)}$ (1)

Where X = C1, Br or I

and conditions are given in Table II, where the reported temperatures are those at the center of the furnace cavity.

Several important observations were made during the course of many experiments. The first of these was that reduction of zirconium(IV) occurred on the surface of the metallic reducing agent to produce a soluble blue species which streamed off the metal surface and eventually was homogeneously dispersed throughout the solvent system. The second was that crystals slowly began to grow at the rim of the melt surface, and that the crystal growth was enhanced by tilting the tube furnace to an angle of about 20 degrees, the completely vertical or horizontal positions giving little or no product deposition. Finally, and after the fact, we found that a natural temperature gradient of about $\Delta 24$ °C existed in the tube furnace, with the higher temperature (T2) occurring at the lip of the melt (middle of the furnace) and the lower temperature (T_1) at the deep end of the melt (the lower end of the furnace) where the metal reducing agent is located. It is this naturally occurring gradient which appears to be implicated in the observed transport of the products to the shallow lip of the melt.

Several other observations should be noted which aid and abet the interpretation of why the synthesis proceeds as it does. The first is the observation that the trihalides are essentially insoluble in pure aluminum halides, but soluble in ZrX_4/Al_2X_6 eutectics (to the extent of 0.3 mole % in the case of the chloride) where they give the same blue color as observed in the original synthesis systems. This suggests that the blue species is the result of an interaction between ZrX_3 and the $ZrX_4 \cdot (AlX_3)_n$ complexes which are probably present in the melts (and which have been verified in both the gas phase (18,19) and the liquid phase (20-22) for the chloride system). It should be noted, however, that even if all of the ZrX4 is completely complexed at the composition of the eutectic melts, the vast majority of the Al_2X_6 is still uncomplexed. (eg. in the chloride system, the mole ratio of ZrCl4 to AlCl3 is 1:6, which in the case of a 1:1 complex would still leave 5 moles of uncomplexed AlCl₃ units or 2¹/₂ moles of Al_2Cl_6).

Lastly, in the case of the chloride and bromide melts, a disproportionation reaction competes with deposition of the ZrX3 product, giving an insoluble brown product of the composition ZrAl2X7. This settles out of the melt and eventually coats the metal reducing agent, inhibiting the reaction from proceeding to completion. Again, it is largely the successful solution phase transport of the desired ZrX3 products from the deep cooler end of the melt, where the reducing agent is located, to the hot shallow lip, which prevents their contamination by these by-products.

THE SOLUBILITY OF ZrX2

Now the question we wish to answer is why ZrX3 is deposited at the hot end of the reaction ampoule rather than at the cooler end. The problem can be formally analyzed as a chemical transport problem (since dissolution of a nonmolecular solid is necessarily a chemical reaction) involving the transport of $ZrX_3(s)$ in the eutectic melt from the cooler end of the melt (T_1) , where it is being generated, to the hotter end of the melt (T_2) , where it is experimentally observed to deposit. This experiment can in fact be carried out as described and pictured in Figure 2, the net equation for the process being:

$$ZrX \underset{(s)}{\overset{\text{eutectic melt}}{\neq}} ZrX \underset{(sol)}{\overset{\text{rt}}{\neq}} T_1 \overset{\text{rt}}{\xrightarrow{}} T_2$$
(2)

and the corresponding equilibrium constant

$$K = a_{ZrC1} (sol.)$$
(3)

Application of the van't Hoff isochore

$$\frac{d\ln K}{dT} = \frac{\Delta H}{RT^2}^{\circ}$$
(4)

predicts that solubility will increase with temperature if the dissolution process is endothermic and decrease if it is exothermic. In the first case, the temperature-dependent shift in solubility should lead to transport from $T_2 \rightarrow T_1$, whereas in the second, it should lead to transport from $T_1 \rightarrow T_2$, as observed in our systems. Thus the simplest interpretation of our observations would be that ZrX3 dissolves exothermically (14).

This conclusion, however, is at variance with the testimony of countless phase diagrams, which show that the solubility of solids almost universally increases with T, rather than decreasing, even in the case of strongly solvated ionic species in highly polar solvents such as water (23). If we adopt the usual rational system of standard states for our melt system, ΔH° in equation 4 becomes equal to the enthalpy of fusion of $ZrX_3(s)$ which is certainly large and endothermic (indeed the ZrX_3 halides generally sublime or decompose long before they melt). Our actual melt is, of course, far from ideal and substitution of equation 3 into 4 gives

$$\frac{d \text{Ling}_{2rCl}(\text{sol})}{dT} = \frac{\Delta \text{H}_{fus}^{\circ}}{\text{RT}^{2}}$$
(5)

Thus the actual solubility of $\text{ZrX}_{3(s)}$ expressed as a mole fraction becomes

$$\frac{d^{lnx}ZrCl_{3(sol)}}{dT} = \frac{\Delta H_{fus}^{\circ}}{RT^{2}} - \frac{d^{ln\gamma}ZrCl_{3(sol)}}{dT}$$
(6)

where we have used the fact that $\ln a = \ln \gamma \cdot x = \ln \gamma + \ln x$, where γ is the activity coefficient of ZrX₃ in the melt. For an ideal solution $\gamma = 1$ and solubility is determined solely by ΔH_{fus}° which is certainly endothermic. Because of the complex formation implicated in the dissolution of ZrX₃ in the eutectic, however, there is little doubt that γ is finite and that the second term in equation 6 makes the overall dissolution process less endothermic than predicted by ΔH_{fus}° alone. Nevertheless, for the reasons mentioned earlier, it is improbable that it makes the overall dissolution process exothermic. Thus we conclude that the probable temperature dependency of the ZrX₃(s) solubility is not sufficient to account for the observed direction of the liquid-phase chemical transport of the products and, indeed, probably opposes it.

VAPOR-PHASE PHYSICAL TRANSPORT OF THE SOLVENT

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The resolution of this difficulty depends on the fact that the Al_2X_6 solvent has a substantial vapor pressure above the reaction melt and must itself be involved in a favorable endothermic transport, via

the vapor phase, from the hotter shallow end of the melt to the deeper cooler end of the melt. Indeed, this process can actually be observed in our systems in terms of the condensing Al₂X₆ films at the cooler end. If again we use rational standard states, ΔH° in equation 4 becomes equal to the enthalpy of vaporization for the Al₂X₆ species in question. These are certainly endothermic and are in keeping with a favorable transport from $T_2 \rightarrow T_1$, though the activity of Al₂X₆ in the melts is certainly far from those of an ideal solution.

It is our postulate that it is this favorable physical transport of the solvent, via the gas phase, which serves to counteract the unfavorable effects of the thermal gradient on the liquid phase transport of the products, the continual removal of solvent at T_2 and its addition at T_1 being sufficient to account for the preferential deposition of the product at T_2 rather than T_1 . Thus the two processes are ultimately "coupled" in the sense that one transport process is driving the other against its preferred thermal gradient.

One of the rules governing transport processes is that the optimal use of a given temperature gradient, ΔT , is obtained if the gradient is evenly spaced on either side of that temperature where the

 K_{eq} describing the "pseudoequilibrium" at the two temperature extremes is equal to 1 (or ΔG° = 0) (9,14). Thus at the temperature in question

$$\Delta H^{\circ} = T \Delta S^{\circ}$$

and

$$T = T_{av} = \frac{T_1 + T_2}{2} = \frac{\Delta H^{\circ}}{\Delta S^{\circ}}$$

(7)

(8)

where ${\rm T}_1$ and ${\rm T}_2$ are the two extremes of the gradient $\Delta {\rm T}$. For our coupled process there should exist a single optimal ${\rm T}_{\rm av}$ which simultaneously maximizes the favorable vapor phase solvent transport and minimizes the unfavorable liquid phase transport. However, since quantitative data are lacking for the liquid phase portion, we cannot calculate this common ${\rm T}_{\rm av}$, though we can calculate the ${\rm T}_{\rm av}$ which will optimize the favorable vapor phase portion of the cycle by itself. This has been done in Table III, where rational standard states have again been used for the Al2X_6 solvents (thus making $\Delta {\rm H}^\circ$ and $\Delta {\rm S}^\circ$ in equation 8 equal to the enthalpies and entropies of vaporization of the pure Al2X_6 species).

As can be seen, the calculated values of T_{av} follow the same trend as the empirically observed orders for our synthesis systems: Al₂I₆ > Al₂Br₆ > Al₂Cl₆ and in absolute terms agree quite well for the bromide and chloride systems. In the case of the iodide systems temperatures of the order of the calculated T_{av} have never been tested experimentally for fear of pressure build up in the reaction ampoules. These results suggest that the vapor phase transport process is indeed the dominant process governing the favorable deposition of the products at T₂ and that the optimal average endothermic transport

temperature for a given melt is roughly the same as the boiling point of the pure solvent itself. This conclusion also serves to rationalize the observation that in order to successfully grow ZrBr3 crystals, reactions in the Al₂Br₆ melts must be run at temperatures above those of the Al2Cl6 melts, even though AlBr3(s) melts nearly 100 degrees lower than AlCl_{3(s)} (98°C vs. 192.6°C) and reduction is observed to commence in both melts (as evidenced by the blue colors) as soon as melting is complete.

PROSPECTS AND CONCLUSIONS

We are not at present aware of any other preparative technique which combines the particular conditions used in our systems. However, the model proposed here strongly suggests that the tilted-tube technique, when combined with the proper thermal gradient, is capable of being generalized to other solvents and reaction systems and that the boiling point of the solvent should play a key role in optimizing the reaction temperatures used.

In several cases we have found that the composition of the product deposited from the Zr/ZrX4/Al2X6 melts varies with temperature. For instance, at temperatures below 210°C the Zr/ZrC14/Al2C16 system gives a mixed-valence Zr(III)-Zr(IV) species having a unique Zr12Al4Cl51 layer structure in which the zirconiums have trigonal prismatic coordination (24). Similarly, at temperatures below 280°C the $2r/2rI_4/Al_2I_6$ system gives the compound $2r_5I_{17}$, which is also a mixed-valence Zr(III)-Zr(IV) species having a defect Zr_{0.882}I₃ structure derived from that of pure ZrI3 (25) (Table IV).

As noted earlier, in terms of the aluminum halide solvents, recent work in our laboratory has extended the technique to the quarternary $Zr/ZrC1_4/Y_8/A1_2C1_6$ systems (where $Y_8 = S_8$ or Se_8) and has led to the preparation of the first known examples of mixed zirconium chalcohalides (1,8) (Table IV). Like the binary halides, these products are deposited as macrocrystals at the shallow end of the solvent lip. Similar studies of the ternary $M/Y_8/A1_2C1_6$ systems (where M = Zr or Ti) give the corresponding binary metal chalcides as products (Table V), which also show preferential transport, though the products are deposited in this case as microcrystalline powders (1).

REFERENCES

- (1) Based on a thesis submitted by W. B. Jensen in partial fulfillment of the requirements for the Ph.D. degree.
- (2)
- (3)
- E. M. Larsen, <u>Adv. Inorg. Radiochem.</u>, <u>13</u>, 1 (1970). E. M. Larsen and J. J. Leddy, <u>J. Am. Chem. Soc.</u>, <u>78</u>, 5983 (1956). S. I. Trayanov, V. I. Tsirel'nikov, and L. N. Korissarova, <u>Izv.</u> (4)
 Vyssh. Uchebn. Zaved. Khim. Khim. Tekhnol., 12, 851 (1969).

 (5) H. L. Schläfer and H. Skoludek, Z. Anorg. Chem., 316, 15, (1962).

 (6) H. L. Schläfer and H-H. Wille, Z. Anorg. Chem., 327, 253 (1964).

- (7) E. M. Larsen, W. J. Moyer, F. Gil-Arnao, and M. J. Camp, Inorg. Chem., 13, 574 (1974).
- (8) J. Wrazel, The Structure of Binary and Ternary Zirconium(III) Halides and the Synthesis of Reduced State Zirconium Polysulfide Chloride Species, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1979.
- (9) H. Schäfer, Chemical Transport Reactions, Academic Press, New York, 1964.
- (10)M. C. Ball, J. Chem. Educ., 45, 651 (1968).
- (11)
- K. E. Spear, J. Chem. Educ., 49, 81 (1972). H. Schäfer in P. Hagenmüller, Ed., Preparative Methods in Solid (12) State Chemistry, Academic Press, New York, 1972, Chap. 6.
- (13)W. L. Jolly, The Synthesis and Characterization of Inorganic Compounds, Prentice-Hall, Englewood Cliffs, N.J., 1970, pp. 209-210.
- (14)
- (15)
- M. F. Pilbrow, <u>Essays in Chem.</u>, 7, 31 (1977).
 J. P. Mc Geer, <u>J. Chem. Educ.</u>, <u>29</u>, 534 (1977).
 P. Ehrlich and H. Kuhnl, <u>Z. Anorg. Chem.</u>, <u>298</u>, 176, 190 (1959). (16)
- (17)Schäfer (9) has in fact used the term coupled-transport in a different context.
- (18)D. R. Taylor and E. M. Larsen, J. Inorg. Nucl. Chem., 41, 481 (1979).
- H. Schäfer and U. Flörke, Z. Anorg. Chem., 479, 84, 89 (1981). (19)
- (20) A. J. Shor, W. T. Smith and M. A. Bredig, J. Phys. Chem., 70, 1511 (1966).
- (21) O. R. Gavrilov, A. S. Krivoshin and L. A. Nisel'son, Russian J. Inorg. Chem., (Engl. Edit.), 11, 1282 (1966).
- (22)N. D. Denisova, E. K. Satronov, and O. N. Bystrova, Russian J. Inorg. Chem., (Engl. Edit.), 11, 1294 (1966).
- (23)G. M. Bodner, J. Chem. Educ., 57, 117 (1980).
- J. Kleppinger, J. Wrazel, J. C. Calabrese and E. M. Larsen, (24)Inorg. Chem., 19, 3172 (1980).
- (25)E. M. Larsen, J. Wrazel and L. G. Hoard, Inorg. Chem., 21, 2619 (1982).
- (26) C. R. Boston, Adv. Molten Salt Chem., 1, 129 (1971).

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Table I

Properties of Aluminum Chloride

Melting Point/(°C)	192.6 (2.4 atm)
Boiling Point/(°C)	192.0
Density Solid/(g/cc)	0.51
Density Liquid/(g/cc)	1.22 (220°C)
Vapor Pressure Liquid/(atm)	3.96 (220°C)

Table II

Summary of	Zr/ZrX ₄ /A1 ₂ X ₆	Reduction Melts	
Composition (mmol)	C1	Br	т
Zr/ZrX4/A12X6	3.3/17.2/75.0	3.2/11.0/52.6	1.2/6.1/28.6
n% ZrX4	18.6	17.6	17.5
Temperature (°C) ^a	230	260	300
Melt Color	blue	blue-green	black
Transport Products	ZrC1 ₃	ZrBr ₃	ZrI ₃
	green	gold	purple

a) Measured at center of furnace cavity.

Table III

Calculated versus Experimental Transport Temperatures

Solvent	∆H v	∆s°v	K _V range ^C	T _{av} /	(°C)
	(kcal/mole) ^b	(e.u.) ^b	(∆24°C)	calc	expta
A12 ^{C1} 6(l)	10.1	21.7	0.74-1.30	192	218
$A12^{Br}6(l)$	11.6	22.0	0.77-1.28	254	248
A12 ¹ 6(l)	14.9	22.6	0.81-1.22	386	288

- a) Calculated by subtracting 12°C from T at the center of the furnace, where T is assumed to correspond to $\rm T_2$ of the $\rm \Delta24\,^\circ C$ gradient.
- b) Data from reference 26.
- c) Values of K_{Vap} at T_1 and T_2 .

Table	IV
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Additional Zirconium Systems

Melt/mmol compn	Time(wks)	Temp.	Product
Zr/ZrC1 ₄ /A1 ₂ C1 ₆ 3.3/17.2/75.0	1	190-210	$2r_{12}^{A1}4^{C1}_{51}$ black
Zr/ZrI ₄ /Al ₂ I ₆ 1.2/6.1/28.6	1	<280	Zr5 ^I 17 black
Zr/ZrCl ₄ /S ₈ /Al ₂ Cl ₆ 1.61/7.72/1.49/38.9	1	210	Zr ₄ Al ₄ S ₇ Cl ₁₈ Apple green
Zr/ZrCl ₄ /Se ₈ /Al ₂ Cl ₆ 1.61/7.72/0.94/38.9	1-2	240	ZrA1Se ₂ C1 ₅ Brown-red

Table V	I
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Additional Titanium Systems

Melt/mmol compn	Time(hrs)	Temp.	Product
Ti/TiCl ₄ /S ₈ /Al ₂ Cl ₆ 1.67/7.7/1.49/38.9	24	220	TiS ₂ ·0.125ALC1 ₃
Ti/S ₈ /A1 ₂ C1 ₆ 4.59/1.49/38.9	24	220	TiS ₂ ·0.125A1C1 ₃
Ti/TiCl ₄ /Se ₈ /Al ₂ Cl ₆ 1.67/7.7/.935/38.9	24	220	^{Ti} 1.18 ^{Se2^{.0.189A1C1}3}
Ti/Se ₈ /Al ₂ Cl 3.13/.935/38.9	24	220	Ti _{1.18} Se ₂ ·0.189A1C1 ₃



Figure 1. Synthesis apparatus showing tilted tube furnace and Pyrex reaction ampoule. a) metal reducing agent, b) transported product, c) insulating plugs.



Figure 2. Reaction tube profile showing the pseudoequilibrium \cdot regions at T_2 and T_1 and the transport directions in the gas phase and liquid phase.

CHEMICAL REACTIONS AMONG THE COMPONENTS IN SbCl3-Alcl3-Sb MELTS

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Abstract

Although mixtures of SbCl₃, AlCl₃ and Sb metal are unreactive and mutually insoluble in the solid state, the electrical conductivity of molten SbCl₃-AlCl₃ mixtures and the substantial solubility of Sb metal in these molten mixtures show that reactions occur in the liquid state. We review research on these and related subjects in an effort to gain insight into what the underlying reactions might be.

Introduction

The SbCl₃-AlCl₃-Sb system is unusual. All available data indicate that the components are thermodynamically unreactive and mutually insoluble in the solid state. However, upon melting, SbCl₃ and AlCl₃ react readily and Sb metal dissolves in this liquid mixture, presumably through a reaction with SbCl₃ to form intermediate oxidation states. In this paper we review evidence pertaining to the kinds of entities that may be formed in these reactions. Our interest in this subject is derived from the use of SbCl₃-AlCl₃ melts as reaction media for organic substances. These melts serve as solvent/catalysts and as solvent/oxidants in which a variety of unusual organic reactions occur (1). When acting as oxidants, the reduced species in the melt are presumably the same as those formed upon dissolving antimony metal.

Properties of Antimony(III) Chloride

Antimony(III) chloride melts at 73.2° C and its normal boiling point is about 222°C (2). The melt is a molecular liquid not unlike water in its physical properties. It has a low viscosity (0.0184 poise at 99°C), a high dielectric constant (34.0 at 99°C), a low

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degree of auto-ionization (specific conductivity, $\kappa \le 8.5 \times 10^{-7}$ S cm⁻¹ at 99°C), and is a good solvent for inorganic solutes.

X-ray and neutron diffraction data on the liquid at $80^{\circ}C$ show it to consist of pyramidal SbCl₃ molecules with a significant degree of intermolecular association (3). Bond distances and angles are 235 pm and 96°, respectively, as compared with 233 pm and 100° for the gas phase species (4). (In this review bond distances are rounded to the nearest pm and bond angles to the nearest deg.) These molecules are associated in short chains with their dipole axes strongly correlated so that, on the average, the first coordination sphere of any given Sb atom contains, in addition to its three intramolecular Cl atoms at 235 pm, three other Cl atoms at 340 pm, which belong to another SbCl₃ molecule. The distance 340 pm is significantly shorter than 400 pm, the sum of the van der Waals radii (5), so that the intermolecular force between associated pairs of molecules must be much stronger than the van der Waals forces between unassociated molecules. The Raman spectrum of liquid SbCl₃ has been measured over wide temperature and frequency ranges, and the results lend strong support to the view that the melt is an associated liquid, not unlike hydrogen-bonded liquids (6).

The association between SbCl₃ molecules in the liquid phase is a manifestation of the general tendency for SbCl₃ to act as a chloride ion acceptor. In recent years a large number of crystal structures have been determined for binary compounds formed between SbCl₃ and chloride ion donors, such as alkali metal chlorides and alkylammonium chlorides (7). The first coordination sphere of antimony usually contains six, sometimes five, chlorine atoms at distances significantly less than the sum of the van der Waals radii. These bonded chlorine atoms are usually arranged with a distorted octahedral geometry. Two complex anions have been found, SbCl₆³⁻ (exactly octahedral) and SbCl₅²⁻, but in most crystals antimony completes its coordination shell by sharing chlorine atoms with other antimony atoms. The result is usually a polymeric chloroantimonate chain or network of infinite extent rather than finite molecular ions.

Bond distances in chloroantimonate(III) compounds span a wide range from about 230 pm to 370 pm without apparent preference for special values. There is, however, a correlation between the lengths of bonds that are trans to one another. Trans bonds of nearly the same length generally lie in the 260-270 pm range, while bonds significantly shorter than this are nearly always trans to bonds that are significantly longer.

Because there are some important analogies between the $SbCl_3-AlCl_3$ system and the $SbBr_3-AlBr_3$ system, we note that bonding in bromoantimonate(III) crystals is qualitatively like that in chloroantimonate(III) crystals (8).

Properties of Aluminum Chloride

The properties of liquid aluminum chloride and its mixtures with chloride ion donors are covered by other papers in this Symposium so that we limit our comments to a few facts. Crystalline AlCl₃ has a compact layer lattice with 6-fold coordination about aluminum but upon melting at 192.4°C a major atomic rearrangement occurs. The resulting liquid phase consists of Al₂Cl₆ molecules with 4-fold coordination about aluminum and with pairs of aluminum atoms linked by two chlorine atom bridges (9). Although liquid aluminum chloride is at most only slightly auto-ionized ($\kappa < 1 \times 10^{-7}$ at 200°C), it readily reacts with chloride ions from donor sources to form ionic melts containing small chloroaluminate anions, such as AlCl₄, Al₂Cl₇ and Al₃Cl₁₀. Liquid aluminum bromide also consists of dimeric molecules, Al₂Br₆, and has a low electrical conductivity, but in this case the crystal also contains these Al₂Br₆ units rather than the close-packed geometry of AlCl₃.

The SbCl₃-AlCl₃ Reaction

The SbCl₃-AlCl₃ phase diagram has a simple eutectic without solid compound formation (10) while the SbBr₃-AlBr₃ phase diagram shows a low-melting 1:1 compound (10a). This formation of a crystalline compound in the bromide system but not in the chloride system has been attributed to the much higher lattice energy of crystalline AlCl₃ as compared with AlBr₃ (11). On the other hand, the liquid phases of both systems show ionic conduction so that in both cases a halide-exchange reaction occurs on melting. Conductivity data are given in References 11 and 12 for the SbCl₃-AlCl₃ system and in References 13-15 for the SbBr₃-AlBr₃ system. Some examples of the conductivity of these melts are shown in Fig. 1. Data for the chloride system are limited to the compositional range shown in this figure while data for the bromide system extend all the way to AlBr₃.

Even before much was known about the structures of haloantimony(III) entities, it was recognized that aluminum(III) is such a strong halide ion acceptor that any ionizing reaction between SbX₃ and AlX₃ (X = Cl or Br) must involve a halide transfer from antimony to aluminum. On this basis it was postulated that the charge transporting entities are SbX₂⁺ and AlX₄⁻. Furthermore, from conductivity data for dilute solutions of AlX₃ in SbX₃ and cryoscopic i values in the bromide case, it was concluded that ionization is incomplete (12, 15). Additional evidence for ion pairing or neutral molecule formation comes from the temperature dependence of the conductivity. As shown in Fig. 2, the conductivity of SbCl₃-AlCl₃ mixtures containing 2.5-10 mole % passes through a maximum with changing temperature (11). The temperature at which the maximum occurs increases with increasing AlCl₃ content so that there

may be a maximum beyond the temperature range investigated for AlCl3 concentrations above 10%.

Temperature dependence data for the bromide system are much more limited but a conductivity maximum was found for an AlBr3-rich melt containing 88.26 mol % AlBr3 (13). Such temperature maxima for conductivity also occur for various other liquid systems, and it is generally believed that these result from ion pairing or neutral molecule formation that is aided by expansion of the liquid with increasing temperature. Substantial support for this view is provided by studies of the effect of pressure on conductivity at elevated temperatures (16).

NQR spectra of the crystalline adduct SbBr₃·AlBr₃ showed the presence of a V-shaped SbBr₂⁺ moiety and a distorted tetrahedral AlBr₄⁻ moiety with antimony also weakly bonded to bromine atoms of AlBr₄⁻ (17). Although crystalline SbCl₃·AlCl₃ is unknown, the crystal structure of the adduct SbCl₃·GaCl₃ serves as a reasonable model since GaCl₃ and its mixtures with chloride ion donors form entities in the liquid phase that have structures quite similar to those formed by AlCl₃. The structure of SbCl₃·GaCl₃ (18) is similar to that of SbBr₃·AlBr₃ and the SbCl₂⁺ and GaCl₄⁻ moieties are strongly bonded through chlorine bridges formed by the chlorine atoms of GaCl₄⁻. A diagram of the coordination sphere of antimony is shown in Fig. 3. It contains 4 chlorine atoms. Two of these with medium bond lengths of 271 and 277 pm are trans related and also belong to the coordination sphere of gallium. The other two, with very short bonds of 230 pm, belong only to antimony and form a bond angle of 97°. The latter have no trans partners. The geometry of the GaCl₄⁻ moiety is bonded to two GaCl₄⁻ moieties so as to form zig-zag chains of indefinite length.

These considerations suggest the following representation for the entities in antimony trihalide-rich melts

$$SbX_2A1X_4 + nSbX_3 \neq SbX_2^+ \cdot nSbX_3 + A1X_4$$

where X = Cl or Br. Solvation is explicitly indicated for SbX_2^+ because it is probably more than a weak association, but the other entities are also probably solvated via long halogen bridge bonds.

Charge Transport Mechanism in SbCl₃-AlCl₃ Melts

The addition of NaCl to SbCl₃-rich melts in amounts equivalent to or less than the AlCl₃ content results in a substantial decrease in the specific conductivity despite the small size of the Na⁺ ion (11). Possibly the presence of these small ions causes some sort of structural lock-up that greatly reduces ionic mobility, but a simpler explanation is that charge transport in SbCl₃-rich SbCl₃-AlCl₃ melts takes place by a non-Stokesian chloride exchange process in which the SbCl₂⁺ moieties play a key role. The addition of NaCl removes these moieties by the reaction

$$SbC1_2^+ + C1^- + SbC1_3$$

and leaves only the less effective diffusive motions of Na^+ as a means of charge transport. The following sequence represents an elementary step in the envisaged exchange process

Initial state: Cl_2Sb^+ ——— $ClSbCl_2$ Transition state: Cl_2Sb^+ — Cl^- — $SbCl_2^+$ Final state: Cl_2SbCl ——— $SbCl_2^+$

The known variability of the Sb-Cl bond length suggests that the transition state does not represent a particularly high activation energy barrier. The fact that SbCl₃ molecules tend to form short chains with their dipoles oriented in the same direction offers the possibility of rapid chloride exchange along such a chain. A more complete set of arguments is given in the original paper (11).

Auto-Ionization of SbCl3

Closely related to the above subjects is the auto-ionization of SbCl₃. The simplest representation of such a process is

SbCl₃ ≠ SbCl₂⁺(solvated) + Cl⁻(solvated)

in which the solvation forces are very strong and could be viewed as intramolecular forces rather than intermolecular forces. However, there is no objective evidence as to specific formulae for the molecular ions formed. Certainly an earlier formulation in which Cl-(solvated) was represented as the anion $SbCl_4$ (2) must be regarded with skepticism since antimony never has such low a coordination number in anionic chloroantimonate(III) complexes in crystals.

The potential of the Sb³⁺/Sb couple was measured at 99°C in molten SbCl₃ containing various amounts of KCl to increase the Cl⁻(solvated) activity and various amounts of AlCl₃ to increase the SbCl₂⁺(solvated) activity (19). Antimony immersed in SbCl₃ saturated with KCl served as the reference electrode. In order to fit these data to a Nernst equation in which the concentration of Cl⁻ served as the only composition variable, the concentration of SbCl₂⁺ was eliminated by choosing a suitable value for the ion product constant

The value log K_i = -7.8 \pm 0.5 at 99°C gave a satisfactory fit. However, this value is inconsistent with that obtained from conductivity data, namely, log K_i < -10.5 at 99°C (2). The reason for such a large discrepancy is unknown but one possibility is the presence of the junction potential.

The solvated Cl⁻ anion has an abnormally high mobility in SbCl₃ and is believed to carry most of the current in mixtures where it is present (2). For solutions of KCl and NH₄Cl in SbCl₃ transport numbers have been directly determined and that for the chloride ion is about 0.9 at 99°C. A non-Stokesian chloride-exchange transport mechanism is clearly a plausible explanation for this high mobility.

Solubility of Antimony Metal in SbCl₃-AlCl₃ Melts

Antimony metal has a very low solubility in molten SbCl₃ [mole fraction of 1.8 × 10⁻⁴ at 273°C (20) and 2.5 × 10⁻⁴ at 405°C (21)] but when AlCl₃ is added to the melt, the solubility of Sb becomes substantial. Measurements have been reported (21) over the temperature range of 235-430°C and representative isotherms are shown in Fig. 4 where $X_{Sb} = n_{Sb}/(n_{Sb} + n_{SbCl_3})$, $X_{AlCl_3}^0 = n_{AlCl_3}/(n_{AlCl_3} + n_{SbCl_3})$ and <u>n</u> is the number of moles. The temperature dependence of this solubility is small and passes through a maximum except at low AlCl₃ concentrations. There is no direct evidence regarding the species formed by Sb in solution, but it is plausible to suppose that a reaction occurs between the metal and SbCl₃ to form entities in oxidation states intermediate to 3+ and zero. The important role of AlCl₃ strongly suggests that the Sb/SbCl₃ reaction is accompanied by a substantial release of chloride ions.

Antimony metal has a much higher solubility in SbI₃ than in SbCl₃ and the addition of AlI₃ to SbI₃ has little effect on this solubility (22). Studies of SbI₃-Sb melts provide strong evidence that the reaction

$2Sb + 4SbI_3 \rightarrow 3I_2Sb-SbI_2$

takes place, where the $I_2Sb-SbI_2$ molecule is presumed to be structurally similar to $I_2As-AsI_2$ and I_2P-PI_2 . It is reasonable to suppose that the chlorine analog, $Cl_2Sb-SbCl_2$, is the dominant species when Sb dissolves in SbCl_3 alone or with a low concentration of AlCl_3 but the occurrence of this neutral species does not account for the large effect that AlCl_3 has on Sb solubility. Bismuth, the Group V element immediately below Sb, forms several homopolyatomic cluster ions with formal oxidation states in between 3+ and zero, and the structures of most of these are known from X-ray crystallography (23). They include Bi_5^{3+} , Bi_8^{2+} , and Bi_9^{5+} . These ions, which are not bonded to chlorine atoms, provide examples of the types of species that should be favored by the addition of AlCl₃ to SbCl₃.

When the solubility data (21) are plotted on a log-log scale, as shown in Fig. 5, a set of parallel straight lines is obtained for $0.05 \le X_{AlCl_3} \le 0.40$. The mean value of the slope is 2.080 ± 0.036 . This result is consistent with the assumption that the solute species is Sb_n^{2+} , a cluster ion with the charge 2+, formed by the reaction

2 SbCl₂⁺ + (n - $\frac{2}{3}$) Sb(metal) \Rightarrow Sb_n²⁺ + $\frac{4}{3}$ SbCl₃

provided that activity coefficients change little with changes in AlCl₃ content. For melts with a mole fraction of AlCl₃ less than 0.05, antimony proves to be much more soluble than is predicted by the above model. This behavior is consistent with the supposition that Cl_2Sb -SbCl₂ is formed (in addition to Sb_n^{2+}) at a low concentration.

The dissolution of Sb in SbCl₃-AlCl₃ is reversible only in the presence of Sb metal (21). Without the metallic phase present, the disproportionation of the dissolved species is kinetically hindered and highly supersaturated solutions can be prepared by evaporating some of the solvent. When an SbCl₃-AlCl₃-Sb melt is solidified in the absence of metallic Sb, a finely divided brown powder is found, dispersed among the clear crystals of SbCl₃ and AlCl₃. This brown substance, presumably an unstable compound, slowly turns black on exposure to light. Although this behavior remains unexplained, it is of considerable importance not only in experimental studies of the SbCl₃-AlCl₃-Sb system but also in the application of this system as a reaction medium for organic substances.

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REFERENCES

- (a) Buchanan, A. C., III; Dworkin, A. S.; Smith, G. P. "Influence of Redox and Lewis Acid Functions of SbCl₃-Rich 1. Molten Salt Catalysts on the Reactions of Coal Model Compounds", This Symposium. (b) Smith, G. P.; Buchanan, A. C., III; Dworkin, A. S., "Proceedings of the Third International Symposium on Molten Salts", edited by Mamantov, G.; Blander, M; Smith, G. P., Electrochemical Society: Pennington, N.J., 1981; pp 393-407.
- 2. For a general review of the properties of molten SbCl₃, see Baughhan, E.C. "The Chemistry of Nonaqueous Solvents", Vol. IV, edited by Lagowski, J. J., Academic Press: New York, 1976; pp 129-165.
- Johnson, E.; Narten, A. H.; Thiesen, W. E.; and Triolo, R. 3. Faraday Discuss. Chem. Soc. 1978, 66, 287.
- Kisliuk, P. J. Chem. Phys. 1954, 22, 86. 4.
- Pauling, L. "The Nature of The Chemical Bond", 3rd ed.; Cornell 5. University Press, Ithaca, N.Y., 1960; p. 260.
- 6. Aliotta, F.; Maisano, G.; Micali, N.; Migliardo, P.; Vasi, C.; Wanderlingh, F.; Triolo, R.; Smith, G. P. J. Chem. Phys. 1982,
- Wanderlingh, F.; Triolo, R.; Smith, G. P. J. CHEM. PHYS. 1902, 76, 3987.
 (a) Edstrand, M.; Inge, M.; Ingri, N.; Acta Chem. Scand. 1955, 9, 122; Webster, M.; Keats, S. J. Chem. Soc. A 1971, 298.
 (b) Porter, S. K.; Jacobson, R. A. J. Chem. Soc. A 1970, 1356.
 (c) Kihara, K.; Sudo, T. Z. Kristallogr. 1971, 134, 142; Acta Crystallogr., Sect. B, 1974, 30, 1088. (d) Schroeder, D. R.; Jacobson, R. A. Inorg. Chem. 1973, 12, 210. (e) Wismer, R. K.; Jacobson, R. A. Inorg. Chem. 1974, 13, 1678. (f) Lipka, A.; Mootz, D.; Z. Anorg. Allg. Chem. 1978, 440, 231. (g) Kruger, F. J.; Zettler, F.; Schmidt, A. Z. Anorg. Allg. Chem., 1979, 218, 229. (i) Ensinger, U.; Schwarz, W.; Schmidt, A. Z. Naturforsch. 1982, 37b, 1584. 7. Naturforsch. 1982, 37b, 1584.
- (a) Lawton, S. L.; Jacobson, R. A. Inorg. Chem. 1966, 5, 743.
 (b) Porter, S. K.; Jacobson, R. A. J. Chem. Soc. A 1970, 1359.
 (c) DeHaven, P. W.; Jacobson, R. A. Cryst. Struct. Commun. 8. <u>1976, 5</u>, 31.
- For a review of the properties of the aluminum halides, see 9. Boston, C. R. "Advances in Molten Salt Chemistry", Vol. 1, edited by Braunstein, J.; Mamantov, G.; Smith, G. P.; Plenum: New York, 1971; Chapter 3.

- (a) Kendall, J.; Crittenden, E. D.; Miller, H. K. J. Am. Chem. <u>Soc. 1923, 45</u>, 963. (b) Nisel'son, L. A.; Orshanskaya, N.; <u>Tret'yakova, K.V. Russ. J. Inorg. Chem. (Engl. Transl.)</u> 1974, <u>19</u>, 580.
- Petrovic, C.; Mamantov, G.; Sørlie, M.; Lietzke, M. H.; Smith, G. P. <u>J. Phys. Chem</u>. <u>1982</u>, <u>86</u>, 4598.
- Jander, G.; Swart, K.-H. Z. Anorg. Allg. Chem. <u>1959</u>, <u>299</u>, 252; <u>301</u>, 54.
- 13. Izbekov, V. A.; Plotnikov, V. A. Z. Anorg. Chem. 1911, 71, 328.
- 14. Gorenbein, E. Va. J. Gen. Chem. USSR 1945, 15, 729.
- 15. Jander, G.; Weis, J. <u>Z. Elektrochem</u>. <u>1957</u>, <u>61</u>, 1275; <u>1958</u>, <u>62</u>, 850.
- Smedley, S. I. "The Interpretation of Ionic Conductivity in Liquids", Plenum, New York, 1980; Chapters 3 and 5.
- 17. Okuda, T.; Yamada, K.; Ishikara, H.; Negita, H. <u>Bull. Chem.</u> <u>Soc., Jpn., 1977, 50</u>, 3136.
- Peylhard, C.; Teulon, P.; Potier, A. <u>Z. Anorg. Allg. Chem</u>. <u>1981</u>, <u>483</u>, 236.
- Bauer, D.; Texier, P. <u>C. R. Hebd. Seances Acad. Sci., Ser. C.</u> <u>1968</u>, <u>266</u>, 602.
- Corbett, J. D.; von Winbush, S.; Albers, F. C. <u>J. Am. Chem.</u> <u>Soc. 1957</u>, <u>79</u>, 3020.
- 21. Sørlie, M.; Smith, G. P. J. Inorg. Nucl. Chem. 1981, 43, 931.
- (a) Corbett, J. D.; Albers, F. C. J. Am. Chem. Soc. <u>1960</u>, 82, 533.
 (b) Bruner, B. L.; Corbett, J. D. <u>J. Inorg. Nucl. Chem.</u> <u>1961</u>, 20, 62.
- For a review, see Corbett, J. D. "Progress in Inorganic Chemistry", Vol. 21; edited by Lippard, S. J., Interscience: New York, 1976; pp 129-137. (a) For structure of Big²⁺, see Krebs, B.; Hucke, M.; Brendel, C. J. <u>Angew. Chem. Int. Ed.</u> Engl. 1982, 21, 445.



Figure. 1. Conductivity isotherms for SbCl₃-AlCl₃ melts at 100-200°C and for SbBr₃-AlBr₃ melts at 100°C.

Figure 2. Temperature dependence of the conductivity of SbCl₃-AlCl₃ melts containing 2.5-25.0 mol % AlCl₃. Curves are labelled according to composition in the order mol % SbCl₃-mol % AlCl₃.





Figure 3. Schematic diagram of the coordination sphere of antimony in the adduct $SbCl_3 \cdot GaCl_3$.



Figure 4. Solubility of Sb in SbCl₃-AlCl₃ mixtures at two temperatures.



Figure 5. Log-log plot of the solubility of Sb in SbCl₃-AlCl₃ mixtures at 5 temperatures for $X^0_{AlCl_3}$ -values of 0.05-0.40.

PHASE DIAGRAM OF LiC1-NaC1-A1C1₃ TERNARY SYSTEM

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ABSTRACT

Phase diagram of LiCl-NaCl-AlCl₃ ternary system has been determined by the use of direct visual observation and DTA methods. Composition ranges studied are 0-100mol% AlCl₃ for LiCl-AlCl₃ and NaCl-AlCl₃ binary systems, and 0-50mol% AlCl₃ for the ternary system.

Chemical compounds LiAlCl₄ and NaAlCl₄ were found in the binary systems and their melting temperatures are 416K and 427K, respectively. The ternary system in the composition range less than 50mol% AlCl₃ shows two liquidus surfaces around LiCl and NaCl, and one boundary line between them. The ternary eutectic composition is considered to be near the eutectic composition of LiAlCl₄-NaAlCl₄ binary system although it could not be found.

It is considered that the ternary system is a reciprocal system of ($\text{Li}^+, \text{Na}^+ \parallel \text{Cl}^-, \text{AlCl}_4^-$) in the composition range less than 50mol% AlCl₃. From the slopes of liquidus surfaces of the reciprocal melt, the standard free energy change of the following ion exchange reaction is estimated to be positive.

 $LiCl(\ell) + NaAlCl_4(\ell) = NaCl(\ell) + LiAlCl_4(\ell)$

INTRODUCTION

Phase diagrams are essential for the evaluation of thermodynamic properties in the study of molten salts, and also the knowledge of liquidus temperatures is indispensable for the practical use of salts.

LiCl-NaCl-AlCl₃ ternary system is attractive because very stable complex anion is formed in it, and it is well known as the electrolyte of new aluminum smelting process. Phase diagrams of LiCl-AlCl₃ and NaCl-AlCl₃ binary systems were previously reported^[1] In this work, liquidus surface of the ternary system is determined in the composition range less than 50mol% AlCl₃. The thermodynamic properties of the ternary melt are discussed.

EXPERIMENTAL

For the determination of the phase diagram of the ternary system, it is desired that a sample salt is sealed in the container in order to prevent the evaporation or hydrolysis of the sample containing $AlCl_3$.

In this study, the direct observation of the phase change was adopted as a principal method, and DTA as a subsidiary method because the conventional thermal analysis is hard to use for the salts containing AlCl₃.

A schematic diagram of the apparatus used for the direct observation is shown in Fig.1. In this method, the sample salt is sealed in a transparent quartz tube under vacuum and heated, and then the appearance of a liquid phase in the solid phase or the disappearance of a solid phase in the liquid-solid coexisting phase was observed directly from the outside of a transparent electric furnace by the use of telescope with low magnification.

The conditions of thermodynamic equilibrium are obtained more easily in this method as compared with conventional thermal analysis, although the present method is also a non-equilibrium method in principle. In this study, the reproducibility was excellent under the conditions that the amount of sample was about 20-30mg and the heating rate was less than 0.1K/min.. The reason why the cooling method was not employed is that the reproducibility was poor because the AlCl₃ melts have the tendency to super cool.

Figure 2 shows the DTA cell arrangement. DTA cells containing the sample and α -Al₂O₃ were fed into the holder made of boron nitride which has high thermal conductance and high electrical resistance. The measurement was made in an argon atmosphere.

AlCl₃ has an extremely high vapor pressure and strong hygroscopicity. The commercial anhydrous reagent grade AlCl₃ contains a fairly large amount of impurities such as HCl, FeCl₃ and others, and cannot be used as it is. In this study, a double distillation method shown in Figs.3 and 4 was used for the purification of the commercial reagent grade anhydrous AlCl₃. Purification was done by the following procedure. The unpurified AlCl₃ on a pyrex boat is placed in the distillation tube shown in Figs.3, and is heated under vacuum at about 390K for one day. Moisture, HCl and other volatile compounds are removed. In this case, the collecting bottle is heated at above 500K. After the heating under vacuum, AlCl₃ is heated to about 480K while dried argon is passed through as a carrier gas, and A1Cl₃ is condensed in the collecting bottle cooled by the water with ice. After the sublimation, the collecting bottle is sealed at both ends. A1Cl₃ obtained is white or slightly yellowish powder and still contains small amount of impurities. $A1C1_3$ powder obtained is sealed in a pyrex tube under vacuum and is melted at about 480K. Then it is cooled slowly in the furnace with the temperature distribution as shown in Fig.4. A1C1₃ condensed at the upper portion of pyrex tube is highly pure and colorless transparent crystal which looks like mica.

For the preparation of LiCl and NaCl, the commercial reagent grade salts were heated at about 600K under vacuum and were melted in a dried HCl atmosphere. After bubbling HCl gas into the melt for one hour, argon was bubbled

into the melt for one hour, and then the melt of LiC1 or NaC1 is solidified under vacuum.

For the determination of chemical composition, the entire sample after measurement is dissolved into distilled water and diluted as required. The analysis was done by the atomic absorption method for Al, and the flame emission method for Li and Na.

RESULTS AND DISCUSSION

Phase diagrams of LiCl-AlCl₃ and NaCl-AlCl₃ binary systems obtained by previous study⁽¹⁾ are shown in Figs.5 and 6, respectively. Figure 7 shows the phase diagram of LiCl-NaCl binary system. In this case, the measurement was done on the liquidus temperatures only. The phase diagram of LiAlCl₄-NaAlCl₄ quasi-binary system having a simple eutectic behavior is shown in Fig.8.

Figure 9 shows the phase diagram of LiCl-NaCl-AlCl₃ ternary system in the composition range less than 50mol AlCl₃. The points show the liquidus temperature measured, and the isothermal lines are shown. As shown in the figure, the liquidus surface consists of two surfaces around LiCl and NaCl. The dotted line, which connects the eutectic composition of LiCl-NaCl binary system with that of LiAlCl₄-NaAlCl₄ quasi-binary system, corresponds to the boundary line in which two liquidus surfaces around LiCl and NaCl sides intersect each other. Ternary eutectic composition is not seen in this figure, but is considered to be present near the eutectic composition of LiAlCl₄-NaAlCl₄ quasi-binary system.

As shown in Figs. 5 and 6, LiC1-A1Cl₃ and NaC1-A1Cl₃

binary systems evidently have the compounds, $LiAlCl_4$ and $NaAlCl_4$. $NaAlCl_4$ is confirmed to be very stable⁽²⁾, and $LiAlCl_4$ is also considered to be stable.

Therefore, LiCl-NaCl-AlCl₃ ternary system is regarded as a reciprocal system of (Li^+ , Na⁺ $\|Cl^-$, AlCl₄⁻). The cationic and anionic fractions are given by the following equation(1).

$$x_{\text{Li}+} = X_{\text{LiCl}} / (1 - X_{\text{AlCl}_3})$$

$$x_{\text{Na}+} = X_{\text{NaCl}} / (1 - X_{\text{AlCl}_3})$$

$$x_{\text{Cl}-} = (X_{\text{LiCl}+} X_{\text{NaCl}-} X_{\text{AlCl}_3}) / (1 - X_{\text{AlCl}_3})$$

$$x_{\text{AlCl}_4} - = X_{\text{AlCl}_3} / (1 - X_{\text{AlCl}_3})$$
(1)

where x means the cationic or anionic fraction of ions in the reciprocal system, and χ means the molar fraction of the compound in the ternary system. Phase diagram of the ternary system obtained is redrawn on the basis of the reciprocal diagram, and is shown in Fig.10.

The thermodynamic properties of a reciprocal system are discussed. At first, the activities of components were calculated for LiCl-LiAlCl₄ and NaCl-NaAlCl₄ quasi-binary systems. In these quasi-binary systems, the activity of LiCl or NaCl in the melt can be obtained by the equation(2) except the composition near to LiAlCl₄ or NaAlCl₄, because the liquidus line from LiCl or NaCl reaches to the composition near to LiAlCl₄ or NaAlCl₄, respectively, and they do not have solid solubility.

$$R \ln a_{MC1} = \int_{T_{f}}^{T} \frac{\Delta H_{f}}{T^{2}} dT$$
 (2)

where M means Li or Na, a_{MCl} is the activity of MC1 in the melt, T and T_f are the temperatures of liquidus and fusion of MC1, R is the gas constant, ΔH_f is the heat of fusion of pure MC1. Heats of fusion used were taken from JANAF table⁽³⁾ for LiC1 and Dawson's data⁽⁴⁾ for NaC1.

Activities of LiCl and NaCl obtained at their melting temperatures are shown in Figs.ll and l2. The activities of LiAlCl₄ and NaAlCl₄ were determined by the use of Gibbs-Duhem's equation and are shown in the figures. The activities of LiCl and NaCl show considerably positive deviation from Raoult's law, and the deviations are more remarkable for LiCl-LiAlCl₄ quasi-binary system. By considering the previously reported result on KCl-AlCl₃binary system⁽⁵⁾ as well as the present results, the following remarks can be made. The mixing of Cl⁻ and AlCl₄⁻ anions

increase the instability of the melt, and the instability decreases with increasing the size of cation.

Thermodynamic properties of a reciprocal melt, for example, $(A^+, B^+ || Y; Z^-)$ are characterized by the standard free energy change of ion exchange reaction⁽⁶⁾ expressed by the equation(3).

$$AY(\ell) + BZ(\ell) = AZ(\ell) + BY(\ell)$$
(3)

The standard free energy change is related closely to the coulombic force between the ions. If the radii of A^+ and Y^- are smaller than that of B^+ and Z^- , respectively, the ion pairs of AY and BZ are stable generally and the standard free energy change of equation(3) is positive.

On the other hand, equation(4) gives the relation between the liquidus temperature of the reciprocal system and the activity of the compound, AY in the melt which equilibrates with pure solid of AY.

$$R \ln a_{AY} = R \ln \gamma_{AY} \cdot x_{A^+} \cdot x_{Y^-} = \int_T^T \frac{\Delta H_f}{T_f T^2} dT \qquad (4)$$

where $\gamma_{_{A\,Y}}$ is the activity coefficient of AY in the melt.

As shown in Fig.10, the liquidus surface around NaCl decreases monotonically toward the direction of LiAlCl₄, but the liquidus surface around LiCl maintains a

high temperature toward the direction of NaAlCl₄. This means that the activity of LiCl in the melt is high, and the standard free energy change of equation(5) is positive. This result agrees with the prediction mentioned above. This indicates that the combination of LiCl and NaAlCl₄ (smaller and larger cation-anion pairs) is more stable than the combination of LiAlCl₄ and NaCl.

 $LiC1(\ell) + NaA1C1_{4}(\ell) = LiA1C1_{4}(\ell) + NaC1(\ell)$ (5)

It is considered that this tendency becomes stronger as the difference between the cationic sizes increases. For example, two liquid region is found in the ternary system of LiCl-KCl-AlCl₃ in the composition range less than 50mol% AlCl₃ as reported by Grothe *et al*⁽⁷⁾, this system has larger difference between the cationic sizes.

CONCLUSION

Phase diagram of LiCl-NaCl-AlCl₃ ternary system was determined by the use of direct visual observation and DTA methods. In the composition range less than $50mol\$ AlCl₃, the ternary system has two liquidus surfaces around LiCl and NaCl, and they intersect on the line which

connects the eutectic composition of LiCl-NaCl binary system with that of LiAlCl₄-NaAlCl₄ quasi-binary system. The liquidus surfaces drop steeply as the content of AlCl₃ approaches 50mol%. The ternary eutectic composition is considered to be near the eutectic composition of LiAlCl₄-NaAlCl₄ quasi-binary system.

By considering that the ternary system is a reciprocal system of ($\text{Li}^+, \text{Na}^+ \parallel \text{Cl}^-, \text{AlCl}_4^-$), the thermodynamic properties were discussed. The activities of components were calculated for the quasi-binary systems containing common cations. From the difference between the slopes around LiCl and NaCl, the standard free energy change of the following reaction is considered to be positive.

 $LiCl(\ell) + NaAlCl_4(\ell) = LiAlCl_4(\ell) + NaCl(\ell)$

REFERENCES

- (1): Y.Sato and T.Ejima: J.Japan Inst.Metals, 42(1978),905.
- (2): L.G.Boxall,H.L.Jones and R.A.Osteryoung: J.Electrochem.Soc., 120(1973),223.
- (3): D.R.Stull and H.Prophet edited:
 'JANAF Thermochemical Tables' 2nd ed., Dow Chem.Co. Midland, Michigan, (1970).
- (4): R.Dawson, E.Brackett and T.E.Brackett: J.Phys.Chem., 67(1963),1669.
- (5): Von W.Fischer and A.L.Simon: Z.anorg.allg.Chem., 306(1960),1. U.I.Shvartsman: Zh.Fiz.Khim., 14(1940),253.
- (6): K.Ichikawa: Bull.Japan Inst.Metals, 16(1977),26.
- (7): Von H.Grothe and C.A.Piel: Z.Elektrochem., 54(1950),210.



Fig.1 Schematic diagram of the apparatus for the direct visual observation method.



- A: Cell holder made of boron nitride
- B: DTA cell made of Pt
- C: Sample
- D: «-Alumina
- E: Thermocouple for temperature measurement
- F: Thermocouple for ⊿T measurement

Fig.2 Schematic diagram of DTA cell arrangement.



Fig.3 Schematic diagram of the apparatus for the first stage distillation of $AlCl_3$.



Fig.4 Schematic diagram of the apparatus for the second stage distillation of $AlCl_3$.







Phase diagram of LiCl-NaCl binary system.



Fig.8 Phase diagram of LiAlCl₄-NaAlCl₄ quasi-binary system.



Fig.9 Phase diagram of LiC1-NaC1-A1C1₃ ternary system.



Fig.10 Phase diagram of (Li⁺,Na⁺ C1⁻,A1C1₄⁻) reciprocal system.



Fig.11 Activities of components in LiCl-LiAlCl₄ quasi-binary melt at 883K.



Fig.12 Activities of components in NaCl-NaAlCl₄ quasi-binary melt at1074K.

TRANSITION METAL CHLORO COMPLEX FORMATION IN ROOM TEMPERATURE CHLOROALUMINATE MELTS

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ABSTRACT

The addition of WC16 to basic aluminum chloride-1-methy1-3-ethy1imidazolium chloride melt results in the formation of the tungsten(V) chloro complex, $[WC1_6]^-$. This species can be reduced electrochemically to the tungsten(IV) chloro complex, $[WC1_6]^{2-}$. The $[WC1_6]^{-}/ [WCl_6]^{2^-}$ electrode reaction is diffusion controlled and exhibits a half-wave potential of ca. 0.46 V in basic melt referenced to aluminum in 66.7-33.3 mol % melt. Neither $[WC1_6]^-$ nor $[WC1_6]^{2-}$ appeared to react with oxide ion, introduced into the melt by dissolution of Li_2CO_3 . Diffusion coefficients for $[WC1_6]^-$ and $[WC1_{6}]^{2-}$, calculated from limiting current data obtained at a glassy carbon rotating disc electrode, were found to be $2.7\pm0.1 \times 10^{-7}$ and $2.2 \pm0.1 \times 10^{-7}$ cm^2/sec . The close agreement obtained between the experimental solvodynamic and calculated structural radii for both $[WC1_6]^-$ and $[WC1_6]^{2-}$ suggests that these two complexes are unsolvated in basic melt.

INTRODUCTION

Aluminum chloride can be combined with certain organic salts to produce ionic liquids at room temperature. Familiar examples of such liquids are mixtures of aluminum chloride with N-(n-butyl)pyridinium chloride (BPC) or 1-methyl-3-ethylimidazolium chloride (MEIC) (1,2). Both systems have been found to be good solvents for electrochemistry and spectroscopy. The Lewis acid-base properties of these ionic liquids can be varied by adjusting the ratio of $AlCl_3$ to organic salt. Melts in which the apparent mole fraction of $AlCl_3$ exceeds 0.5
are acidic, owing to the presence of the heptachloroaluminate ion, while those with an AlCl₃ mole fraction less than 0.5 are basic, since they contain uncomplexed chloride ion.

The solvation properties of these melts with regard to transition metal solutes are not well known. However, the results obtained during previous studies do suggest that some transition metal ions form very stable anionic chloro complexes in basic $AlCl_3$ -BPC or basic $AlCl_3$ -MEIC. Tetrahedral MCl_4 (n-4) ions were the dominant chloro complexes found for cobalt(II) (3), nickel(II) (4,5), iron(II) (5,6), and iron(III) (5,6). Potentiometric data indicated that both copper(I) and silver(I) formed mononuclear complexes of the type MCl_p (1-p), $2 \le p \le 4$, as a function of melt composition in basic $AlCl_3$ -BPC and $AlCl_3$ -MEIC. Linear MCl_2^- species were favored in basic melt at low chloride ion activity, while tetrahedral MCl_4^{3-} species were dominant in very basic melts(7,8). Unsolvated $Mocl_6$ (n-6) chloro complexes were found for molybdenum(III) and molybdenum(IV) in basic $AlCl_3$ -MEIC (9).

The investigation reported herein concerns chloro complex formation for tungsten ions with various oxidation states in basic $A1C1_3$ -MEIC. Techniques used for this study include cyclic voltammetry, rotating disc electrode voltammetry, and absorption spectroscopy. The chemistry of tungsten chloro complexes has been examined previously in molten $A1C1_3$ -NaC1 mixtures in the temperature range from 120 to 220°C (10). In addition, the electrochemistry of hexachlorotungstate(IV) and (V) has been studied in acetonitrile (11). EXPERIMENTAL

<u>Apparatus</u>. - The dry box system and electrochemical instrumentation used for this study were identical to those employed previously (3,5,7-9). The procedure for monitoring the moisture and oxygen content of this dry box has been described (5).

A glassy carbon disc electrode (area = 0.07 cm^2), constructed according to the procedure given by Phillips et al. (12), was used as the working electrode during voltammetric experiments. The cell used for these experiments consisted of a Pyrex cup with a tapered bottom,

fitted with a Teflon lid. The reference electrode was an aluminum wire spiral (Alfa, m5N) immersed in 66.7-33.3 mol % AlCl₃-MEIC melt. This melt, together with the aluminum wire, were placed in a Pyrex tube which had a fine porosity fritted disc sealed in one end. This tube was inserted into the bulk melt through a hole provided in the cell top. The counter electrode was a molybdenum wire spiral. It was isolated from the bulk melt in a similar fashion. A small glassy carbon crucible served as the working electrode during controlled potential coulometry experiments.

The cell was thermostated in a furnace constructed from an aluminum block heated by means of a Vulcan cartridge heater. The heater was controlled by using an ACE Glass 12105 proportional temperature controller equipped with a platinum temperature sensor. All measurements were performed at $40.0\pm0.2^{\circ}$ C.

<u>Chemicals.</u> - The procedures used for purification of $A1Cl_3$ by sublimation, synthesis of MEIC, and preparation of the $A1Cl_3$ -MEIC melt were similar to those described in previous publications (3,5,13). Tungsten(VI) chloride, WCl₆, (Alfa Ventron, 99%, resublimed) was purified further by heating it to 130-150°C under vacuum for several hours to remove oxychloro contaminants. Potassium hexachlorotungstate(V), KWCl₆, was prepared from WCl₆ and KI according to the procedure recommended by Dickinson et al. (14). Potassium hexachlorotungstate(IV), K₂WCl₆, was synthesized according to Kennedy and Peacock (15).

The oxide content of the $A1Cl_3$ -MEIC melt used in this study was determined by using pulse polarography at a slowly rotating glassy carbon electrode (GCRDE) according to the procedure developed by Osteryoung and coworkers (16). Melts that contained more than 5 ppm oxide were discarded. For conciseness, the melt compositions specified throughout this paper are expressed in terms of the apparent mole fraction of $A1Cl_3$, X_{A1C1} , or the apparent mole percent, mol %, of $A1Cl_3$ in each $A1Cl_3^2$ MEIC melt.

RESULTS AND DISCUSSION

WC16 and KWC16. - The addition of either WC16 or KWC16 to basic A1C12-MEIC melt resulted in a canary yellow solution. However, both solutions turned green after standing for several hours. Cyclic voltammograms of fresh solutions of $WC1_6$ and $KWC1_6$ at a glassy carbon electrode in 44.4 mol % melt are shown in Figure 1. These voltammograms are very similar and both exhibit two major redox processes with reduction peak potentials, $E_p^{\ c}$, at about 0.43 and -0.83 V. (The oxidation current that occurs at potentials greater than 0.7 V is believed due to oxidation of chloride ion in the melt.) The similarity of these cyclic voltammograms supports the contention that the addition of either WCl_6 or $KWCl_6$ to basic melt results in the same solute species. However, the rest potential of the working electrode changed to more negative potentials with time in fresh solutions prepared by using WCl₆ or KWCl₆, suggesting that the electroactive species introduced by addition of these compounds was unstable.

Cyclic voltammetric data for the redox process with $E_n^c = 0.43$ V are collected in Table I. These data were produced in a solution prepared from WCl₆; however, identical results were obtained in a solution made with KWCl₆. The voltammetric peak potential separation for these cyclic voltammograms averaged 0.067 V over the range of scan rates tested. (The theoretical value for a one-electron reversible charge transfer is 0.062 V at 40.0°C). In addition the peak current ratio, ip^a/ip^c, calculated using Nicholson's procedure (17), was close to one. Both i_n^{a}/i_n^{c} and the current function, $i_n^c/v^{1/2}$, were constant over the same range of scan rates. The limiting current at a GCRDE varied linearly with the square root of rotation rate during reduction of a solution containing WCl_6 or $KWCl_6$ (Figure 2). The information presented above indicates that the charge transfer reaction at $E_n^c = 0.43$ V is reversible. These observations also point to an absence of homogeneous chemical reactions coupled to the charge transfer process (18). The data collected in Table II suggest that the redox process with $E_n^c =$

0.43 V is essentially independent of pC1 in basic melt, also.

Controlled potential coulometry was performed on fresh solutions of $WC1_6$ in basic melt. Exhaustive reduction at potentials of -0.3and -0.5 V gave n values of 1.0 and resulted in a pale green solution. A cyclic voltammogram of the former solution initiated 0.082 V positive of the working electrode rest potential is shown in Figure 3a. This voltammogram indicates that the reduced form of the redox couple is present and that no new electroactive species appear to be produced during electrolysis.

Absorption spectra of fresh solutions of WCl_6 and $KWCl_6$ in 44.4 mol % melt are shown in Figure 4. Data taken from these spectra are recorded in Table III. It can be seen readily from this table and figure that the spectral characteristics of WCl_6 and $KWCl_6$ solutions are very similar. Furthermore, these spectra have many features which are similar to those observed for $KWCl_6$ dissolved in organic solvents (Figure 4 and Table III). Spectra originating from the latter solutions have been attributed to the hexachlorotungstate(V) ion. It should be noted that it was not possible to record the spectrum of solutions made with basic melt below ca. 270 nm, since the UV cut-off of the melt occurs in this region. Also, accurate values of the absorptivities for the maxima appearing in the WCl_6 and $KWCl_6$ spectra could not be calculated because the absorbancies of these maxima changed significantly over a relatively short time.

 $\underline{K_2WC1_6}$. - Solutions of $\underline{K_2WC1_6}$ in basic melt were pale green. It should be noted that dissolution of $\underline{K_2WC1_6}$ in liquid ammonia is reported to result in a solution of similar color (15). A cyclic voltammogram of a solution of $\underline{K_2WC1_6}$ in 44.4 mol % melt is shown in Figure 3b. An absorption spectrum of a similar, but more dilute solution of $\underline{K_2WC1_6}$ is depicted in Figure 5. Also shown in this figure is a spectrum of the solution resulting from the coulometric one-electron reduction of WC1_6 (vide supra).

Considered together, the evidence presented above suggests that the addition of WCl_6 to basic melt results in the formation of the tungsten(V) chloro complex, $[WCl_6]^-$. The redox process that appears

in Figure 1 with $E_p^{c} = 0.43$ V must therefore correspond to the reversible, pCl independent $[WCl_6]^{-}/[WCl_6]^{2-}$ redox couple. However, melt solutions containing $[WCl_6]^{-}$ do not appear to exhibit long term stability. The negative shift in the working electrode rest potential and the spectral similarity of aged solutions of WCl₆ and $KWCl_6$ to solutions prepared from K_2WCl_6 (Figure 5) suggest that $[WCl_6]^{-}$ is reduced to $[WCl_6]^{2-}$ by a component of the melt, most likely chloride ion, after standing for several hours.

The $[WCl_6]^{2-}$ species can be reduced at $E_p^{c} = -0.83$ V, as shown in Figures 1 and 3. Cyclic voltammetric data for this process are given in Table IV. A plot of the GCRDE limiting current for the reduction of $[WCl_6]^{2-}$ is linear with the square root of rotation rate (Figure 2). Controlled potential electrolysis at -1.10 V gave an n value of 1.0 for this electrode reaction. Thus, the reduction of $[WCl_6]^{2-}$ appears to be a diffusion controlled, one-electron process.

<u>Addition of 0^{2^-} to $[WC1_6]^-$ and $[WC1_6]^{2^-}$ Solutions. - The</u> addition of Li₂CO₃ to basic chloroaluminate melts has been shown to result in the formation of A10C1₂⁻ according to the reaction (21,22):

$$\omega_3^{2-} + \text{Alcl}_4^- \rightleftharpoons \text{Alocl}_2^- + 2\text{Cl}^- + \omega_2 \qquad [1]$$

Both $[\text{TiCl}_6]^{2-}$ and $[\text{MoCl}_6]^{2-}$ appear to react with $A10Cl_2^-$ to form oxychloro complexes (9,23). Li_2CO_3 was added to basic melt containing $[\text{WCl}_6]^-$ or $[\text{WCl}_6]^{2-}$. However, the formation of the corresponding oxychloro complexes via interaction of $A10Cl_2^-$ with $[\text{WCl}_6]^-$ or $[\text{WCl}_6]^{2-}$ does not seem to be favored in this case, since no outward change in the voltammetric properties of these solutions could be detected, e.g., no new peaks were observed and no changes in the heights of existing peaks were noted. These results are surprising since numerous tungsten(IV) and tungsten(V) oxychlorides and oxychloro complexes are known (24). Apparently, reactions of $A10Cl_2^-$ with $[\text{WCl}_6]^-$ or $[\text{WCl}_6]^{2-}$ in basic $A1Cl_3^-$ MEIC are not thermodynamically favorable or they occur very slowly.

<u>[WC1₆]⁻ and [WC1₆]²⁻ diffusion coefficients</u>. - Diffusion coefficients were calculated for $[WC1_6]^-$ and $[WC1_6]^{2-}$ from GCRDE

limiting current data. The average values obtained from several determinations for each complex are $2.7\pm0.1 \times 10^{-7}$ and $2.2\pm0.1 \times 10^{-7}$ cm²/sec, respectively. Solvodynamic radii of 3.9 and 4.8 Å were calculated for $[WCl_6]^-$ and $[WCl_6]^{2-}$, respectively, from these diffusion coefficients by using the Stokes-Einstein equation:

$$\frac{\mathbf{kT}}{\mathbf{D}\pi\mathbf{r}\eta} = 6$$
 [2]

An estimate of the structural radius for $[WC1_6]^{2-}$, calculated from the crystal radii of W^{4+} and C1⁻, was about 4.3 Å. The structural radius of $[WC1_6]^-$, which contains W^{5+} , should be approximately the same, since there are little differences in the values of the crystal radii of W^{4+} and W^{6+} . The good agreement between the solvodynamic and structural radii observed for both $[WC1_6]^-$ and $[WC1_6]^{2-}$ suggests that solvation of these ions is negligible in basic melt. Similar results were found for $[MC1_6]^{2-}$ and $[MC1_6]^{3-}$ (9).

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REFERENCES

- H. L. Chum and R. A. Osteryoung in "Ionic Liquids", D. Inman, and D. G. Lovering, Eds., Plenum, New York, 1981, pp 407-423.
- C. L. Hussey in "Advances in Molten Salt Chemistry", Vol. 5,
 G. Mamantov, Ed., Elsevier, New York, 1983.
- 3. C. L. Hussey and T. M. Laher, Inorg. Chem., <u>20</u>, 4201 (1981).
- R. J. Gale, B. Gilbert, and R. A. Osteryoung, Inorg. Chem., <u>18</u>, 2723 (1979).
- 5. T. M. Laher and C. L. Hussey, Inorg. Chem., 21, 4079 (1982).
- C. Nanjundiah, K. Shimizu, and R. A. Osteryoung, J. Electrochem. Soc., <u>129</u>, 2474 (1982).
- 7. T. M. Laher and C. L. Hussey, Inorg. Chem., 22, (1983).
- 8. T. M. Laher and C. L. Hussey, Inorg. Chem., in press.
- T. B. Scheffler, C. L. Hussey, K. R. Seddon, C. M. Kear, and P. D. Armitage, Inorg. Chem., in press.

- D. L. Brotherton, Ph.D. Dissertation, University of Tennessee, Knoxville, TN, 1974.
- H. F. Hagedorn, R. T. Iwamoto, and J. Kleinberg, J. Electroanal. Chem. Interfacial Electrochem., <u>46</u>, 307 (1973).
- J. Phillips, R. J. Gale, R. G. Wier, and R. A. Osteryoung, Anal. Chem., <u>48</u>, 1266 (1976).
- J. S. Wilkes, J. A. Levisky, R. A. Wilson, and C. L. Hussey, Inorg. Chem., <u>21</u>, 1263 (1982).
- R. N. Dickinson, S. E. Feil, F. N. Collier, W. W. Horner, S. M. Horner, and S. Y. Tyree, Inorg. Chem., <u>3</u>, 1600 (1964).
- 15. C. D. Kennedy and R. D. Peacock, J. Chem. Soc., 3392 (1963).
- Z. Stojek, H. Linga, and R. A. Osteryoung, J. Electroanal. Chem. Interfacial Electrochem., <u>119</u>, 365 (1981).
- 17. R. S. Nicholson, Anal. Chem., <u>38</u>, 1406 (1966).
- 18. R. S. Nicholson and I. Shain, Anal. Chem., <u>36</u>, 706 (1964).
- B. J. Brisden, D. A. Edwards, D. J. Machin, K. S. Murray, and R. A. Walton, J. Chem. Soc. (A), 1825 (1967).
- 20. R. A. Walton, P. C. Crouch, and B. J. Brisdon, Spectrochim. Acta, 24A, 601 (1968).
- J. Robinson, B. Gilbert, and R. A. Osteryoung, Inorg. Chem., <u>16</u>, 3040 (1977).
- B. Gilbert and R. A. Osteryoung, J. Am. Chem. Soc., <u>100</u>, 2725 (1978).
- H. Linga, Z. Stojek, and R. A. Osteryoung, J. Am. Chem. Soc., <u>103</u>, 3754 (1981).
- C. L. Rollinson in "Comprehensive Inorganic Chemistry",
 Vol. 3, J. C. Bailar, H. J. Emeléus, R. Nyholm, and A. F. Trotman-Dickenson, Eds., Pergamon Press, Oxford, 1975, Chapter 36.

v, V sec ⁻¹	ΔΕ _p , V	ip ^a /ip ^c	$i_p^{a}/v^{1/2}$, A sec ^{-1/2}
0.01	0.065	1.1	6.1×10^{-5}
0.02	0.065	1.1	6.0×10^{-5}
0.05	0.065	1.1	6.0×10^{-5}
0.10	0.068	1.1	6.2×10^{-5}
0.20	0.072	1.1	6.0×10^{-5}
0.50	0.063	1.1	6.0×10^{-5}
1.00	0.069	1.1	6.1×10^{-5}

Table I. Cyclic Voltammetric Data for the $[WC1_6]^{-7}/[WC1_6]^{2-}$ Electrode Reaction.

Table II. pC1 Dependence of the $[WC1_6]^{-7}/[WC1_6]^{2-7}$ Electrode Reaction

$(E_p^{c}+E_p^{a})/2^{a},V$	$E_{1/2}^{b}$, V	mole fraction AlCl ₃	pC1
0.457	0.455	0.458	0.156
0.457	0.456	0.464	0.218
0.460	0.458	0.471	0.300
0.462	0.460	0.476	0.382
0.463	0.460	0.482	0.492
0.465		0.487	0.639
0.467		0.493	0.901

^ascan rate was 0.05 V/sec.

^bGCRDE voltammetric half-wave potential at a rotation rate of 157 rad sec⁻¹.

solute	solvent	λ_{max} , nm (ϵ , 1/mol-cm)	ref.
WC1 ₆	44.4 mol %	$275^{a}, 299(\sim 1.5 \times 10^{4}), 347(\sim 8 \times 10^{3}), 2008$	this work
KWC1 ₆	A1C1 ₃ -MEIC "	10°),390° 275 ^a ,298(~1.3x10 ⁴),350(~7x 10 ³) 390 ^a	this work
KWC16	CH ₃ CN	246(7.5x10 ³),~275 ^a ,297(1.2x 10 ⁴), 347(7.0x10 ³),~390 ^a	this work
в RWC1 ₆	CH ₃ CN or CH ₂ C1 ₂	$242(4.3 \times 10^3), 270^{a}, 297(1.5 \times 10^4), 345(1.1 \times 10^4), 380(2.6 \times 10^3)$	(19) ³),
[wc1 ₆] ^{2-°}	44.4 mol %	429 (4x10 ²) 287(7.9x10 ³),308 ^a ,350 ^a	this work
K₂₩C1 ₆	// // AICI3-MEIC	287(7.7x10 ³),308 ^a ,350 ^a	this work
K₂₩C1 ₆	ch ₃ cn	237 ^a ,249(1.5x10 ⁴), 287(7.0x10 ³),~307 ^a ,~342 ^a	this work
K₂₩C1 ₆	mu11	233,259,285,314	(20)

Table III. Absorption Spectroscopic Data for [WC16]^{X-} Chloro Complex Anions

 $b_{R} = (Et_{4}N)$ celectrolytic reduction of [WC1₆]⁻

Table IV.	Cyclic	Voltammetric	Data	for	the	$[WC1_6]^{2-}/W(III)$	Electrode
Reaction						Ŭ	

$v, V sec^{-1}$	ΔE _p ,V	ip ^a /ip ^c	$i_p^{c}/v^{1/2}$, A sec ^{-1/2}	
0.01	0.067	1.1	5.8×10^{-5}	
0.02	0.069	1.1	5.8 x 10^{-5}	
0.05	0.070	1.1	5.7×10^{-5}	
0.10	0.074	1.1	5.7×10^{-5}	
0.20	0.073	1.1	5.6 x 10^{-5}	
0.50	0.071	1.1	5.4 x 10^{-5}	
1.00	0.080	1.1	5.5 x 10^{-5}	





Figure 2. Plots of the limiting current at a GCRDE as a function of rotation rate in 44.4 mol % melt at 40.0°C: a. 9.3 x 10^{-3} M in [WC1₆]⁻, E = 0.25 V; b. 6.9 x 10^{-3} M in [WC1₆]²⁻, E = -0.98 V.



Figure 3. Cyclic voltammograms at a glassy carbon electrode in 44.4 mol % melt at 40.0° C: a. product obtained after exhaustive electrolytic reduction of a 7.1 x 10^{-3} M solution of WCl₆ at E = -0.30 V; b. 6.1 x 10^{-3} M in K₂WCl₆. Sweep rates were 0.020 V sec⁻¹.



Figure 4. Absorption spectra: ----, 6.3 x 10^{-5} M WCl₆ in 44.4 mol % melt (vs. pure melt); ----, 6.5 x 10^{-5} M KWCl₆ in 44.4 mol % melt (vs. pure melt); ----, pure 44.4 mol % melt (vs. air); ..., 7.5 x 10^{-5} M KWCl₆ in CH₃CN (vs. pure CH₃CN).







PROSPECTS FOR ALKYL PYRIDINIUM ALUMINUM CHLORIDE MELTS

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ABSTRACT

N-butyl pyridinium chloride: aluminum chloride (BPC:AC) melt mixtures have been synthesized under rigorously pure and dry conditions. The phase diagram and preliminary conductivity data are presented. Purified aluminum chloride, AlCl₃, has been found to be chloride, Altij, has been found to be non-stoichiometric, that is, chloride deficient. In acidic melts (e.g. mole fraction of $AlCl_3 > 0.5$), the metals Li, Mg, In and Al are active; Pt, Mo, C and Zr are passive; and Cu, Ag and Ti are transitional. Less overall activity occurs in neutral (0.50 mole fraction $AlCl_3$) and basic (<0.5) melts. Preliminary electrochemical studies on Li, Mo and Cu in the 0.67 mole fraction melt at various temperatures permit some understanding of the different mechanisms operable. Suggestions for further fundamental investigations and prospects of these melts as battery electrolytes are discussed.

INTRODUCTION

The recent preparations of molten salts which are liquids at room metallurgy or surface

chemical cells whether for batteries, electrotemperature and below has preparation. These melt led to speculation about systems (1), in partic-their potential uses as ular, the alkyl pyridinium electrolytes in electro- chloride-aluminum chloride system developed by King et al (2) and Osteryoung et \overline{al} $\overline{(3)}$ and the alkyl imidazolium-aluminum chloride system developed by Wilkes et al (4) have advantages over conventional electrolytes and/or molten salts in that, 1) they can exist as liquids to below -50°C, 2) they are non-aqueous media, 3) they exhibit better conductivity relative to aprotic electrolyte systems and 4) they do not necessarily require solute However, if material. their suitability for use with active metal anode materials is required, close attention must be paid to both purity and details of preparation.

Many electrochemical investigations at several laboratories have been completed on molten salts liquid at room temperature since first reported by Hurley and Weir (5) in For example, 1951. Suchentrunk (6) has shown that aluminum can be plated on nickel Electro-deposited aluminum has also been observed in pre-electrolysis cells for purifying melts (7); and anodic dissolution of aluminum is possible with 100% current efficiency (2). The results obtained with aluminum as well as other electrochemical investigations (8, 9) have shown the "potential" usefulness of melts as electrolytes in electrochemical cells. In

a specific instance, an alkyl pyridinium-aluminum chloride melt showed suitability as a battery electrolyte (10, 11).

It has been the focus of this investigation to prepare pure, anhydrous n-butyl pyridinium chloride-aluminum chloride melts, to assess the relationship of composition and temperature and to examine the thermodynamics and kinetics of redox reactions which can occur on a variety of metals. These efforts will ultimately uncover new phenomena which could possibly be exploited in metallurgy, batteries or catalysis.

EXPERIMENTAL METHODS

General. - All phases of the preparation and purification of melts and melt materials were carried out, wherever possible, under the argon atmosphere of a Vacuum Atmosphere dry box equipped with a Model He-493 Dri Train (RPC). The dri box atmosphere was further purified by an additional recirculating chamber loaded with pre-treated molecular sieve and activated The atmosphere carbon. was periodically checked with a cracked light bulb which generally operated for at least 30 days under continuous use. Material

handling outside of the dri box for transfers and other procedures such as recrystallizations were carried out on a glass vacuum line with the appropriate accessories. The electrochemical measurements (DREO), in large part, were carried out under conditions similar to that above but less rigorous with respect to the removal of oxygen and/or moisture.

A Varian ESR spectrometer was used to determine the presence of free radicals. A Model 31YSI Conductivity Bridge and a micro-cell (K = 1.0)were used for conductivity studies. Cyclic voltammograms were obtained using a PAR 173 potentiostat/galvanostat and PAR 175 universal programmer. Open circuit potentials were measured with an electrometer (having an impedence of ${\sim}10^{14}$ ohms). Other potentials, currents, etc., were measured with a Fluke digital multimeter (Model 8010A).

Preparation of AlCl₃. -AlCl₃ (Alfa Ventron) was sublimed by a modified method of Seegmiller <u>et al</u> (12). 20g AlCl₃ was placed in a sublimation apparatus (designed and constructed in-house) containing lg NaCl and 4-5 1/4" pieces of aluminum. The apparatus was then removed from the dry box and heated to 220-230 °C under an HCl gas

flow of approximately 1 ml/min. Translucent to white crystalline material was collected on the cool areas of the apparatus. After \sim 5h., the apparatus was sealed, cooled and residual HCl gas was removed under vacuum. The crystals were removed from the apparatus in the dri box, crushed and stored in glass vials. The material was analyzed for Cl and Al and consistently gave a ratio of Al to Cl of 2.8 to 2.9 and less than 1% impurity (e.g., oxide material).

Preparation of BPC. -N-butyl pyridinium chloride (BPC) was synthesized by condensing, in a typical experiment, 324 ml of pyridine (Burdick and Jackson) and 418 ml of n-butyl chloride (Aldrich, distilled before use) as outlined by Osteryoung et al (3). The reagents were refluxed in a standard R.B. flask in the dark for $\sim 2d$. The red oil product formed in the reaction crystallized on cooling. The crystals were filtered, recrystallized from acetonitrile, MeCN, and dried under vacuum. The crystals were further purified by recrystallization in a vacuum sealed filtering apparatus using specially purified and dried MeCN. The preparation and purification of dry MeCN has been reported elsewhere (13, 14). These procedures yielded highly crystalline,

pure BPC, the purity of which was verified by elemental analysis (Theoretical: C = 63.01, H = 8.16, N = 8.16, C1 = 20.66%; Found: C = 62.84, H = 8.33, N = 8.13; C1 = 20.88). The crystalline BPC prepared as above was ground, pumped under vacuum overnight and stored in glass vials.

Preparation of Melts. -AlCl3:BPC melts (e.g., 2:1, 3:2, 1:1, 2:3, 1:2) were prepared by placing the appropriate molar quantities of each melt component in separate chambers of a melt apparatus (constructed in-house). The loaded apparatus was removed from the dri box and the lower portion (containing BPC) was immersed in liquid N2. The valve separating the two melt components was then opened allowing small portions of AlCl₃ to contact BPC. The lower portion was then thermally cycled to room temperature at various intervals until all the AlCl₃ had been added. In some cases, the melts had to be cycled to 75-90°C for complete reaction to take place. Clear colourless liquids were obtained except for the acid rich melts (e.g., 2:1, AlCl₃:BPC) which always showed some discoloration.

The melts were characterized by proton nmr, laser Raman spectra and 27 Al nmr and no significant features were found using these methods beyond those reported by Wilkes <u>et al</u>. (15), Gray <u>et</u> <u>al</u>. (16)., and Osteryoung <u>et al</u>. (17).

The 2:3 and 1:2 AlCl3: BPC melts exist in two phases at R.T. Preliminary analytical data would suggest that the liquid phases are 1:1.2-1.3 AlCl3 :BPC melts.

RESULTS AND DISCUSSION

Melt Phenomena. -Analytical evidence has established that the AlCl3 is chlorine-deficient, the Cl/Al ratio being typically 2.8-2.9. Both a powdery and crystalline material are observed as sublimation products. Attempts to relate these results to a possible second phase structure of AlCl3 remain inconclusive. For example, x-ray diffraction and 27 Al NMR show only marginal differences, if any. The observation that a yellowish-amber tinge increased in the melt with increasing mole fraction of AlCi3 may also be related to chlorine deficiency. Although it has been reported that the yellow discoloration can be eliminated using pre-electrolysis procedures (7), it should also be noted that the discoloration reappears in several weeks. Obviously, further study in this area is required.

The melting and freezing points were determined for each melt mixture to yield the phase diagram in Figure 1. The figure shows an A-B compound at 0.50 mole fraction (1:1 AlCl3: BPC), as others have reported (2). However, not only supercooling to as much as 60°C below the mp, but also metastability of the super-cooled melt for protracted periods of time were observed. For example, the .67 AlCl3 mole fraction melt (2:1 AlCl3 :BPC) was used as an electrolyte for anodic oxidations and cathodic reductions while supercooled by 20°C for up to two weeks without freezing. The ability of these pure, chlorine deficient melts to supercool and remain so while being "seeded" by structural changes occurring at the electrode-electrolyte interface, needs theoretical attention. We suggest that, as in the molten polysulfide system which also shows supercooling phenomena (18), there may exist repetitive molecular structures which could promote meta-stable chains. Chain structures have been inferred from nmr studies of nitrogen heterocycles by Quereshi et al. (19) and more recently for these melts by Wilkes et al. In the case of the (15). melts, the chain structures have been postulated to be

polymers of anion-cation complexes. The specific complexes are dependent on the AlCl₃ concentration. The free energy of formation of these chains need not be large to effect considerable meta-stability and it is possible that the non-stoichiometry in the AlCl₃ leads to chain-breaking.

Cyclic voltammetry shows generally that the melts are stable over a potential range of about 2.0V. This range has been observed on Al, Ag, Ti and Li in our case and on glassy carbon and W by other workers (7). For example, the cyclic voltammogram in a 1:1 AlCl₃ : BPC melt taken on Ti with a Al reference (see Figure 2) shows the major reduction wave at about -0.8V and the major oxidation at about +1.2V. The oxidation wave occurs between +0.8 and +1.2V with different metal surfaces. Figure 2 also demonstrates X, Y and Z oxidation processes by Ti, but no corresponding reduction activity. By contrast, as will be seen later, the X, Y, Z oxidation processes are not clear during anodic sweeps on Mo but can be separated on reduction. The major reduction at about -750mV versus an Al reference at R.T. on Li, Ti, and Ag produced a blue-colored transient product which reacts further and disappears. The blue product has an

absorption peak at 610 nm and was spin-active, as demonstrated by its 18-line ESR spectrum (see Figure 3). We have tentatively assigned the spin-active product to be the butyl pyridinium radical formed by reduction of the butyl pyridinium cation, BP⁺. The disappearance of the blue product is probably due to radical dimerization or formation of a dihydropyridine. Naarova et al (20) have also observed blue colours during electrochemical reduction of a series of alkyl pyridinium ions. However, although they were unable to identify the main one-electron reduction products, they were able to detect and characterize a secondary dimeric radical product.

Preliminary

conductivity measurements of the BPC:AlCl3 melts gave values ranging from 3.3 x 10⁻³ (ohm.cm)⁻¹ (AlCl₃- BPC 2:3 melt) to a high of 8.0 $x 10^{-3}$ (ohm.cm)⁻¹ for the 2:1 AlCl₃ - BPC melt. These results are consistent with those of King et al (2) where a specific conductivity of 8.9×10^{-3} (ohm om) $^{-1}$ was obtained for the 2:1 AlCl3 -BPC melt. These values are comparable to those obtained for nonaqueous aprotic battery electrolyte systems.

Electromotive Series -Silver and copper metal

electrodes show a potential difference of Aq positive to Cu by 30±2mV. Both show small anodic and cathodic over-potentials and are suitable as reference electrodes, although the Ag electrode is preferred. Tn preliminary work, Al was selected as the stable reference electrode since its activity in the melts is expected to be fixed. However, the Al potential against both Cu and Ag was found to drift slowly for several hours or days at room temperature. The drift may be due to slow dissolution of an oxide film on Al. Ti showed similar but more irreproducible open-circuit potential drift. Measurements of open-circuit voltages of several metals taken on a multi-electrode cell and on individual M/Aq cells yield a preliminary electromotive series (see Figure 4) for M/M^{+X} in the 2:1 melt at 25°C. For example, the Li/Ag couple gave a potential close to the theoretical value given in redox tables, ≃iz Li + AqCl = LiCl + Aq; E = 2.70V.

Metal Dissolution and

Displacement. - Of the group of metals studied in the acidic 2:1 AlCl₃- BPC melt, the alkali metals are easily corroded in the order Li>Na>K. For example, Na is destroyed in a few minutes, Li and Ca passivate, and K appears to passivate. A 0.5mm Li foil reacts immediately on contact with the 2:1 melt (turns black). Mg tarnished after a few hours and appears to be protected by a loose reaction product. Al reacts slowly, showing tarnish after a few Other metals studied days. showed relatively no signs of corrosion. In fact, Mo appeared to be cleaned of darkening air-formed oxide by the melt; and Ti likewise at elevated temperatures, $\sim 60^{\circ}$ C. Generally, the reaction initiation period may be days. Pt and C showed no evidence of reaction.

By contrast with behavior in the 2:1 AlCl3-BPC melt, Li is stable in the 1:1 melt, even at 60°C, over a period of three months. Li, however, does react with the liquid phase of the 2:3 AlCl3- BPC melt to give the blue butyl pyridinium radical.

In a Al-Cu cell, a powder Cu deposition on the Al was observed. In a Ti-Cu cell, Cu deposition could be observed after stripping the protective oxide coating. Copper powder could be made by electrochemical reduction of Cu⁺² dissolved in a 2:1 AlCl₃- BPC melt.

As in aqueous systems all the metals examined showed anodic passivation at current densities or anodic potentials higher than some critical value. Electrochemical Studies. -(a) Active metals: Li, Mg, In, Al.

The critical current density for anodic oxidation of pure Li foil at R.T. in a 2:1 AlCl₃- BPC melt was found to be 10 mA/cm^2 and much less, about 2 mA/cm^2 in a supercooled 1:1 melt (see Figure 5). Although LiCl is quite soluble to 0.1 mole fraction LiCl (15) (1 M; a LiCl/BPC/AlCl3 ratio of 1:1:2), it is probably the ratio of dissolution of the LiCl formed by anodic reaction which determines the critical current density. On the other hand, the corrosion reaction which proceeds in parallel with the anodic reaction probably aids the removal of reaction product, baring fresh Li surface for reaction. Independent measurements of the rates of these processes are needed.

The reversibility of the system, with respect to reduction of the reaction product LiCl to Li while still on the surface or nearby in solution, remains suspect although the reversibility of one or more species in solution is indicated. For example, in Figure 5, it has been observed that the potential remains within $\sim 200 \text{mV}$ of the open circuit potential for at least ten minutes if the current density during oxidation/reduction steps does not exceed 4 mA/cm². Obviously, the corrosion

reaction militates against on Mo are shown in the alkali metals (Li, Na, Figure 6a. Critical K) being a dependable, current density was ab rechargeable anode in the $10 \ \mu \text{A/cm}^2$ for both an 2:1 electrolyte. As in the Li/organic-electrolyte reduction at room systems, a non-porous, temperature. During t adherent inhibiting anodic oxidation, pote corrosion-reaction product may be necessary.

The highly functional reduction occurred at Mg alloy, Mg AZ61A (6% Al, potentials strongly 1% Zn, high purity) dependent upon current supports current densities of up to 5 mA/cm² at 25°C in the 2:1 AlCl3-BPC melt but corrodes slowly. It in the cathodic reduction may redeposit under special conditions. Some of this stored charge

(b) Passive metals: Pt, C, Mo.

Oxidation and the overpotential at any current density decreases with agitation; during an open-circuit rest (21, 22) have recently (Figure 6a) further store reported work on soluble organic and inorganic redox and the potential returns systems, and Koch et al (7) to about 1090mV following polarization to higher or

In a cell containing freshly prepared 2:1 AlCl3 :BPC melt, Pt, C and Mo were positive 0.86, 0.82 and 0.31 initially against an Ag reference. Pt and C were steady while Mo was fluctuating and climbing. After aging the highest potential was observed for Mo at 1090 [±]5mV.

Pt and Mo metals in a 2:1 AlCl3-BPC melt were chosen for polarization and potential decay measurements. Anodic and cathodic charging currents

on Mo are shown in Figure 6a. Critical current density was about $\mu A/cm^2$ for both anodic 10 reduction at room temperature. During the anodic oxidation, potential arrests X, Y, Z were observed, at about 0.5, 1.1 and 1.2V. Cathodic reduction occurred at potentials strongly dependent upon current density; however, the charge stored in the anodic oxidation and retrievable in the cathodic reduction Some of this stored charge may be in surface Mo compounds, but most will be in the electrolyte: thus the overpotential at any current density decreases with agitation; during an open-circuit rest (Figure 6a) further stored charge becomes available; to about 1090mV following polarization to higher or lower values (Figure 6b).

The nature of the active redox system on Mo is not yet established. Similar behavior was found on Pt and on spec-pure (no metals) graphite. Candidate redox systems include Cl2/Cl⁻ and OCl⁻/Cl⁻.

Attempts were made via ESR to detect any long-lived free radical formed as a result of anodic oxidation of the 2:1 AlCl3-BPC melt on Mo and on C. Special care was taken to eliminate the potentially spin active species Ag⁺ or Cu⁺⁺ from the anolyte which could originate from the reference electrodes. No active species were found.

(c) Transitional Metals: Cu, Fe. The redox system Cu/Cu⁺² does not display simple behavior. The anodic oxidation is much faster than cathodic reduction, even in a 2:1 AlCl3-BPC melt saturated with Cu₂Cl₂. Both active and passivated copper were studied. At anodic potentials more positive than about 0.22V at room temperature the metal passivates (see Figure 7). The dependence of peak current iap, and of passivating current ia (at a potential 3.0V at which passivation was assured), was measured from -30° up to +80°C. The anode and reference were separated by a glass frit from reduction product(s) which might be formed at the Cu counter electrode, and the anode potential was swept at lmV/sec from 0 to 3.00V and held there. After ia had stabilized and had been measured, the potential was swept at 5mV/s up to 3.50, then down to 2.50 and back to 3.00, and the average slope $\Delta V / \Delta i$ determined. Thus two measurements ia and $\Delta V / \Delta i$, related to the resistance of the passivated electrode, were in hand. Then the temperature was re-set, up

or down several degrees, and after stabilization of ia, the $\Delta V / \Delta i$ Between -30° redetermined. to +45°C this procedure gave a systematic measure of "resistance" as a function of temperature (see Figure 7). Repeated returns to 21 °C gave values which indicated that no irreversible changes had occurred at higher or lower temperatures (although this observation does not prove that the films were not different at the different temperatures).

The activation energy for the peak rate ia^p is very low (20 KJ/mol) indicating mass transfer control in the electrolyte and perhaps diffusion of Cu^{+2} away from the anode. The value of 20 KJ/mol compares favourably with Osteryoung's (22) for diffusion controlled mass transfer of the Fe²⁺/Fe³⁺ couple in these melts. The mechanism changes below -20°C to a process with an activation energy of ~50 KJ/mol.

Above 46 °C the activation energy for the anodic oxidation process for the passivated copper (held at 3.0V) is about 50 KJ/mol (slopes plus or minus 2.5 for resistance $\Delta V/\Delta i$ or rate i_a). This suggests that a different, perhaps liquid crystal medium, controls transport processes at or in the surface film. Above 46 °C the film apparently is much thinner because of dissolution. Some chemical-activation process with much higher activation energy (130 KJ/mol⁻¹), such as $Cu^+ = Cu^{++} + e^-$, must be rate-determining.

The i/V sweeps in the range $3.0 \stackrel{+}{=} 0.5V$ at temperatures greater than about 40°C show a minimum in the i/V curve right at the formation potential of 3.00V. From this fact it could be argued that the resistance is really a back-emf due to concentration gradient of the conducting species in the film. Under these steady-state conditions the electrolyte should be saturated with the Cu^{+2} . Solubility is low. By means of ESR Cu⁺² was detected in the electrolyte, although there was no appearance of the characteristic blue color of Cu^{+2} in any of these experiments. The role of the Cu^+/Cu^{++} couple in the melt remains unknown.

PROSPECTS - FUNDAMENTAL AND APPLIED

Several opportunities for fundamental electrochemical work on metals in AlCl₃-BPC melts have been identified. They include: (a) redox processes on Pt and Mo; (b) anodic electrocrystallization on Cu and Ag; (c) dissolution of Li, Mg; (d) stripping of surface films from Al, Ti and Zr; (e) identification of electrolyte complexes and of anodic and cathodic reaction products. Attention to purity and analytical content is seen to be of primary importance, and is stressed.

The stability of supercooled melts is of fundamental interest, as well as is the effect of soluble metallic chlorides. The most fundamental question to be answered remains: Why are these mixtures liquid at R.T. and below?

Other melt systems such as the imidazolium based systems developed by Wilkes et al (15) may have the same prospects suggested for BPC based melts. The theoretical basis for the identification of alternate, more stable nitrogen heterocycles has been LUMO calculations. Our preliminary investigations indicate additional "potential" systems suitable for future study.

From a technological application viewpoint, the use of R.T. melts is limited by stability and electrical conductivity. Metallurgical uses such as the removal of scales or oxides from metals like Mo and Ti may be feasible. There is evidence for electrodeposition of Cu and Al.

Primary batteries based on Li, Ca or related alloys as anodes are possible. However, preliminary estimates indicate that the performance is not likely to exceed that of a good Zn-AgO reserve primary. As an alternative to organics now used in conventional lithium primaries, these melts may offer a useful alternative for special applications. Prospects for melts as media for electro-oxidizing oily organic wastes and recovering metals from them needs to be examined, as does the possibility of conducting more selective organic coupling reactions than are possible with the Friedel-Crafts reactions.

In the present work, we have concentrated on the acidic, low-freezing point melts. If low f.p. is not an important consideration, the neutral or basic melts become interesting. As would be expected, both the molecular structures and electrode processes vary with melt composition.

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REFERENCES

- (1) "Chemical and Electrochemical Studies in Room Temperature Aluminum-halide-containing Melts" by H.L. Chum and R.A. Osteryoung in <u>IONIC LIQUIDS</u> edited by D. Inman and D.G. <u>Lovering</u>, Plenum Press, New York, 1981, p. 407.
- (2) R.A. Carpio, L.A. King, R.E. Lindstrom, J.C. Nardi and C.L. Hussey, J. Electrochem. Soc., 126, 1644 (1979).
- (3) J. Robinson and R.A. Osteryoung, J. Amer. Chem. Soc., 101, 32 (1979).
- (4) J.S. Wilkes et al, <u>Inorg. Chem.</u>, <u>21</u>, 1263 (1982).
- (5) F.H. Hurley and T.P. Wier, J. Electrochem. Soc., <u>98</u>, 203 (1951).

REFERENCES Cont'd

- (6) R. Suchentrunk, "Corrosion Protection by Electrodeposited Al", in <u>Materials Coating Techniques</u>, <u>NATO/AGARD-LS-106</u>, p. 7-12 (1980).
- (7) V.R. Koch, L.L. Miller, and R.A. Osteryoung, <u>J. Amer. Chem. Soc.</u>, <u>98</u>, 5277 (1976).
- (8) C.L. Hussey, L.A. King and J.S. Wilkes, J. Electroanal. <u>Chem.</u>, 102, 321 (1979).
- (9) R.J. Gale and R.A. Osteryoung, <u>Inorg. Chem.</u>, <u>18</u>, 1603 (1979).
- (10) A.A. Fannin, Jr. and L.A. King, F.J.S. R.L. Technical Report SRL-TR-76-19 (1976).
- (11) J.C. Nardi, C.L. Hussey and L.A. King, U.S. Patent No. 4,122,245, Oct. 1978.
- (12) D.W. Seegmiller, G.W. Rhodes, and L.A. King, <u>Inorg. Nucl. Chem. Letters.</u>, <u>6</u>, 885 (1970).
- (13) M. Walter and L. Ramaley, <u>Anal. Chem.</u>, <u>45</u>, 165 (1973).
- (14) G.A. Heath, G.T. Hefter, T.W. Boyle, C.D. Desjardins, and D.W.A. Sharp, J. Fluorine. Chem., 11, 399 (1978).
- (15) J.S. Wilkes, J.L. Pflug, J.A. Levisky, C.L. Hussey, A.A. Fannin and L.A. King, F.J. Seiler Research Laboratory Technical Report, TR-82-0005, June 1982.
- (16) J.L. Gray and G.E. Maciel, J. Amer. Chem. Soc., <u>103</u>, 7147 (1981).
- (17) R.J. Gall, B. Gilbert, and R.A. Osteryoung, <u>Inorg. Chem.</u>, <u>18</u>, 2723 (1979).
- (18) G.J. Janz and D.J. Rogers, Extended Abstracts of the 162nd Electrochem. Soc. Meeting, Volume 82-2, p. 536 (abstract no. 333), Oct. 1982.
- (19) M.S. Quereshi and I.M. Walker, <u>Inorg. Chem.</u>, <u>14</u>, 2187 (1975).

REFERENCES Cont'd

- (20) J. Volke and M. Naarova, <u>Coll. Czech. Chem. Commun.</u>, <u>38</u>, 2670 (1973).
- (21) G.T. Cheek and R.A. Osteryoung, J. Electrochem. Soc., <u>129</u>, 2488 (1982).
- (22) C. Nanjundiah, K. Shimizu and R.A. Osteryoung, J. Electrochem. Soc., <u>129</u>, 2474 (1982).





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FIGURE 4 - Open Circuit Voltages of several metals vs an Ag reference.





FIGURE 5 - Cyclability and Passivation of Li foil in a 1:1 melt.

FIGURE 6a - Oxidation and Reduction Behavior of a Mo electrode in a 2:1 AlCl₃-BPC melt.









REDUCTION OF AROMATIC KETONES IN AN ALUMINUM CHLORIDE : DIALKYLIMIDAZOLIUM CHLORIDE MOLTEN SALT SYSTEM

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ABSTRACT

The electrochemical reductions of benzil, benzoin, and benzophenone have been studied in the 1-methyl-3-butylimidazolium chloroaluminate molten salt system. For benzil, the primary two-electron reduction process in the basic melt produces a complexed stilbenediolate intermediate which undergoes rearrangement to the benzoin dianion. In the acidic melt, a 1.8 volt shift in benzil reduction to more positive potentials is observed due to complexation of the carbonyl oxygens by aluminum chloride. Benzophenone and benzoin, both of which undergo a two-electron reduction in the basic melt, also exist in the acidic melt as aluminum chloride complexes.

INTRODUCTION

Previous studies of anthraquinone (1) and chloranil (2) in the aluminum chloride : 1-butylpyridinium chloride molten salt system have established that the electrochemical characteristics of these compounds depend markedly upon melt acidity. On the basis of these results, it was decided to investigate other compounds containing carbonyl groups in order to assess the generality of the phenomena involved. The compounds benzil, benzoin, and benzophenone were chosen since they represent aromatic ketones with some degree of structural variation. The fact that these compounds typically undergo reduction at more negative potentials than do quinones (3), however, prevented their study in the above molten salt system. With the discovery and characterization by Wilkes et al. of chloroaluminate molten salts based on dialkylimidazolium chlorides (4,5), a system became available which retains the advantage of room-temperature operation while possessing a much wider potential window for voltammetric studies, particularly in the basic region. Our results for ketone reduction in this molten salt system are presented in this paper.

EXPERIMENTAL

All experiments were carried out in a Forma Scientific Company glovebox, the argon atmosphere being purified by continuous passage through molecular sieves and both Ridox (Fisher Scientific Company) and BTS (BASF Corporation) oxygen removal catalysts. Total oxygen and moisture content is estimated to be below 10 ppm based on the absence of fumes from samples of titanium tetrachloride and diethylzinc kept in the glovebox.

Aluminum chloride (Fluka Chemical Corp., puriss.) was sublimed three times, giving small colorless crystals. 1-Methyl-3-butylimidazolium chloride was prepared by reaction of 1-methylimidazole with 1-butylchloride followed by threefold recrystallization of the salt from acetonitrile/ethyl acetate mixtures (4). After drying at 50° C in a vacuum oven for two to three days, the salt was placed on a vacuum line in the molten state for several hours prior to introduction into the glovebox. Melt compositions are denoted by the aluminum chloride: 1-methyl-3-butylimidazolium chloride molar ratio.

Benzil, benzophenone (Aldrich Chemical Company), and benzoin (Matheson, Coleman and Bell) were used as received, the melting points of the compounds agreeing with the literature values.

Electrochemical experiments were carried out using a Princeton Applied Research (PAR) Model 174A Polarographic Analyzer for voltammetric experiments and a PAR Model 170 Electrochemistry System for coulometry and preparative electrolysis. In some cases a microprocessor-based function generator was employed in cyclic voltammetric studies. The cell system used has been described previously (6). A 3 mm diameter vitreous carbon rod was used as the working electrode, with potentials referred to an aluminum wire immersed in a 2.0 : 1.0 aluminum chloride : 1-methyl-3-butylimidazolium chloride melt. Unless otherwise indicated, experiments were carried out at a temperature of 25 + 1°C.

Preparative electrolyses were run in a 35 mm diameter vitreous carbon crucible (Atomergic Chemetals Corp.). Product isolation from these electrolyses involved hydrolysis of the melts with distilled water followed by extraction with either benzene or hexane.

RESULTS AND DISCUSSION

Benzil

As seen in Figure 1, benzil reduction in the 0.8 : 1.0 basic melt occurs at -1.05 V, with a subsequent reduction at -1.27 V and oxidation processes at +0.22 V and +0.55 V also apparent. The initial reduction process was studied in some detail by means of several electrochemical techniques. Variation of the cyclic voltammetric scan

rate over the range 10 mV/second to 200 mV/second produced a linear dependence of peak current on square root of scan rate, indicating that the reduction is diffusion-controlled on this time scale. Coulometry at -1.10 V showed that two electrons are involved in the reduction, while hydrolysis of the melt following a preparative electrolysis at this potential led to the isolation of benzoin in approximately 90 % yield.

In carrying out the cyclic voltammetric survey, it was found that, as the scan rate was increased, the current observed for the reduction process at -1.27 V decreased relative to that for the initial reduction process while a corresponding increase in the oxidation peaks at +0.22 V and +0.55 V occurred. At scan rates above 20 V per second, the second reduction process was not observed, leaving only the single reduction peak with subsequent oxidation process, seen as one broad peak, in a peak current ratio (cathodic to anodic) of 3.0. Upon lowering the scan rate to 10 mV/second, a small amount (approximately 10%, based on the above peak current ratio) of the species undergoing oxidation was still observed on the return sweep, with the second reduction process now greatly predominant. It is evident from these results that the species responsible for the oxidation processes are intermediates formed upon reduction of benzil and undergo a transformation to a substance the reduction of which is observed at -1.27 V.

The most plausible interpretation of these results involves the initial two-electron reduction of benzil to form a complexed stilbenediolate intermediate followed by a rearrangement to the benzoin dianion as depicted in Figure 2. It should be noted that a similar pathway has been proposed by Stapelfeldt and Perone for benzil reduction in aqueous media (7,8). In the basic melt, benzil reduction apparently occurs as an ECEC process since the uptake of two electrons occurs in a single reduction process. As is the case for chloranil and anthraquinone reduction in basic aluminum chloride : n-butylpyridinium chloride melts (1,2), the chemical step following the first electron transfer involves an interaction of the anion radical produced with the tetrachloroaluminate ion, leading to the formation of the complexed species shown in Figure 2. The complexed stilbenediolate undergoes oxidation at +0.22 V $\,$ and +0.55 V, the two processes corresponding to the oxidation of the trans and cis isomers, respectively, by analogy to the situation in aqueous media (7,8). An approximate value of the rate constant for the rearrangement involved in benzil reduction was obtained by the method of Nicholson and Shain (9) as 0.01 sec^{-1} . The reduction of the complexed benzoin dianion, formed upon rearrangement of the stilbenediolate intermediates, is responsible for the cathodic process at -1.27 V. This assignment is supported by the fact that reduction of benzoin added to the basic melt, which will be described in greater detail in a later section, occurs at -1.25 V. The series of voltammograms obtained at various temperatures, shown in Figure 3, shows qualitatively the increasingly rapid formation of the benzoin dianion as the temperature is raised.

In the 1.2 : 1.0 acidic melt, a large shift (1.8 V) of the potential for benzil reduction occurs (Figure 1), as has been observed in the 1-butylpyridinium chloroaluminate system for quinones (1,2) and amines (10) for which complexation by aluminum chloride in the acidic melt took place. Further evidence for such an interaction for benzil in the present system was obtained by comparing infrared spectra of benzil in the 0.8 : 1.0 basic melt and 1.2 : 1.0 acidic melt. As seen for anthraquinone complexation (1), a complete shift in carbonyl stretching frequency from 1670 cm⁻¹ (basic melt) to 1545 cm⁻¹ (acidic melt) was observed, indicating that the carbonyl groups are both complexed by aluminum chloride in the acidic melt. In contrast to the complexed anthraquinone, however, the complexed benzil is very soluble, to the extent of at least 0.5 M, in the acidic melt.

More quantitative electrochemical experiments involved coulometry at +0.50 V, indicating a two-electron process, and preparative electrolysis at the same potential, giving rise to benzoin as isolated from the hydrolyzed melt. The fact that the voltammogram in Figure 1 (acidic melt) shows only one reduction process suggests that the initial benzil reduction product in the acidic melt does not undergo rearrangement as it does in the basic melt. Voltammetry of reduced benzil solutions showed an oxidation peak at +1.72 V, corresponding to that shown in Figure 1, upon an initially positive potential sweep from +1.20 V. This information, coupled with the above coulometric study, strongly indicates that the reduced benzil in the acidic melt exists as the complexed stilbenediolate dianion. The peak current corresponding to its oxidation showed a slight (10%) decrease over a period of two days, indicating that the species is not completely stable in the acidic melt. As in the basic melt, one complexed stilbenediolate species, probably the trans isomer, predominates in the acidic melt.

The separation in potentials observed for the benzil redox processes in the acidic melt is an indication that benzil undergoes further complexation upon reduction. This interaction can be represented by the equation

$$B(A1C1_3)_2 + mA1_2C1_7 + 2e^- = B(A1C1_3)_{2+m}^{2-} + mA1C1_4,$$

in which $B(AlCl_3)_2$ refers to benzil the oxygen atoms of which are complexed with aluminum chloride and m is the number of additional aluminum chloride molecules acquired in the reduction process. The value of m was determined by a potentiometric study in which the potential of a coulometrically produced mixture containing equal amounts of the oxidized and reduced benzil species was measured as a function of the melt composition according to the Nernst equation

$$E = E + \frac{RT}{2F} \ln \frac{[B(AlCl_3)_2]}{[B(AlCl_3)_{2+m}^2]} + \frac{mRT}{2F} \ln \frac{[Al_2Cl_7]}{[AlCl_4]}$$

The slope of a plot of E against $\log \frac{[Al_2Cl_7]}{[AlCl_4]}$ (Figure 4) over the

acidity range 1.05 : 1.00 to 1.70 : 1.00 was found to be 49 mV per log unit, indicating that somewhat less than two (1.7) $\rm Al_2Cl_7^-$ ions

are involved in the reductive complexation process. The corresponding value for anthraquinone reduction as previously studied (1) was found to be 2.0, suggesting that each oxygen atom in the reduced quinone is complexed by two aluminum chloride molecules; in the present case, the smaller value for m may indicate that some sharing of the complexing aluminum chloride between the oxygen atoms occurs as a result of their rather close proximity. The slope of the curve increased somewhat to 74 mV per log unit in the acidity range 1.70 : 1.00 to 2.00 : 1.00, suggesting that a more extensive interaction occurs at higher acidity levels. Finally, cyclic voltammetric sweeps in both directions from the rest potential following the potentiometric study indicated little if any decomposition of the reduced form of benzil had taken place.

A brief study was also made of benzil electrochemistry in the neutral melt, typical results being shown in Figure 1. It is interesting to note that the situation in the neutral region is not as welldefined as is the case for anthraquinone, in which a process attributed to the singly complexed quinone was observed (1). It is thought that the present results again reflect the fact that the complexation sites of benzil are both much closer together than those of anthraquinone and not as constrained in their orientation to one another, a situation which apparently leads to some lack of definition in the electrochemical properties of the singly complexed benzil species.

Benzoin

The formation of the benzoin dianion from benzil reduction in the basic melt prompted a study of the electrochemical behavior of benzoin itself in the molten salt. In Figure 5, the cyclic voltammogram of benzoin added to a basic melt shows the main reduction process at -1.25 V, preceded by a smaller process at -1.10 V. Since the peak height for this smaller system did not appear to depend directly on the scan rate, it was assumed that it did not indicate product adsorption in the benzoin reduction but that the response was due to the presence of another electroactive species in the melt. Support for this conclusion was obtained from a voltammogram taken at platinum rather than vitreous carbon, under otherwise identical conditions, which showed a larger peak at -1.10 V than at -1.25 V. Given the higher overpotential for proton reduction at vitreous carbon compared to platinum (11), the most logical assignment for the more positive process is that of proton reduction. It should be noted here that a smaller response at this potential was observed in background scans (before benzoin addition) at platinum, and apparently is due to protons formed from interaction of trace amounts of moisture with the chloroaluminate melt (12). The larger proton concentration observed after benzoin addition indicates a displacement of chloride ion from the tetrachloroaluminate ion by the benzoin hydroxyl group, giving a complexed benzoin and a proton. It should be stressed at this point that this complexation occurs not at the carbonyl oxygen but at the hydroxyl oxygen. The structural difference between this complexed benzoin, with its C-H bond intact, and the benzoin diamion produced in benzil reduction (Figure 2) is rather slight, a fact which is consistent with the similarity in reduction potentials for these species.

The voltammograms in Figure 5 illustrate the shift in potential observed for benzoin reduction as a result of complexation of the carbonyl oxygen by aluminum chloride as the melt acidity is increased into the neutral and acidic regions. The fact that no additional processes were observed between those illustrated is most probably due to the presence of only one site on the molecule at which additional complexation can occur. In the 1.2 : 1.0 acidic melt, it is seen that the aluminum deposition process partially obscures the peak for reduction of the benzoin : aluminum chloride complex.

Benzophenone

As is evident from the voltammetric curves in Figure 6, only one process is observed for benzophenone reduction in the basic melt. The potential at which this reduction occurs is considerably more negative than that for benzoin or benzil reduction, an observation which reflects the existence of other electron-withdrawing centers near the carbonyl group in the latter cases. Coulometric investigations revealed that two electrons are involved in the reduction; therefore, it again appears that a rapid complexation of the intermediate anion radical takes place by displacement of chloride from tetrachloroaluminate, followed by the uptake of another electron by the system. Benzhydrol (diphenylmethane) was isolated from the hydrolyzed melt following a preparative electrolysis at -1.70 V, indicating that the electrolysis product in the melt is the complexed form of the alcohol in which the oxygen and carbon of the C-O bond are each complexed with aluminum chloride. In the neutral and acidic melts, a simple shift in reduction potential to -0.30 V is observed, again characteristic of complexation of the carbonyl group prior to reduction. As in benzoin reduction, the reduction process here occurs immediately positive of aluminum deposition in the acidic melt.

CONCLUSIONS

Perhaps the most general aspect of this work is the complexation of ketone reduction products, whether in the basic or acidic region, by interaction with species in the melt. More specifically, displacement of chloride from the tetrachloroaluminate ion by oxygen anions upon carbonyl reduction occurs in the basic melt, whereas in the acidic melt the interaction is probably with the more acidic heptachlorodialuminate species with resultant displacement of tetrachloroaluminate. These interactions appear to be extremely fast and result in ECEC twoelectron processes as characteristic reduction pathways for the systems studied. The rapidity of this complexation is such that intermolecular coupling of any intermediate radicals is effectively prevented, as seen by the formation of the complexed benzhydrol from benzophenone reduction, whereas coupled products, typically pinacols, result from reduction of ketones in other nonaqueous solvents (13).

Another common feature seen in this study involves the complexation of the carbonyl groups of the ketones by aluminum chloride upon their introduction into the acidic melt. A shift in reduction potential was observed for all the ketones studied in this work, as has been found previously for quinones (1,2) and amines (10) in chloroaluminate melts. In the case of benzil, a corresponding shift in carbonyl infrared stretching frequency confirmed that both carbonyl oxygens undergo complexation.

The rearrangement observed upon benzil reduction in the basic melt allows some correlation of the properties of the molten salt solvent system with those of aqueous systems by comparing the rates of the rearrangement in the two systems. In aqueous buffers, it was found that the rearrangement of the stilbenediolate intermediate is rather slow in acidic solutions (0.0011 sec^{-1} at pH 1.0) and increased as the solutions were made more basic (7). The rate in neutral aqueous solutions (0.0073 sec^{-1} at pH 7.2)(7) appears to correspond rather closely with that observed in the basic molten salt, indicating that the complexation of the stilbenediolate, whether by protons or aluminum chloride, is not sufficiently strong to prevent rearrangement to the benzoin dianion with its conjugated carbonyl group. At low pH and in the acidic melt, the greater complexing ability of these media slows the rearrangement markedly and, in the melt, allows the existence of the stilbenediolate species as a rather stable entity.

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REFERENCES

- 1. G.T. Cheek and R.A. Osteryoung, J. Electrochem. Soc., <u>129</u>, 2488 (1982).
- G.T. Cheek and R.A. Osteryoung, J. Electrochem. Soc., <u>129</u>, 2739 (1982).
- H. Siegerman, in "Techniques of Electroorganic Synthesis," N.L. Weinberg, ed., Volume V, Part II of "Techniques of Chemistry," John Wiley and Sons, New York, 1975. Appendix, p. 720.
- J.S. Wilkes, J.A. Levisky, M.L. Druelinger, and C.L. Hussey, in Proceedings of the Third International Symposium on Molten Salts, G. Mamantov, M. Blander, and G. Smith, eds., The Electrochemical Society, Inc., Princeton, NJ, p. 245.
- 5. J.S. Wilkes, J.A. Levisky, R.A. Wilson, and C.L. Hussey, Inorg. Chem., <u>21</u>, 1263 (1982).
- J. Robinson and R.A. Osteryoung, J. Electrochem. Soc., <u>125</u>, 1454 (1978).
- H.E. Stapelfeldt and S.P. Perone, Analytical Chemistry, <u>40</u>, 815, (1968).
- H.E. Stapelfeldt and S.P. Perone, Analytical Chemistry, <u>41</u>, 623, (1969).
- 9. R.S. Nicholson and I. Shain, Analytical Chemistry, 36, 706 (1964).
- 10. J. Robinson and R.A. Osteryoung, J. Am. Chem. Soc., <u>102</u>, 4415 (1980).
- 11. D.T. Sawyer and J.L. Roberts, "Experimental Electrochemistry for Chemists," John Wiley and Sons, New York, 1974, p. 69.
- 12. R.A. Osteryoung, personal communication.
- M.R. Rifi, in "Techniques of Electroorganic Synthesis," N.L. Weinberg, ed., Volume V, Part II of "Techniques of Chemistry," John Wiley and Sons, New York, 1975, Chapter VIII, pp. 87-95.



Figure 1. Cyclic voltammograms of benzil (20 mM) in 0.8:1.0 basic melt (top scan), neutral melts (middle scans), and 1.2:1.0 acidic melt (bottom scan). Scan rate = 100 mV/second. Temperature = 25° C.



Figure 2. Mechanism of benzil reduction process in 0.8:1.0 basic melt.



Figure 3. Cyclic voltammograms of benzil (20 mM) in 0.8:1.0 basic melt at various temperatures.

Figure 4. Nernst plot of coulometrically produced benzil (7.5 mM)/ reduced benzil (7.5 mM) mixture in acidic melt. Composition was varied by additions of aluminum chloride.



Figure 5. Cyclic voltammograms of benzoin (28 mM) in 0.8:1.0 basic melt (top scan), neutral melt (middle scan), and 1.2:1.0 acidic melt (bottom scan). Scan rate = 100 mV/second. Temperature = $25^{\circ}C$.



Figure 6. Cyclic voltammograms of benzophenone (28 mM) in 1.2:1.0 acidic melt (top scan), neutral melt (middle scan), and 0.8:1.0 basic melt (bottom scan). Scan rate = 100 mV/second. Temperature = 25° C.

ORGANIC REACTIONS IN LOW MELTING CHLOROALUMINATE MOLTEN SALTS

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ABSTRACT

Mixtures of 1, 3-dialkylimidazolium chlorides and aluminum chloride are liquid considerably below room temperature, and they promote certain organic reactions. Acidic mixtures of 1-methyl-3-ethylimidazolium chloride and AlC1₃ act both as a solvent and a catalyst for alkylation and acylation of aromatic compounds. The rate of reaction may be controlled by changing the Lewis acidity of the melt and the temperature. The melts that were used permit reactions at sub-zero temperatures. Spectroscopic experiments showed the identity of the catalytic species in the melt and the reactive intermediate.

INTRODUCTION

The behavior of organic compounds in chloroaluminate molten salts has been studied by several groups in the last decade. Early work involved the relatively high temperature (approximately 175° C) NaCl-AlCl3 molten salts, but problems with solubility, thermal stability and volatility were experienced. Later, low temperature melts comprised of 1-alkylpyridinium chloride and aluminum chloride were used to study the electrochemistry of a variety of organics at or near room temperature. As a rule, these electrochemical reactions took advantage of the ability of the AlCl3-rich melts to stabilize positive oxidation states of aromatic compounds (1). Numerous types of organic reactions employing chloroaluminate melts have been reviewed by Jones and Osteryoung (2). Surprisingly, reactions in the new low temperature melts have not been as extensively studied as those in the high temperature NaCl-AlCl3 melts.

Recently, we have been studying the structure, physical properties and chemistry of chloroaluminate melts consisting of mixtures of 1,3-dialkylimidazolium chloride and aluminum chloride (3). These mixtures are liquid at room temperature and some compositions melt substantially below room temperature. In addition, they demonstrate a much wider range of Lewis acidity than the NaCl-AlCl₃ mixtures. The binary mixture of 1-methyl-3-ethylimidazolium chloride and AlCl₃ ("MEETIM melt") has a particularly favorable combination of physical properties and ease of preparation. We noted that the MeEtImCl-AlCl₃ mixtures dissolved a wide variety of organic compounds and stabilized organic radical actions. We report here that the low melting MeEtImCl-AlCl₃ molten salts can act as catalyst and/or solvent for classic Friedel-Crafts alkylation and acylation of aromatic compounds.

EXPERIMENTAL

All melts were prepared as reported previously (3). In a glove box the appropriate amount of melt and aromatic compound were added to an "airless-ware" reaction flask (Kontes), usually 50 mL, equipped with a magnetic stirring bar. All further operations were done outside the glove box, using a dry nitrogen flow to exclude moisture. The reaction mixtures were usually cooled to 0° C in an ice/water bath. The organic chloride was added to the aromatic/melt mixture by pipet and the reaction was allowed to proceed for the appropriate time, after which the reaction was quenched by pouring over ice. The mixture was made alkaline with a concentrated NaOH solution until all precipitate was dissolved. The mixture was extracted with diethyl ether, dried over magnesium sulfate and analyzed by GC/MS.

RESULTS AND DISCUSSION

The venerable Friedel-Crafts electrophilic alkylation and acylation reactions are normally run in an inert solvent and catalyzed by suspended or dissolved AlCl₃. In this report we describe the reactivity and extent of these simple reactions employing the unusual MeEtImCl-AlCl₃ catalyst and solvent system. Since an acidic species is required to catalyze the reactions, compositions of the MeEtIm melt where AlCl₃ was in excess over the MeEtImCl was the most effective catalyst. We usually express the melt composition as apparent AlCl₃ mole fraction, N, realizing that free AlCl₃ does not exist in the melt. An N = 0.67 melt is prepared by adding 2 moles of AlCl₃ to 1 mole of MeEtImCl and is acidic. Likewise an N = 0.50 melt is prepared by combining 1 mole of each, and is neutral. N ≤ 0.50 implies a basic melt. A combination of the two solids produces a liquid that has the unique dual character of catalyst and solvent for Friedel-Crafts reactions.

A series of alkylating agents was investigated. Primary and secondary alkyl halides were added to mixtures of melt and benzene under anhydrous conditions. Alkylated benzenes were observed after reactions with methyl chloride, ethyl chloride, n-propyl chloride, n-butyl chloride, cyclohexyl chloride and benzyl chloride. Gaseous HCl was evolved during all of the alkylation reactions. In addition to mono-alkylation products, poly-alkylated benzenes were present in the reaction products. For example, excess ethyl chloride reacted with benzene to produce the following ethylbenzenes: mono-(12%), di-(11%), tri-(33%), tetra-(24%), penta (17%) and hexa-(2%). Methyl chloride produced an interesting array of products (Table 1). Note that the odd substitutions are virtually absent under the reaction conditions described. We have no explanation for this and we could not find any reports of similar phenomena in the literature.

Polyalkylation can be accounted for by considering the enhanced activity of the alkylated product. An excess of aromatic substrate would minimize polyalkylation. Thus, a ten fold excess of benzene over n-propyl chloride, in the presence of the 0.67 melt, produced predominately mono-propylbenzene (95%) with only 5% poly-propylated products. The mono-propylbenzene consisted of 70% iso-propylbenzene and 30% n-propylbenzene. The presence of iso-propylbenzene gives evidence of rearrangement of the primary carbonium ion to the more favorable secondary carbonium ion prior to ring substitution. The predominance of the rearranged product is an indication that the carbonium ion is formed, since reactions where ionization does not take place (i.e. where a "polarized covalent complex" is formed) show primarily the unrearranged product (4). Rearrangement of n-butyl carbonium ion to secondary butyl carbonium ion also occurs in alkylation reactions with n-butyl chloride. Rearrangements such as these are common in classic Friedel-Crafts electrophilic aromatic alkylation Spontaneous formation of carbonium reactions. ions in 1-(1-buty1)pyridinium chloride-AlCl3 melt has been reported (5), so we believe that the alkylation proceeds by way of the completely dissociated carbonium ions in the reactions described here.

Comprehensive positional isomerization studies of the polyalkylated benzenes have not been done in the melt to detect intramolecular rearrangements. Under usual Friedel-Crafts conditions intermolecular migrations among polyalkylated benzenes can also occur, especially in the presence of excess catalyst, to produce a non-thermodynamically controlled product distribution (6). The intermolecular migration usually occurs following protonation of the polyalkylbenzene at the carbon bearing an alkyl group with subsequent dissociation of the carbonium ion. The same process should not be possible in the aprotic MeEtIm melts. An equimolar mixture of benzene and hexamethylbenzene in an acidic MeEtIm melt (N = 0.67) resulted in no toluene, xylenes, mesitylenes, etc., thus there is no dissociation of the methyl substituents, probably due to lack of H^+ in the medium. Koch et al. (7) observed that Friedel-Crafts transalkylations could be initiated electrochemically in ethylpyridinium bromide/AlCl3 melts, which are chemically similar to the MeEtIm melt described here.

The versatility of the MeEtImCl-AlCl₃ melt in Friedel-Crafts reactions was demonstrated by attempting the alkylation reaction with different aromatic compounds. Table 2 lists the compounds and the alkylated products. The reactions showed the expected behavior towards activated and deactivated aromatic substrates, with no reaction occurring with nitrobenzene. The classic nature of Friedel-Crafts electrophilic aromatic substitution reactions in chloroaluminate melts was further demonstrated through relative reactivity measurements. In competitive propylation, toluene was found to be 1.9 times more reactive than benzene, and chlorobenzene was approximately 0.55 times as reactive as benzene. The relative rates suggest that a highly reactive electrophile is produced during the reaction. Such reactive attack by electrophiles is relatively non-selective for aromatic compounds that are activated or deactivated by substituents, therefore, relative rates are usually within the same order of magnitude.

Friedel-Crafts acylation of aromatic compounds with MeEtImCl molten salts proceeds with relative ease. Acylation proved simpler than alkylation because the first substitution product deactivates the aromatic nucleus towards further ring substitution. As a result, mono-substitution is observed with essentially no poly-substitution when benzene and acetyl chloride are reacted in acidic MeEtIm melt. A competitive rate experiment similar to that described for alkylation was done and the expected order of reactivity for benzene, toluene and chlorobenzene was observed. The relative rates were 1, 37, and 0.015 respectively. Note that the substituents are exerting more kinetic control in the case of acylation.

The simplest of the acylation reactions, i.e., MeEtImC1-AlCl3 catalyzed reaction of acetyl chloride with benzene to produce acetophenone was studied in detail. The rate at which acetophenone was produced was dependent on the composition (hence Lewis acidity) of the melt. In the melts described here, Lewis acidity is determined by the proportions of AlCl₃ to MeEtImCl used to prepare the melt, and is expressed as the quantity N (vide infra). In chloroaluminate melts, the Lewis acidity is known for any given composition. Melts of greater Lewis acidity demonstrated greater catalytic activity than those of weaker acidity or neutral and basic melts. A series of experiments using constant weights of reactants and melt but variable melt composition demonstrated the expected dependency. Figure 1 shows the initial rate of acetylation of benzene plotted vs N. The reactions were run at 0° C, and progress monitored by GC/MS analysis of aliquots. No substitution occurred in melts where N < 0.5, and the initial rates or reactions were found to increase as the acidity of the melt increased. These observations are almost certainly due to the increasing concentration of the actual catalytic species in the melt. The concentration of Al_2Cl_7 in the melts also is plotted in Figure 1, and the dependence of $[Al_2Cl_7^-]$ on N suggests that $Al_2Cl_7^-$ may be the catalyst responsible for promoting the reaction.

We examined the reaction between the melt and acetyl chloride by nuclear magnetic resonance (NMR) spectrometry in order to learn some details about the nature of the catalyst in the melt and the electrophile that is produced from the acetyl chloride. Observation of the proton NMR resonance of the methyl group in the acetyl chloride (or its reaction product) was useful, since it was a singlet well separated from the proton resonances of the imidazolium ions in the melts. Figure 2 shows the dependence on the acetyl proton chemical shift on the relative concentrations of acetyl chloride ([CH₃COC1]) and Al₂Cl₇ in the mixture. At low concentrations of acetyl chloride, the acetyl resonance was shifted downfield, and did not change much with increasing concentration. At high [CH₃COC1], the resonance moved upfield with increasing relative concentration. The threshold that delineated these two types of behavior was where [CH₃COC1] was equal to the [Al₂Cl₇] in the mixture (zero on the plot in Figure 2). This is very suggestive of a stoichiometric reaction between the CH₃COC1 and Al₂Cl₇, which is probably the actual catalyst in the melt. This is a very useful fact, because we can now easily select the reactivity of the medium toward Friedel-Crafts substitution by adjusting the <u>N</u> of the melt used. The product of the reaction between CH₃COC1 and Al₂Cl₇ is still an open question. The simplest case would be complete transfer of the chloride in acetyl chloride to produce the acetyl cation (1-oxoethylium):

$$CH_3COC1 + Al_2Cl_7 \rightarrow CH_3CO^+ + 2AlCl_4$$

Alternatively, a reactive complex of $CH_3COC1 \cdots Al_2Cl_7^$ might be the species formed. The ¹H NMR chemical shift of CH_3CO^+ has been measured (8), but in an entirely different solvent and with a different reference. Olah reported that CH_3CO^+ was shifted 1.9 ppm downfield from its parent CH_3COF . We see a 1.0 ppm downfield shift from the parent CH_3COC1 , which we cannot interpret unambiguously as the completely dissociated CH_3CO^+ . ¹³C NMR measurements are being done to clarify the matter.

From the results of the experiments described above we suggest the reaction scheme outlined in Figure 3. Note that Al_2Cl_7 is regenerated and that the observed products (acetophenone and HCl are accounted for). We have written the reactive electrophile as CH_3CO^+ ; but it may not be completely dissociated, as discussed above.

We have not yet established the full scope of Friedel-Crafts reactions in the MeEtImCl-AlCl₃ molten salts. At this point we know that alkylations and acylations are promoted by the melt, the reactions are homogeneous, and the work-up is relatively simple. The melt is easily prepared in two steps from commercially available materials, so it may be a generally useful reagent and solvent.

REFERENCES

1. J. Robinson and R. A. Osteryoung, J. Amer. Chem. Soc., <u>101</u>, 323-7 (1979).

- H. L. Jones and R. A. Osteryoung, Adv. Molten Salt Chem., <u>3</u>, 121-76 (1975).
- J. S. Wilkes, J. A. Levisky, R. A. Wilson and C. L. Hussey, Inorg. Chem., <u>21</u>, 1263-4 (1982).
- G. A. Olah and R. E. A. Dear, in "Friedel-Crafts and Related Reactions", vol. I, G. A. Olah, ed., Interscience Publishers, New York, 1963; p. 68.
- 5. G. D. Luer and D. E. Bartak, J. Org. Chem., 47, 1238-43 (1982).
- D. A. McCaulay, in "Friedel-Crafts and Related Reactions", vol. II, part 2, G. A. Olah, ed., Interscience Publishers, New York, 1963; p. 1066.
- V. R. Koch, L. L. Miller and R. A. Osteryoung, J. Amer. Chem. Soc., <u>98</u>, 5277-84 (1976).
- G. A. Olah, S. Kuhn, W. Tolgyesi and E. Baker, J. Amer. Chem. Soc., 84, 2733-84 (1962).

TABLE 1 ALKYLATION OF BENZENF

Alkylating Agent	N of	Mole Ratio R-C1:Benzene:			% Alkyla	ted Produc	ts	
(R-c1)	Melt	Melt	Mono-	Di-	Tri-	Tetra-	Penta-	Неха-
R=methy1 ^a	0.67	xs:1:1	1.5	58.5	1.5	26.8	1.4	10.2
R=ethy1a	0.67	xs:1:1	11.5	10.8	33.4	24.4	1	1.5
R=n-propy1 ^b	0.60	1.25:1.25:1	24.8	19.9	55.3	1	ł	;
R=cyclo- hexyl	0.60	10:10:1	35.0	30.0	34.4	1	!	! 1
R=benzy1 ^c	0,60	0.78:1.17:1	50.0	34.5	15.6		1	ł

a. Run at reflux temperature of alkyl chloride

b. Room Temperature, dry box conditions, exothermic with evolution of gas

c. Tar formation, small amount of alkylated product isolated

Aromatia	N of	Reagant Ratios	Draduat
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Benzene	0.67	10:1:1	95% Mono-, 5% Poly-
Toluene	0.67	10:1:1	73% Mono-, 27% Poly-
Chlorobenzene	0.67	10:1:1	96% Mono-, 4% Poly
Nitrobenzene	0.67	10:1:1	no reaction

TABLE 2 PROPYLATION OF AROMATIC COMPOUNDS^a

a. Reactions run at 0° C for 10 min.





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0.46 0

ELECTROCHEMICAL PROPERTIES OF THE SOLVENT SbCl3-AlCl3-N-(1-BUTYL)PYRIDINIUM CHLORIDE AND ELECTROCHEMICAL AND SPECTROELECTROCHEMICAL STUDIES OF THE SOLUTE 9,10-DIMETHYLANTHRACENE

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ABSTRACT

Physical and electrochemical properties were determined for ternary mixtures of SbCl₃, AlCl₃ and N-(1-buty1)pyridinium chloride (BPC1) that are liquid at ambient temperatures. Specific conductivities of the compositions (mole %) 60:19:21 (basic) and 60:21:19 (acidic) SbCl₃-AlCl₃-BPCl, measured over the temperature range 24 – 100° C, varied from 0.00395 to 0.02759 S cm⁻¹. Viscosities of the 60:21:19 and 60:19:21 melts were 22.8±0.7 and 31.5±0.9 cp, respectively, at 25.1±0.5°C. For a potentiometric titration between the compositions 60:18:22 and 60:22:18 with SbCl₃ fixed at 60 mol %, the potential of the Sb(III)/Sb(0) couple increased by 0.43 V at 27°C. Current-overvoltage curves for the oxidation of antimony metal in a 60:21:19 melt at an Sb rod electrode displayed Tafel behavior. The feasibility of performing electrochemical studies in these media was demonstrated using cyclic voltammetry, differential pulse polarography and double potential-step chronocoulometry to elucidate the electrochemical behavior of 9,10-dimethylanthracene (DMA) in the 60:19:21 melt. The solute was reversibly oxidized to its radical cation at an anodic peak potential of +0.50 V relative to the reference electrode SbCl3-BPCl(1), sat. SbCl₃/Sb at 27°C. Spectroelectrochemical experiments on DMA using an optical multichannel spectrometer over the range 479-984 nm are reported. The spectrum of the DMA radical cation has four bands with the most intense at 678 nm.

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Introduction

It has recently been shown (1) that certain SbCl₃-rich mixtures of SbCl₃, AlCl₃ and N-(1-butyl)pyridinium chloride (BPCl) are molten at room temperature and act as solvent-catalysts for hydrogen transfer reactions of anthracene, and that the 9H-anthracenium ion is stable in some of these media. These results suggest that lowmelting SbCl₃-AlCl₃-BPCl mixtures may have chemical properties similar to those of higher-melting binary SbCl₃-AlCl₃ and SbCl₃-MCl systems (where MCl is a strong chloride ion donor such as KCl or $[CH_3]_4NCl$). These higher melting salts have been shown to have unique catalytic properties and to provide environments in which arenium ions and arene radical cations are quite persistent and readily studied (2-9). The room temperature melts are more easily handled than the higher-melting mixtures, and carbocations may prove to be even more persistent at ambient temperatures than they are in the binary mixtures at elevated temperatures.

As a next step toward utilizing the ternary room temperature melts, we measured some of their physical and electrochemical properties, and studied the electrochemical oxidation of 9,10-dimethylanthracene (DMA). In studies of the higher-melting SbCl₃-rich mixtures, information on the potential of the Sb(III)/Sb(0) couple as a function of composition together with El_2 values for arene solutes proved to be of key importance in elucidating the chemistry of arenes in these media and we anticipate similar benefits from electrochemical studies of the ternary melts.

Experimental

Materials. — Purification of the melt constituents has been described (1). 9,10-Dimethylanthracene (Aldrich, >99%) was used without further purification. Antimony metal (Bradley Mining Co., 99.99%) was vacuum cast into 3-mm diameter single crystal rods that were drilled and threaded to serve as electrodes.

<u>Cells and Electrodes.</u> — The spectroelectrochemical cell, electrodes and fittings have been described (9) except that tungsten (Alfa, 99.98%) was substituted for platinum wire as a working electrode material, and the reference electrode was fitted with a Pyrex screw joint, FETFE o-ring and teflon bushing (Ace Glass) for easy assembly. The electrolyte in the reference electrode was a binary SbCl₃-BPCl melt saturated with solid SbCl₃. This reference electrode is designated SbCl₃-BPCl(ℓ), sat. SbCl₃/Sb. The indicator electrode for the EMF measurements was an Sb metal rod which was machined to expose a fresh surface and cleaned with methanol.

The acid-base titration (described below) was performed by pipetting a known volume of acidic melt into a known volume of basic melt.

The conductivity cells, instrumentation and experimental procedures were the same as described previously (10). Viscosity measurements were made at ambient temperature in a glove box using a Sargent-Welch Model S-83400D falling ball viscosimeter. Calibration of the viscosimeter (cell constant = $4.07\pm0.01 \times 10^{-4} \text{ cm}^2 \text{ s}^{-2}$) was accomplished as described in the literature (11).

Instrumentation. — The electrochemical instrumentation consisted of a Princeton Applied Research Model 174A Polarographic Analyzer, a Model 173 Potentiostat/Galvanostat equipped with a Model 179 Digital Coulometer, and a Model 175 Waveform Generator. Data were recorded with either a Hewlett-Packard Model 7045A X-Y recorder or a Nicolet Model 2090-III digital storage oscilloscope.

Absorption spectra for the spectroelectrochemical (SE) experiments were measured in the visible region with the following equipment. Radiation from a 10-W quartz/halogen lamp was filtered with neutral-density filters to control intensity and a 470-nm long-pass filter to eliminate second-order light. An image of the filament was focused on a square aperture to crop the edges, and a 4×4-mm image of the aperture was focused on the optical cell, which had a 1-mm path length. Light transmitted through the cell was focused on the entrance slit (0.025 mm) of a flat-field, 0.32-m spectrograph (Instruments SA, Inc. Model HR-320) equipped with a 152.5 grooves mm⁻¹ grating. Dispersed light was focused on the face of a linear silicon photodiode array detector (EG&G/PAR Model 1412). The detector array consisted of 1024 photodiodes and was thermoelectrically cooled to -20°C. Detector control and read-out were performed with an EG&G/PAR Model 1218 detector controller and Model 1215 system processor. Spectra were stored on 8-in. floppy disks, and hard copy was obtained with a Hewlett-Packard 9872B plotter and a Data Access Systems, Inc. Model 360 line printer. Wavelength calibration and resolution verification were performed with Hq, Ne, Ar, and Xe atomic lamps.

With the equipment described above a wavelength window 505 nm wide was spread over the 1024 photodiodes to give a maximum of 1024 optical channels at 0.5-nm resolution with a read-out time of 16.4 ms per spectrum. However, in the experiments described here neither such resolution nor such speed was required. By allowing the signal to accumulate and then reading the photodiodes in pairs, a 512-channel spectrum with high signal/noise ratio was obtained in \sim 0.2 s at a resolution of 1.0 nm. The spectra were corrected for dark current and a slight drift in lamp intensity. A Cary Model 219 spectrophotometer was used for non-SE optical measurements.

Experimental Procedures. — All material transfers were performed in an argon-filled glove box where 0₂ and H₂O were continuously monitored and kept below 1 ppm by circulation of the atmosphere through a purification train. Weighings were performed on an analytical balance in the glove box. Positive feedback circuitry was employed during voltammetric measurements to compensate for solution resistance. The SE experiment was computer controlled in such a way that a spectrum (intensity vs. wavelength) was measured every 60 s. The integration time per spectrum was 0.183 s, and the wavelength window was 479 - 984 nm. Absorbance was calculated by using a spectrum taken just prior to electrolysis as a reference. In order to remove gas bubbles trapped in the optically transmitting electrode (OTE), the SE cell was partially evacuated for a short period prior to the experiment and refilled with argon.

All temperatures (unless otherwise noted) were measured with copper/constantan thermocouples which were calibrated against a platinum resistance thermometer with a Minco RT 88078 bridge, the calibrations of which are traceable to NBS standards.

Results and Discussion

<u>Reactions Among Components.</u> — The SbCl₃-AlCl₃-BPCl mixtures considered here were restricted to the following formal compositions: 60 mol % SbCl₃, (20+a) mol % AlCl₃ and (20-a) mol % BPCl where $-2 \le 4 \le 2$. Aluminum trichloride is a strong chloride ion acceptor, SbCl₃ is a much weaker acceptor while BPCl is a chloride ion donor. Therefore, the dominant chloride-exchange reaction was

$$BPC1 + A1C1_3 \rightarrow BP^+ + A1C1_4$$
(1)

Since the AlCl_3:BPCl mole ratio was close to unity for all melts, one can regard the liquid as consisting of the binary mixture $SbCl_3-BP(AlCl_4)$ (75-25%) to which small amounts of AlCl_3 or BPCl were added. The acidic and basic species in these solutions have been discussed elsewhere (1) so that we shall do no more here than summarize the principal equilibria that have been proposed to occur among them, namely:

 $SbCl_3 \neq SbCl_2^+(solvated) + Cl^-(solvated)$ (2)

 $2A1C1_{4} \neq A1_{2}C1_{7} + C1^{-}(solvated)$ (3)

 $SbCl_2^+(solvated) + 2AlCl_4^- \neq SbCl_3 + Al_2Cl_7^-$ (4)

$$SbCl_{2}^{+}(solvated) + AlCl_{4}^{-} \neq SbCl_{2}(AlCl_{4})$$
 (5)

where $SbCl_2^+$ and Cl^- are strongly solvated by $SbCl_3$ molecules. It is expected that equilibria (2), (3) and (4) are displaced strongly

to the left so that $SbCl_2^+$ (solvated), rather than $Al_2Cl_7^-$, is the dominant Lewis acid in melts for which $AlCl_3:BPCl > 1$.

<u>Physical Properties</u>. — The viscosities of the 60:21:19 (acidic) and 60:19:21 (basic) melts were determined at $25.1\pm0.5^{\circ}$ C to be 22.8 ± 0.7 and 31.5 ± 0.9 cp, respectively. The viscosity of the acidic melt is comparable to viscosities measured for AlCl₃:alkylpyridinium chloride (AlkPC) melts with an AlCl₃:AlkPC mole ratio of 2:1 (12).

The electrical conductivities of the 60:19:21 and 60:21:19 melts were measured over the temperature range 24 to 100°C with results that are shown in Fig. 1. The specific conductivities of the two ternary mixtures are almost equal at ambient temperatures, but at higher temperatures the basic melt becomes more conducting. The conductivities are comparable to those reported for binary AlCl_3:AlkPC (2:1) mixtures (12), but are about one order of magnitude less than the conductivities reported for acidic alkali metal chloroaluminate melts at slightly higher temperatures (13).

For comparison with SbCl₃-AlCl₃ melts, we have included in Fig. 1 the conductivity of the binary melt whose composition most closely resembles the SbCl₃:AlCl₃ ratio in the ternary melts (10). As can be seen in Fig. 1, the conductivity <u>vs</u> temperature function for the ternary melts has a curvature (slope increasing with temperature) opposite to that of the binary melt curve.

<u>Current-Overvoltage Studies</u>. — In an earlier investigation (14) of the acid-base dependence of the potential of an Sb metal rod immersed in SbCl₃-AlCl₃ (>90 mol % SbCl₃) an appreciable irreversibility was observed. Furthermore, in a preliminary study using cyclic voltammetric and chronocoulometric measurements of the electroreduction of SbCl₃ at inert microelectrodes in acidic AlCl₃-NaCl melts, we found the process to be kinetically hindered. Therefore, we investigated the electrochemical reversibility of the Sb(III)/Sb(0) couple in an acidic 60:21:19 melt by means of currentovervoltage curves.

In the absence of mass transfer effects the Butler-Volmer equation (15) may be used to predict current-overvoltage behavior. For large overpotentials ($\eta > 0.118/n$ mV) the equations

$$\ln i = (-\alpha n f_{\eta}) + \ln i_{\rho} \tag{6}$$

for cathodic currents, and

$$\ln i = \{ (1 - \alpha) n f n \} + \ln i_0$$
 (7)

for anodic currents should be valid (15). The data are plotted in Fig. 2; the anodic branch displays Tafel behavior for n > 40 mV. The apparent exchange current obtained from the intercept of this

curve is 13 μ A cm⁻², and the transfer coefficient determined from the slope is 0.8. The cathodic branch is somewhat more complicated, and the electrode process may involve more than one fundamental step (16). The possible complications are not significant in potentiometry as long as the current densities are low, as is the case with the high-impedance circuits used in the present investigation. For potentiometric purposes (including the use of antimony as a reference electrode) the electrode was considered to behave reversibly.

Equilibrium Studies. — The overall reduction of SbCl₃ releases Cl- ions according to Eq. (8)

$$1/3 \text{ SbCl}_3 + e^- \rightarrow 1/3 \text{ Sb} + \text{Cl}^-$$
 (8)

Thus, the potential of the Sb(III)/Sb(0) couple is dependent on the chloride ion activity. An acidic medium will drive reaction (8) to the right, thereby increasing the "oxidizing power" of $SbCl_3$.

The change in the potential of an antimony electrode resulting from changes in ternary melt composition was measured using the following concentration cell:

Sb/SbCl3(solid), SbCl3-BPCl(liquid):frit:

SbCl3-AlCl3-BPCl(60:x:y mole %)/Sb

where x:y varied from 22:18 to 18:22. The lack of information regarding the transference numbers of charge carriers prevented a calculation of the junction potential. No attempt was made to analyze the data for the purpose of establishing an acidity scale.

The EMF data are shown in Fig. 3 and demonstrate that the potential of the Sb(III)/Sb(0) couple may be tuned over a potential range of 0.43 V for the compositions indicated. For comparison, the Sb(III)/Sb(0) couple may be varied over a 0.44 V range by titrating SbCl₃-KCl (90:10) with AlCl₃ (14). These data provide information for estimating the extent to which a dissolved solute will be oxidized by a given solvent composition, provided that the half-wave potential of the solute is known.

Voltammetry and Chronocoulometry. — The available electrochemical window in the SbCl₃-AlCl₃-BPCl mixtures (Fig. 4) is somewhat larger than that reported for SbCl₃-CSCl and SbCl₃-AlCl₃ (>90 mole % SbCl₃) melts at 100°C (9). The potential span for both the 60:21:19 and 60:19:21 compositions is about 1.8 V, compared to 1.4 V for the binary melts. [The total potential span available in AlCl₃-BPCl binary mixtures between the cathodic limit of the 1:1 melt and the anodic limit of the 2:1 melt is roughly 3 V. (17)] The negative potential limit in the ternary melts is the reduction of Sb(III) to

Sb metal. As can be seen in Fig. 4, overpotentials for the reduction process at an inert electrode exist for both ternary melts. The anodic limit for the liquids is the oxidation of Sb(III) to Sb(V).

DMA is soluble only to a limited extent in a 60:19:21 melt and the dissolution rate is slow. Solutions were prepared by adding DMA to the melt and heating to $80-100^{\circ}C$ with stirring in a closed container for a period of about an hour.

A voltammogram obtained on a basic melt containing DMA at a glassy carbon electrode is shown in Fig. 5. The peak potentials (E_p) and half-peak potentials $(E_{p/2})$ for both waves are listed in Table I along with the difference in peak potentials (ΔE_p) . The experimental values of ΔE_p correspond well with the theoretical value for a one-electron Nernstian process of 60 mV (18). Also included in the Table are half-wave potentials $(E_{1/2})$ calculated from the expression (18)

$$E_{1/2} = E_{n/2} + 1.09 \text{ RT/nF}$$
 (9)

and values of n calculated from

$$E_p - E_{p/2} = 2.2 \text{ RT/nF}$$
 (10)

Scan rates up to 20 V s⁻¹ revealed no significant shift in the anodic peak potential, and the half-wave potentials determined by differential pulse polarography (19) (average = 0.47 V) corresponded well to the values calculated from Eq. (7).

The integrated Cottrell equation (20) predicts that for diffusion controlled electrode reactions, a linear relationship holds between the charge (Q) and the square root of time (t 1 2). Fig. 6 shows a plot of Q vs t 1 2 for times up to 20 s; it is clearly linear. The intercept of the plot yields a value of the apparent doublelayer capacitance of approximately 5 μ F cm⁻², while the slope (uncorrected for impurities) gives an upper limit on the diffusion coefficient of neutral DMA of 2.5 \times 10⁻⁷ cm² s⁻¹. Finally, the technique of double potential-step chronocoulometry (20) demonstrates that the charge consumed around a square potential cycle obeys theoretical predictions (Q_{2T}/Q_T = 0.414) (21) for 10 and 20 s pulse widths. Thus, there is no significant reaction of the DMA radical cation on a voltammetric time scale.

<u>Spectroelectrochemical Studies</u>. — Measurements of absorption spectra at an OTE during electrolysis of ~ 1 mM DMA in a basic 60:19:21 melt and during subsequent open-circuit decay verify the formation of the DMA radical cation and demonstrate that it is very persistent under these conditions.

Fig. 7 shows spectra measured during electrolysis and Fig. 8 shows spectra measured during open-circuit decay. Bands assigned to the DMA radical cation are at 550, 600, 656 (sh) and 678 (max) nm. Weak, broad shoulders at about 620, 760 and 850 nm are attributed to other species, probably subsequent reaction products because they develop at a much slower rate during electrolysis and are more persistent under open-circuit conditions than those assigned to DMA. In a previous investigation (22) transient spectra of DMA radical cations were measured in benzonitrile solutions at a much lower optical resolution than reported here. To within experimental uncertainty, these spectra show the same profiles as those in Figs. 7 and 8.

From the values of $E_{1/2}$ for DMA and the formal potential of the Sb(III)/Sb(0) couple in the 60:21:19 melt at 25°C, it is estimated that DMA should be partially oxidized with the simultaneous reduction of Sb(III) in this medium. The optical spectrum of DMA in the acidic melt revealed weak absorption bands due to DMA⁺⁺, but the lack of accurate values for the molar extinction coefficients of the optical transitions prevented a quantitative determination of the concentration. Nevertheless, it is significant to note that solutes with $E_{1/2}$ values more negative than that of DMA will be appreciably oxidized in acidic melts.

Conclusion

The electrochemical properties of novel ternary molten salts as media in which reactive intermediates may be readily studied are reported in this paper. The principal advantages of these ternary melts as compared to SbCl₃-KCl and SbCl₃-AlCl₃ mixtures are ease of handling and a wider electrochemical window. The melts possess tunable redox and Lewis acid-base functions which may be exploited to initiate or suppress reactions in which Sb(III) serves as an oxidant.

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REFERENCES

- S. P. Zingg, A. S. Dworkin, Morten Sørlie, D. M. Chapman, A. C. Buchanan, III, and G. P. Smith, "Reactivity of Anthracene 1. in Liquid SbCl3-AlCl3-N-(1-Butyl)Pyridinium Chloride Mixtures," this Symposium.
- A. S. Dworkin, M. L. Poutsma, J. Brynestad, L. L. Brown, 2. L. O. Gilpatrick, and G. P. Smith, J. Am. Chem. Soc., 101, 5299 (1979).
- A. C. Buchanan, III, A. S. Dworkin, J. Brynestad, L. O. Gilpatrick, M. L. Poutsma, and G. P. Smith, <u>J. Am. Chem.</u> 3. <u>Soc., 101</u>, 5430 (1979).
- A. C. Buchanan, III, A. S. Dworkin, and G. P. Smith, J. Am. 4. Chem. Soc., 102, 5262 (1980).
- 5. A. C. Buchanan, III, A. S. Dworkin, G. P. Smith,
- M. V. Buchanan, and G. Olerich, <u>Fuel</u>, <u>60</u>, 694 (1981). A. C. Buchanan, III, A. S. Dworkin, and G. P. Smith, J. Org. 6. Chem., 46, 471 (1981).
- A. C. Buchanan, III, A. S. Dworkin, and G. P. Smith, J. Org. 7. Chem., 47, 603 (1982).
- A. C. Buchanan, III, R. Livingston, A. S. Dworkin, and G. P. 8.
- M. Sørlie, G. P. Smith, V. E. Norvell, G. Mamantov, and L. N. Klatt, <u>J. Electrochem. Soc.</u>, 128, 333 (1981). C. Petrovic, G. Mamantov, M. Sørlie, M. H. Lietzke, and G. P. 9.
- 10. Smith, <u>J. Phys. Chem., 86</u>, 4598 (1982). C. Nanjundiah, K. Shimizu, and R. A. Osteryoung,
- 11.
- J. Electrochem. Soc., 129, 2474 (1982). R. A. Carpio, L. A. King, R. E. Lindstrom, J. C. Nardi, and C. L. Hussey, J. Electrochem. Soc., 126, 1614 (1979). R. A. Carpio, L. A. King, F. C. Kibler, Jr., and 12.
- 13.
- A. A. Fannin, Jr., <u>J. Electrochem. Soc.</u>, 126, 1650 (1979). D. Bauer and P. Texier, <u>C. R. Hebd. Seances Acad. Sci., Sec. C</u>, 14. 266, 503 (1968).
- A. J. Bard and L. R. Faulkner, "Electrochemical Methods: Fundamentals and Applications," p. 103, John Wiley & Sons, New 15. York (1980).
- P. Delahay, "Double Layer and Electrode Kinetics," Chap. 8, 16. Interscience, New York (1965).
- J. Robinson and R. A. Osteryoung, J. Am. Chem. Soc., 101, 323 17. (1979).
- R. S. Nicholson and I. Shain, <u>Anal. Chem.</u>, <u>36</u>, 706 (1964). 18.
- E. P. Parry and R. A. Osteryoung, Anal. Chem., 37, 1634 (1965). 19.
- J. H. Christie, R. A. Osteryoung, and F. C. Anson, J. 20. Electroanal. Chem., 13, 236 (1967).
- J. H. Christie, J. Electroanal. Chem., 13, 79 (1967). 21.
- A. Kira, S. Arai, and M. Imamura, J. Phys. Chem., 76, 1119 22. (1972).

ν(mV/s)	E _{pa} (V)	E _{pc} (V)	∆E _p (mV) ²	E _p /2 _a (V)	E _{1/2a} (V) ³	n ⁴
10	0.505	0.440	65	0.445	0.473	0.95
20	0.500	0.440	60	0.443	0.471	0.95
50	0.503	0.440	63	0.443	0.471	1.0
100	0.503	0.443	60	0.445	0.473	0.98
200	0.505	0.445	60	0.447	0.477	0.98

Table I. Electrochemical parameters determined from a 1.2 mM solution of DMA in a 60:19:21 melt at 27°C. Glassy carbon working electrode area = 0.071 cm².

¹All potentials relative to liq. SbCl₃-BPCl (£), sat. SbCl₃/Sb ²Theory = 60 mV (18) ³Calculated from $E_{1/2} = E_{p/2} + 1.09$ RT/nF (18) ⁴Calculated from $|E_p - E_{p/2}| = 2.2$ RT/nF (18)



Fig. 1. Specific conductivities of (a) SbC1₃-AlC1₃-BPC1 (60:21:19); (b) SbC1₃-AlC1₃-BPC1 (60:19:21); (c) SbC1₃-AlC1₃ (3:1) (Ref. 10).



Fig. 2. Tafel plot for the Sb(III)/Sb(0) couple in a SbC13-AlC13-BPC1 (60:21:19) melt at 27°C. Sb metal working electrode, area = 1.51 cm². (a) cathodic branch; (b) anodic branch.



Fig. 3. EMF of Sb(III)/Sb(0) couple at 27°C for ternary melts. Sb metal working electrode.



Fig. 4. Background cyclic voltammograms of (a) SbCl3-AlCl3-BPCl (60:21:19); (b) SbCl3-AlCl3-BPCl (60:19:21). Glassy carbon, electrode, area = 0.071 cm². Sweep rate = 100 mV/s, temp. = 20°C.



Fig. 5. Voltammogram of DMA (saturated solution) in SbCl₃-AlCl₃-BPCl = 60:19:21. Glassy carbon electrode, area = 0.071 cm². Sweep rate = 500 mV/s, temp. = 27°C.



Fig. 6. Charge-time^{1/2} plot for a 1.4 mM solution of DMA in SbCl3-AlCl3-BPCl (60:19:21). Potential step: +0.35 V to +0.65 V. Glassy carbon electrode area = 0.071 cm². Temp. = 27°C.



Fig. 7. Spectra measured every 60 s during 20-min electrolysis at 0.65 V of 1.2 mM DMA in a 60:19:21 melt. Pre-electrolysis spectrum used as reference. Pt-screen OTE and 1.0-mm pathlength.



Fig. 8. Spectra measured every 180 s during 57-min open-circuit decay following electrolysis in Fig. 7. Reference same as in Fig. 7.

USE OF A1C1₃-CONTAINING MOLTEN SALTS FOR CARBONIZATION AS SOLVENT AND CATALYST

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ABSTRACT Liquid-phase carbonization was studied using two kinds of molten salts, NaCl 26 -KC1 14 -A1C13 60 mo1% (MS-A)] and [ethylpyridinium bromide 33 -A1C13 67 mo1%(MS-B)], as the reaction solvent and catalyst. As the raw material aromatic compounds such as naphthalene, substituted naphthalenes, anthracene, etc. were mainly used. A raw material dissolved in one of the molten salts was heated at 250 to 300°C for a few to 10 hours yielding coke in the form of powder or flakes. An equimolar mixture of naphthalene with a polychloroethane also gave coke at a temperature as low as 200°C when heated in MS-B. Generally the graphitizability of the resulting cokes ranged widely depending mainly on the nature of the raw material. When stopped halfway, the reaction sometimes yielded a kind of pitch which was easily changeable to mesophase pitch. Some other variations of the procedure and the basic chemistry of these reactions were also studied.

INTRODUCTION

Our study was undertaken in order to gain a better understanding of carbonization in terms of organic chemistry. For this purpose we thought it advantageous to carry out carbonization in solution at least during its earlier stage and decided to employ molten salts as the reaction medium. Here we would like to review briefly our work on a new method of carbon and pitch preparation using two kinds of AlCl₃-rich molten salts. Some researchers have reported on organic reactions using molten salts where tar, pitch, and/or coke were produced. However, these substances have only been regarded as undesirable by-products.

Among many carbon products our interest was focused on recently developed, so-called fine carbons such as carbon fiber, biocarbons, high quality pencil-lead, and so on. Pitch is an important raw material of carbon, and its characteristics directly determine the properties of the resulting carbon. Therefore, its selection has been one of the most important problems in the production of carbon. Recently its blending and chemical modification have been actively investigated. However, our aim was to obtain the most suitable pitch for the production of a given carbon product by <u>synthesis</u> from pure substances. This process was thought more suitable for the production of fine carbons.

The compositions of our two molten salts, MS-A and MS-B,were as follows:

 $\frac{MS-A \text{ (mp. 95°C)}}{[A1C1_{z} 60 \text{ mo1}\% : \text{NaCl 26 mo1}\% : \text{KCl 14 mo1}\%]}$

and <u>MS-B</u> (room-temperature molten salt) (1) [AlCl₃ 67 mol% : ethylpyridinium bromide 33 mol%].

These molten salts both contain more than 50 mol% $AlCl_3$ and, therefore, are strong acids.

Carbonization of low-molecular-weight compounds is a process of polymerization consisting of a very complicated series of reactions. However, these reactions can be classified into two categories. One is the C-C bond formation including the rearrangement. The other is the elimination of elements other than carbon. It was expected that both types of reaction could be catalyzed by a strong acid and that, as a result, the carbonization temperature would be lowered.

1. COKE AND PITCH FROM AROMATICS (2)

One of the molten salts was placed in a glass flask in an argon stream. A raw material was added while being stirred. The mixture was then heated to the desired temperature. Naphthalene and other aromatic compounds were mainly used as the raw material. The quantities of raw material used were 0.05 to 1 in molar ratio to the free AlCl₃. Near the end of reaction a deposition of resulting product was usually observed. After cooling, the reaction mixture was poured into a mixture of ice and diluted hydrochloric acid. The resulting precipatates were filtered, washed, and dried. The crude products were separated by hot-benzene extraction into benzene-soluble(BS) and benzene-insoluble (BI) fractions.

In Table 1 some of the results obtained using MS-A are given, and in Fig.3 the X-ray 002-diffraction profiles

of the coke from naphthalene are given as an example.

No	. Raw	Yield	Atomic	X-Ray pa	rameters	;a)
of	material	(%)	ratio			
ru	ns		H/C	d ₀₀₂ (Å)	L _c (Å)	
1	Anthracene	96	0.50	3.42	150	
2	Phenanthrene	71	0.48	3.37	700	
3	Naphthalene	92	0.47	3.37	700	
4	1-Bromonaphthalene	e 98	0.40	3.40	200	
5	1-Nitronaphthalene	e 99	0.35	3.52	20	

Table 1. BIs from Aromatics Obtained by Reactions at 300°C for 10 Hours in MS-A

a) After heat-treatment at 2800°C; $d_{\rm 002}$ and $\rm L_{C}$ of graphite: 3.354Å and 1000Å, respectively.

In most cases the BIs were a kind of coke. They are insoluble and infusible. The X-ray analysis showed that they had a layer structure which is characteristic of carbon material. These properties and their H/C atomic ratios were very close to those of so-called green coke and carboid coke. We shall call this type of BI "coke" for short hereafter. Quite similar results were obtained when MS-B was used.(3)

Graphitizability is an important property of carbon and it is estimated from the structural parameters measured by X-ray 002-diffraction analysis of a carbon material after a heat-treatment at a temperature usually above 2000°C. The X-ray analysis data, partly given in Table 1 and Fig.3, show that the graphitizabilities of the BIs ranged widely depending mainly on the nature of the raw material; for example, naphthalene gave a highly graphitizable BI, and nitronaphthalene gave a non-graphitizable BI. This indicates that cokes of various graphitizabilities are now available by this method.

Fig.1 shows the photographs of the coke obtained from 1-bromonaphthalene as an example. One can see the thin, wavy film structure.

Some preliminary experiments of carbonization of materials other than aromatics were also examined. Of these, cotton fiber gave the most interesting results (4). It was carbonized by immersing it in MS-B at 150°C for

No. of melt	Compo A1C1 ₃ -	ositio •ZnCl ₂	n (mol -NaCl-	L%) -KCl	Yield(%) of BI
1	0	60	20	20	No reaction
2	60	0	26	14(MS-A)	96
3	49	0	35	16	84
4	40	0	30	30	76

Table 2. Effects of Composition of Molten Salt on the Yield of BI Obtained from Anthracene by Reaction at 300°C for 10 hours

Monomethylnaphthalenes were isomerized at 100° C - monomethylnaphthalenes were isomerized at 100° C. The reactions were very quick and reached equilibrium within two minutes. The α/β isomer ratio at equilibrium was 4.4. Small amounts of by-products such as naphthalene, dimethylnaphthalenes, tetralin, and polymers were produced. This indicates that, besides the rapid intramolecular $\alpha = \beta$ rigration of methyl groups, intermolecular methyl groups and hydrogen-transfers and polymerization also occurred.

1,2-Dimethylnaphthalene produced isomeric dimethylnaphthalenes and trimethylnaphthalenes when heated in MS-A as shown in Eq. 2. All these products are considered to be the intermolecular rearrangement products because the intramolecular migrations of the methy groups from 1- to 8-position and from



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1 hour. Unfortunately the resulting carbon fiber was not strong, but improving its mechanical properties seemed possible. When treated similarly with either sulfuric acid or oleum, cotton fiber was destroyed, and the yield was only black powder.

When aromatics were treated under moderate reaction conditions, various pitches were obtained. After separation from the molten salt, the pitches were subjected to an additional heat-treatment. In most of the cases the pitch yielded so-called mesophase pitch.

Fig.2a) and b) are the photographs(5), taken under polarized light, of the pitches obtained from naphthalene by the reaction at 230°C for 5 hours using MS-B followed by an additional simple heat-treatment at 300°C and 400°C, respectively, for 1 hour. The spherical particles appearing in a) are mesophase, and it is reasonablly assumed that under a higher heating temperature of 400°C these particles grew larger and unite with each other to a continuous structure of mesophase as shown in b). Such a pitch as easily changing to mesophase pitch at a temperature as low as 300°C was quite new, and is expected to be suitable for producing, e. g., carbon fiber. For comparison Ashland 240 Pitch, a famous commercial product, was also examined similarly, but it did not behave in this way.

The reactivities of the aromatic compounds used were as follows; anthracene > naphthalene > phenanthrene > stilbene > biphenyl > benzene > quinoline. This sequence is similar to those generally observed in electrophilic aromatic substitutions.

Table 2 shows the effect of the composition of molten salt on the BI-yield from anthracene. The use of zinc chloride instead of $AlCl_3$ made the melt quite inactive. The decreasing $AlCl_3$ -content in the molten salts resulted in decreasing Bl-yield. However, it is interesting to see that in the case of No.4 the melt was still active enough to produce an appreciable amount of BI in spite of its $AlCl_3$ -content lower than 50 mol%.

ISOMERIZATION, DISPROPORTIONATION, AND POLYMERI-ZATION OF METHYLNAPHTHALENE(6)

The reactions of mono- and dimethylnaphthalenes in MS-A were studied. Methylnaphthalenes were regarded as simple models of the constituents of tar and pitch. 2- to 3-position are both inhibited.

On the other hand, according to Suld and Stuart(7), the same compound did not react in a superacid of composition of $[HF-BF_3]$. These facts indicate MS-A is a fairly strong superacid. This high acidity is attributable to the combination of the free AlCl₃ with HCl generated from the water as contaminant. Furthermore, an addition of a strong protic acid trifluoromethylsulfonic acid accelerated the reaction.

3. CARBONIZATION OF 1,2-DI- and 1,1,2-TRICHLOROETHANE SUPPLIED IN THE FORM OF VAPOR(8)

Vaporized di- and trichloroethane mixed with a carrier gas of argon were bubbled separately into MS-B at 100, 200, and 300°C yielding cokes although the yields were low. Trichloroethane was more reactive than dichloroethane. The product derived from trichloroethane by the reaction at 300°C was a mixture of a powdery and a film-shaped coke. As given in Fig.4, the latter showed, after heat-treatment at 2500°C, an X-ray 002-diffraction angle $20(K\alpha)$ of 26.5°, which is practically the same value to that of natural graphite.

4. COKE AND PITCH FROM NAPHTHALENE AND POLYCHLOROALKANES THROUGH THE FRIEDEL-CRAFTS CO-POLYMERIZATION(9)

According to our view on the nature of carbonization, polymerization deliberately introduced into the earlier stage of carbonization must accelerate the whole reaction, and as a result the carbonization temperature must be lowered. To prove this hypothesis we undertook the following experiments.

Naphthalene was mixed with equimolar amounts of a polychloroalkane in MS-B at room temperature, and the temperature was raised gradually. Interesting results were achieved with polychlorinated methanes and ethanes. The latter's reactions yielded cokes

R: Methylene and Ethylene

at a temperature as low as 200°C, and when the reactions were stopped at 100°C, the products were pitches. The experiments showed that in the earlier stage, below 80°C, the main reaction proceeded through the path of the Friedel-Crafts reaction yielding a co-polymer as shown in Eq.3. Following this stage intra- and inter-molecular condensations of the co-polymer took place, accompanied by dehydration, resulting in coke formation.

For comparison naphthalene and dichloroethane were heated to 150°C with AlCl₃ by the standard Friedel-Crafts procedure without molten salt. However, almost no reaction took place. This indicates that the molted salt was essential to these reactions.

Table 3 shows the properties of some of the products. Without chloroalkane only pitch was produced. However, when chloroalkanes were used, the end products were coke. This supports our working hypothesis. The d_{002} -values show that dichloroethane acted to yield non-graphitizable carbon, and trichloroethane, graphitizable carbon. This indicates that we can control the important property of the resulting carbon by adjusting the combination of the raw materials.

Table 3. Products through the Friedel-Crafts Co-polymerization of Naphthalene and Chioroalkanes

Chloroalkane	Reaction	temp. and	products	
Chiloroarkane	100°C	200°C	[BI-Content;	d ₀₀₂ a)]
None	Tar	Pitch	[53%;	3.39Å]
C1-CH ₂ CH ₂ -C1	Pitch	Coke	[77%;	3.45Å]
C1-CH ₂ CH-C1 C1	Pitch	Coke	[91%;	3.38Å]

a) By X-ray 002-diffraction analysis after heattreatment at 2500°C.

CONCLUSION

Although our study on the chemistry of carbonization is still far from completion, we have already established a new method of making carbon and pitch. The main features of the process can be summarized as follows:

First, the use of this process results in lowtemperature carbonization. Secand, it consists of solution reactions which proceed through an acid-catalyzed ionic Third, it can produce either graphitizable or mechanism. non-graphitizable carbon, and it can prepare mesophase pitch.

REFERENCES

(1)R. A. Osteryoung, J. Am. Chem. Soc., 98, 5277(1976).
(2)a)E. Ota and S. Otani, Chemistry Lett., 1975, 241;
b)E. Ota, S. Inoue, M. Horiguchi, and S. Otani, Bull.

Chem. Soc. Japan, 52, 3400(1979).
(3)E. Ota, S. Hagiwara, and S. Otani, International Symposium of Carbon, Extended Abstracts, p. 333, <u>1982</u>; Toyohashi, Japan.

(4)Unpublished data.

(5)Unpublished data.

- (6) E. Ota, S. Inoue, M. Domae, and S. Otani, Nippon Kagaku Kaishi, 1979, 1210.
 (7) S. Suld and A. P. Stuart, J. Org. Chem., 29, 2936(1964).
 (8) E. Ota, S. Hagiwara, and S. Otani, The 8th Annual Meeting of Carbon Society of Japan, 1981, Preprint, 1997.
- p. 10; Kiryu, Japan.
- (9)E. Ota, S. Hagiwara, and S. Otani, The 47th National Meeting of the Chemical Society of Japan, <u>1983</u>, Preprint II, p. 1449; Kyoto, Japan.



Fig.1 a) Coke obtained from 1-bromonaphthalene by the reaction at 300°C for 10 hours in MS-A;b) The same coke photographed with transmitted light. (cf. Sec.1)



Fig.2 Pitch obtained from naphthalene by the reaction at 230°C for 5 hours in MS-B and following heattreatment, after separation from MS-B, at a)300°C and b)400°C, respectively, for 1 hour. (cf. Sec.1)



- Fig.3 X-Ray 002-diffraction profiles of BI obtained from naphthalene by the reaction at 300°C for 10 hours in MS-A; a) as obtained,
 - b) after heat-treatment at 2800°C.(cf. Sec.1)



Fig.4 X-Ray 002-diffraction profiles of two types of BI obtained from 1,1,2trichloroethane by bubbling it into MS-B at 300°C followed by heat-treatment at 2500°C. (cf. Sec.3)
SUBSTITUENT EFFECTS ON TRANSPORT AND THERMODYNAMIC PROPERTIES OF MOLTEN PYRIDINIUM SALTS

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ABSTRACT

The conductivities, viscosites and densities of a series of molten dimethylpyridinium chlorides were measured as a function of temperature. The conductivity, viscosity and density of 4, t-butylpyridinium chloride were also measured as a function of temperature. The substitutent effect of the bulky t-butyl group as well as the effect of a second methyl group on transport and thermodynamic properties were assessed by comparing these properties at a constant multiple of the salts' boiling point. The presence of a t-butyl group as well as the specific location of the methyl groups strongly influences the melts' properties as does the presence or absence of hydrogen bonding.

INTRODUCTION

Molten pyridinium salts, either alone or in mixtures, are useful solvents for a variety of chemical reactions including the alkylation of coal and model coal compounds (1) and various electrochemical oxidation-reductions (2,3). However, from a theoretical perspective pyridinium salts are perhaps more important because their low melting points, ease of handling, and enormous variety, allow all sorts of correlations to be made between structure, transport properties, spectra and thermodynamic properties. From these correlations of experimental results, a theoretical scaffolding to support ideas about the nature of pyridinium melts in particular, and organic melts in general, may be constructed.

In earlier studies (4,5) of molten methylpyridinium halides we found that the effect of a methyl substituent on the melts' properties depended markedly on its ring

position. We also observed that the presence or absence of hydrogen bonding affected a melts' ¹HNMR spectrum, viscosity and conductivity. The viscosity data were particularly enigmatic when viewed in context with the conductivity data because those isomeric melts with the highest conductivity also had the highest viscosity. For example, N-methylpyridinium chloride (N-mepyr-Cl) had an equivalent conductance, $\boldsymbol{\Lambda}$, of 10.5 cm² ($\boldsymbol{\Omega}$ eq)⁻¹ and an absolute viscosity, η , of 6.24 cp whereas its isomer 4-methylpyridinium chloride (4-mepyr-Cl) had a Λ of 6.68 cm^2 ($\hat{\mathbf{R}}$ eq)⁻¹ and an $\boldsymbol{7}$ of 3.26 cp, all at a constant temperature of 425 K. Similar results were observed in the bromide and iodide melts. Strong hydrogen bonding between the 4-mepyr⁺ ion and the $C1^{-}$ ion would account for the relatively low conductivity by causing complexes to form which have long enough life times to effectively remove charge carriers from the electric field. However, 4-mepyr-Cl would seem to be more highly associated than N-mepyr-Cl (which presumably cannot hydrogen bond) and consequently would be expected to be more viscous. But 4-mepyr-Cl is considerably less viscous, which means additional factors are affecting the viscosity.

Part of the explanation for the low viscosity originated from the work of Bauge and Smith (6) who measured the dipole moments of several tri-n-butylammonium and triethyl-ammonium salts in benzene solution at 25°C. These authors observed a substantial reduction in the measured dipole moment, \mathcal{M}_D , of the ternary salt relative to the \mathcal{M}_D of the corresponding quarternary salt. They attributed this reduction in *M*_D to hydrogen bonding between the trialkylammonium cation and the appropriate anion. The H-bonding forces the trialkylammonium ion to be oriented with the $\mathbf{\bar{y}}N-\mathbf{H}^+$ pointed toward the anion. The mean interionic distance would be smaller than in the tetraalkyl salt and the measured dipole moment correspondingly smaller. Shortening of the interionic distance through hydrogen bonding and stabilization of the resulting ion pairs would partially account for the relatively low viscosity and concomitant low conductivity in the hydrogen bonded pyridinium melts. However, we think an additional microscopic process is affecting these viscosities. The nitrogenic proton has been shown to be quite labile by 1 HNMR measurements (7) and is most likely hopping back and forth between cation and anion. We and other authors suggested that the labile proton might be contributing to the conductivity of pyr-Cl (7,8) and we specifically presented this mechanism as a rationale for 3-mepyr-Cl and 3-mepyr-Br being better conductors than the corresponding 2-methyl salts (5). Since the 2-methyl pyridine molecule is more basic than 3-methyl pyridine (9)

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and a CH₃ group in the two position partially blocks the nitrogen site, if protons were contributing they would do so less in the 2-methyl melt than in the 3-methyl melt. Alternatively, steric factors and exigencies of packing resulting from a combination of spacial orientation and electrostatic forces may be causing the conductivity differences. The labile proton may, in fact, be playing an entirely different role. Since it is not possible to separate these "hydrogen bonding effects" from substitutent effects in 2,3 and 4-mepyr-Cl because the two effects are intertwined, we have extended our investigation to include 1,2 and 1,3 dimethylpyridinium chloride (dimepyr-Cl) because hydrogen bonding is eliminated, but asymmetry is preserved. We have also studied the three symmetrical dimethylpyridinium chlorides, 2,4 dimepyr-Cl and 4-t-butylpyridinium chloride (4-t-bupyr-Cl) in order to reach a better understanding of substituent effects.

EXPERIMENTAL DETAILS

All salts were synthesized by bubbling HCl or CH_3Cl through a solution of the substituted pyridine in pet. ether. The synthetic details are described elsewhere (10).

Conductivity measurements were made at 1 kHz using a Pyrex capillary cell fitted with cylindrical platinum electrodes. A Canon-Fenske viscometer was used for viscosity measurements and a modified Lipkin bicapillary arm pycnometer was used to measure density. All of the experimental details have been described earlier (8,11).

Elemental analyses were performed at Galbraith Laboratories, Knoxville, TN.

All transfer operations were performed in a dry box through which nitrogen gas circulated.

RESULTS

The normal boiling and melting points of the six dimethylpyridinium chlorides and 4-t-butpyr-Cl are listed in Table I. Also listed are the melting and boiling points of pyridinium chloride to serve as references.

TABLE I

Normal Melting and Boiling Points of Pyrdinium Chloride

т _m (°С)	т _b (°С)
102	163
148	185
216+2*	218+2*
232	239*
239*	239*
230	242*
154	240*
144	219
	T _m (°C) 102 148 216 <u>+</u> 2* 232 239* 230 154 144

*slight decomposition

It is evident that the three symmetrical dimethylpyridinium chlorides have no appreciable liquid range at atmospheric pressure. Therefore their transport properties could not be measured. It is also evident that the hydrogen bonded liquids have substantially higher boiling points than liquids without hydrogen bonds.

Carbon, H and Cl analysis of the salts whose transport properties were measured were within 0.1% of theoretical for t-butpyr-Cl and 2,4-dimepyr-Cl and within 2% of theoretical for 1,2 and 1,3 dimepyr-Cl.

Figure 1 shows the density of each of the four salts plotted as a function of temperature. Included in the figure for reference are the densities of pyr-Cl and 2-methyl-pyridinium chloride (2-mepyr-Cl) taken from earlier studies (5,11). It can be seen from these curves that steric effects determine the relative densities to a greater extent than do molecular weights or electrostatic effects. The bulky 4-t-butpyr-Cl is the least dense liquid, even though it has the highest molecular weight, while pyr-Cl is the most dense, but has the lowest molecular weight. The ionic radius seems to be the principal factor that governs the relative densities.

The logarithms of the equivalent conductances of the four salts plotted as a function of T^{-1} are shown in Fig. 2 and Fig. 3 shows the logarithms of their absolute viscosities plotted as a function of T^{-1} . The \bigwedge s for pyr-Cl and the viscosities for 2-mepyr-Cl are included for reference.

DISCUSSION

To validly assess substituent effects each substituted molecule must be in the same thermodynamic state. The "practical" standard state is, of course, a common temperature at which the salts being compared are liquids. The "natural" standard state for liquids seems to be the ideal glass transition state, T_0 , or the normal boiling point, T_b (12). T_0 is the temperature where the configurational entropy vanishes and T_b is the temperature at which it is maximized for the liquid state. We have chosen to use T_b as the reference state.

Referring first to the conductivity data in Fig. 2 it is evident that 4-t-butpyr-Cl, 1,2-dimepyr-Cl and 2,4-dimepyr-Cl all have similar Λ s at their respective T_b's. The Λ for 1,3-dimepyr-Cl is considerably higher at its T_b and also higher at any "common" temperature. This means 1,3-dimepyr-Cl is a better conductor than 1,2 dimepyr-Cl and a CH₃ group in the 3 position enhances conductivity relative to a CH₃ group in the 2-position. Comparing Λ 's at 425 K, which was the common temperature used in earlier studies when neither T₀ nor T_b data were available (5), gives the results shown in Table II.

TABLE II

Equivalent Conductances at 425 K

Salt	∧ cm ² (∩ eq) ⁻¹	% difference	actual difference
3-mepyr-Cl	8.58		
		22	1.9
2-mepyr-Cl	6.68		
1,3-dimepyr-Cl	10.91		
, ,,		14	1.52
1.2-dimepyr-Cl	9.32		
4-t-butpyr-Cl	2.92		

These data indicate that protonic contribution to the conductivity in the 3-mepyr-Cl is probably very small or nonexistent.

In all likelihood, if the more valid T_b reference state were used it would increase the differene between a CH₃ on the 2 position and one on the 3-position (as it does in the 1,2 and 1,3 dimethylpyr-Cl melts) and there would no longer be a need for a "protonic contribution" to explain the conductivity differences. Comparing the \bigwedge 's of pyr-Cl with those of 1,3 dimethylpyr-Cl (23 vs 18 cm² (\Re

eq)⁻¹) at the respective boiling points, again shows that a protonic contribution seems to be unnecessary. The difference in Λ would be expected from differences in mass and ionic radius alone. In fact, if ln Λ vs T⁻¹ for 1,3 dimepyr-Cl is extrapolated to 219°C the Λ 's are virtually indistinguishable. The principal role of a nitrogenic proton is to hydrogen bond and by so doing form neutral species (ion pairs or molecules) that do not contribute to the conductivity. This is almost certainly the reason why the 1,2 and 1,3 dimethyl chlorides are respectively better conductors than the 2 and 3 methyl chlorides despite their greater molecular weights.

Focusing attention on the viscosity data in Fig. 3 it can be seen that the viscosities of the two dimethylpyridinium isomers are, within experimental error, the same at their respective boiling points. This is especially reassuring since it is expected that at T_b , where Δ S is a maximum and the interionic attractive forces are approximately equal to the thermal forces, the viscosities would be equal for isomers with nearly the same radii. Furthermore, these results support the contention that, at least for viscosity, T_b is a valid standard state.

It is also evident that for 1,2-dimepyr-Cl and for 1,3 dimepyr.Cl the γ 's are about equal at lower temperatures. For example, at 0.95 T_b (a temperature in common to both melts and hence a valid standard state) corresponding to 435 K for 1,3-dimepyr-Cl and 415 for 1,2-dimepyr-Cl, the γ 's are 3.06 cp and 3.00 respectively. As the temperature drops, the viscosities diverge a bit. A much larger difference, but in the same direction, is obtained if a practical constant temperature standard state is used. In any case, the sizeable difference in conductivity between the isomers cannot be attributed to viscosity differences nor to protonic contributions and therefore must arise out of a distinctive charge transfer mechanism.

Extrapolating γ of t-butpyr-Cl to its T_b, a value of 0.9 cp is obtained. This is clearly much lower than the viscosities of either di-methyl isomer at its T_b. At 0.95 T_b, a more reasonable standard state since no decomposition is occurring, γ is only 1.04 cp. What is perhaps more striking is that at 425 K 4-t-butpyr-Cl has an γ of 5.52 cp while N-mepyr-Cl has an γ of 5.24 cp. The large 4-t-butyl ion is actually less viscous than the smaller N-mepyr-ion despite the fact that the t-butyl moiety is about the same size as the pyridinium moiety and the molecular weight of 4-t-butpyr-Cl is greater than that of either the dimethyl isomer or the methyl isomer. Since it bears on the discussion that follows, the relevant dipole moment data of Bauge and Smith are reproduced in Table III. It is evident from these data

TABLE III

Measured Dipole Moments of Alkyl Ammonium Salts in Benzene Solution at 25°C

Salt

₩_D(D) ⊭_D(corresponding quarternary salt)

Tri-n-butylammonium	bromide	8.50	12.2
Tri-n-butylammonium	picrate	11.79	15.3
Tri-n-butylammonium	chloroacetate	6.41	14.8
Tri-n-butylammonium	benzoate	4.27	12.1

that a shortening of the principal interionic axis will not completely explain the reduction of μ_D in the chloroacetate and benzoate solutions even though it is adequate to explain much of the reduction of μ_D in the bromide and picrate solutions.

The mechanism we propose to account for the unusual viscosities of the H-bonded pyridinium melts (and possibly for some of the data of Bauge and Smith) assumes that the equilibrium shown below persists in the H-bonded melts but not in the N-methyl melts.

 $C1^{-} + \frac{R}{pyr-R^{+}} = \frac{R}{pyr-R^{+}--C1^{-}} = \frac{R}{pyr+R-C1}$ ion pair neutral molecules

When R^+ is a proton this "mobile equilibrium" (7) lies considerably further to the right (favoring a higher ion pair and neutral molecule concentration) than when R^+ is a CH₃ group. The labile proton jumps back and forth between pyridine and Cl⁻ and may remain at the bottom of a potential well for perhaps 10^{-6} or 10^{-7} sec. This is too short a time span to be detected by ¹HNNR, but represents perhaps 10,000 translational or rotational movements of the molecule. The model is shown schematically in Fig. 4. The cation and anion are initially drawn together via H-bonding along the principal interionic axis. The proton hops from pyridine to Cl⁻ creating two neutral species and a modicum of empty space. The neutral species rotate and translate relatively freely thus lowering the viscosity, but not increasing the

conductivity. The extra free space increases the probability of an appropriate density fluctuation and thereby decreases the absolute viscosity. In other words, charge neutralization causes local liquid relaxation and local liquid expansion. Without this sort of microscopic process it is very difficult to account for the fact that 4-t-butpyr-Cl is less viscous than N-mepyrCl. The extremely low viscosity of 4-t-butpyr-Cl at T_b is not unreasonable if, on a fast time scale, a high enough concentration of HCl and 4-t-butylpyridine persists.

The energies of activation for viscosity and equivalent conductance are listed in Table IV.

TABLE IV

Energies of Activation

Salt	E $\gamma^{(kJ/mole)}$	E∧ (kJ/mole)	^E ୩ ^{/ E} ∧
t-butpyr-HCl	47.4	33.2	1.42
1,3 dimetpyr-Cl	37.6	26.7	1.40
1,2 dimetpyr-Cl	33.6	24.5	1.36
2,4 dimetpyr-Cl	(66.4)	27.6	2.4

With the exception of E ϕ for 2,4-dimepyr-Cl which is probably unreliable because of the small liquid range and partial decomposition, the values are not, especially remarkable. The large E ϕ for 4-t-butpyr-Cl is expected because of the cations' size and the H-bonding in the melt. The ratios are lower than those for inorganic melts which generally range between 2 and 5 and are a bit higher than the values for typical methylpyridinium halides and alkylammonium salts which range between 1.09 and 1.4, with the bulk of the ratios clustering around 1.1. The dominance of attractive forces, coupled with the need for cooperative movement for large ions to move past one another in an environment containing relatively little free space, ensures that neither viscosity nor conductance will require substantially different amounts of energy.

REFERENCES

 D.S. Newman, R.E. Winans, R.L. McBeth, Reactions of Coal and Model Coal Compounds in Room Temperature Molten Salt Mixtures, "Proceedings of the Third International Symposium on Molten Salts," G. Mamantov, Editor, The Electrochemical Society, Softbound Proceedings Series, Princeton, N.J. 1981, pp 425-438.

- 2.
- C. Nanjundiah, K. Shimizu, R.A. Osteryoung, <u>J.</u> Electrochem. Soc. 129 2474 (1982). G.T. Cheek, R.A. Osteryoung; <u>J. Electrochem. Soc 129</u> 2489 (1982). 3.
- D.S. Newman, R.T. Tillack, D.P. Morgan, Wai-Ching Wan, Correlations Between ¹HNMR Spectroscopy and 4. Transport Properties in Molten Pyridinium Salts, J.
- Electrochem. Soc. 124 856 (1977). D.S. Newman, R.R. Rhinebarger, D. Siconolfi, O.A. 5. Banjoko, The Relationship of Transport Properties and ¹HNMR Spectra to the Structure of Molten Methypyridinium Halides, J. Electrochem. Soc. 128 2336 (1981).
- K. Bauge, J.W. Smith; <u>J. Chem. Soc.</u> (A) 616 (1966). J.W. Shuppert, C.A. Angell, <u>J. Chem. Phys. 67</u> 3050 6.
- 7. (1977).
- D.S. Newman, W. Rohr, D. Kirklin, H.D. Frame, <u>J.</u> Electrochem. Soc. 119 797 (1972). 8.
- A. Albert, E.P. Sergeant, "Ionization Constants of 9. Acids and Bases" p. 145, Methuen and Co. Ltd. London (1962).
- 10. M.S. Rozhdestvenskii, L.M. Brode; J. Appl. Chem. USSR 10 722 (1937).
- D.S. Newman, D.P. Morgan, R.T. Tillack, J. Chem.Eng. Data 21 279 (1976). 11.
- J. Wong, C.A. Angell, "Glass Structure by Spectroscopy," Chpt. 1 Marcel Dekker Inc., New York 12. (1976).



Fig. 1 Density as a function of temperature



Fig. 2 Equivalent conductance as a function of temperature



Fig. 4 Model of hydrogen bonded pyridinium melts

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STRUCTURES IN MOLTEN METAL HALIDES

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Abstract: Cesium tetrabromoaluminate complexes show identical line-widths of the A₁-mode in melt and in crystal. This means that their life-span is longer than 10^{-11} sec. In the melts of LiInBr₄ to CSInBr₄ the line-width increases. In all these cases the life-span is shorter than 10^{-11} sec.

Raman spectra of molten magnesium and calciumbromides and iodides mixed with alkali halides are discussed. In the mixture of CaBr₂ with KBr the life-span of the complex is so short that no Raman spectrum can be obtained. In CaI₂-KI mixtures the CaI₄²-complex has a life-span of approximately 10^{-13} sec.

The life-span $\Delta\tau$ of a complex is related to the line-width by the Heisenberg uncertainty principle

$$\Delta \tau \cdot \Delta E = \frac{\Pi}{2\pi} \qquad \Delta E = h \Delta v C$$

h is Planck's constant, c the velocity of light and Δv is the increase in the half-width of a Raman line in cm⁻¹.

 $\Delta \tau = \frac{1}{2\pi\Delta\nu c} \text{ [sec]} \qquad \Delta \tau = \frac{0.5}{\Delta\nu} \text{ 10-11 [sec]}$

With our spectrograph it is impossible to measure an increase of less than 0.5 cm⁻¹ in the half-width of the Raman line. As the last equation shows, an increase of 0.5 cm⁻¹ in the half-width results in a life-span $\Delta \tau$ of 10⁻¹¹ sec. A longer life-span cannot be measured by this method. To hold the influence of asymmetric electric fields on the line-width as low as possible, we examined the pulsation of tetrahalogeno complexes. These cause no electrical moment in vibration.

In Fig. 1 the Raman spectra of aluminum tetrabrom complexes of Cs, K, Na and Li are shown. In all cases, using an entering slit of 8 cm⁻¹ on the spectrograph, the line-width of the pulsation is 9 cm⁻¹ in the crystal at room temperature. In the liquid state we observe the same line-width for aluminum tetrabromo complexes of Cs, K and

Na within the margin for error. This shows that the lifespan of these complexes is 10^{-11} sec or longer. Only the lithium complex with a line-width of 11.4 cm⁻¹ shows an increase of 2 to 3 cm⁻¹ which demonstrates that, as a result of contrapolarization, the life-span of this complex is reduced to just under 10^{-11} sec.

In Fig. 2 Raman spectra of molten alkali tetrabromoindates are shown. With a slit-width of 8 cm⁻¹, CsInBr₄ in the crystal has a line-width of 10.3 cm⁻¹ at room temperature. At 400°C, the pulsations of the alkali tetrabromoindates show line-widths of 12, 18, 19 and 20 cm⁻¹, respectively. This increase in the line-widths, compared with line-widths in the crystal enables us to calculate the following life-spans:

CsInBr4	3•10-12	sec	KInBr4	0.7.10-12	sec
NaInBr ₄	0.6.10-12	sec	LiInBr4	0.5.10-12	sec

The comparison of AlBr4- with InBr4- in the melt shows that both the increase in the polarity of the bond and the increase in the contrapolarization caused by the cation reduce the life-span of the complexes.

In Fig. 3 Raman spectra at 550°C of Cs2MgBr4, K2MgBr4, Na2MgBr4 and Li2MgBr4 are shown. In these cases also an increase in the line-widths of 8.9, 13.5, 17.2 and 20.9 cm⁻¹ is observed. Assuming the same conditions as for $InBr_4^{2-}$, we estimate the life-span of these complexes to be as follows:

Cs2MgB:	r4 0.6•10-12 sec	K2MgBr4 0.4 •10 ⁻¹² sec
Na ₂ MgB:	r4 0.3•10-12 sec	Li2MgBr4 0.25.10-12 sec
The heigth o	of the pulsation	of the $MgBr_4^{-2}$ complexes shows
a gradual de	ecrease as noted	below:

Cs2MgBr4	157 cm ⁻¹	K2MgBr4	156 cm-1
Na ₂ MgBr ₄	147 cm-1	Li2MgBr4	144 cm-1

Through the increase in the contrapolarization, the pulsation assumes more and more the character of a Li-Br-Mgbridge-mode. The characteristic Mg-Br-Mg-bridge-mode is observed in molten MgBr₂ at 140 cm⁻¹. MgBr₂ has coordination number four in the melt.

In the melt of CaBr2.2KBr no Raman bands could be observed. In this case, the difference in polarity between Ca and Br is so great that the life-span becomes so short that the complexes can no longer be observed by spectroscopy. This means that the life-span of the complex is shorter than one mode.

Fig. 4 shows the Raman spectrum of Cs2MgI4 in molten state at 500°C. The slit-width of the spectrograph is now 4 cm⁻¹. The pulsation of MgI4²⁻ at 106 cm⁻¹ is polarized. The F₂ deformation mode at 61 cm⁻¹ is depolarized. The line-width of the pulsation in the melt is 9 cm⁻¹. The Cs2MgI4 crystal also contains the MgI4²⁻ tetrahedron and shows the same spectrum as the melt except that the linewidth is now 5 cm⁻¹. The difference in line-width of 4 cm⁻¹ between the melt and the crystal allows us to calculate the life-span of MgI4²⁻ in the melt to be $0.6 \cdot 10^{-12}$ sec.

Fig. 5 shows the Raman spectrum of a mixture consisting of two mols CsI and one mol CaI₂. The slit-width of the spectrograph is again 4 cm⁻¹. In the solid state there are two compounds: Cs4CaI₆ and CsCaI₃. Both have coordination number six. Cs4CaI₆ contains CaI₆⁴⁻ octahedra and CsCaI₃ has perowskite structure. According to our experience, all iodides of divalent cations have the coordination number four in the melt. We assume that the very broad Raman line in the CaI₂·2CsI melt is the pulsation of the CaI₄²⁻ tetrahedron. Its line-width is 30 cm⁻¹. Assuming a standard line-width identical to that of Cs₂MgI₄ (5 cm⁻¹), we estimate the life-span of the CaBr₄²⁻ complex in the melt to be 2.0·10⁻¹³ sec. This is the shortest life-span we have ever observed.

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Fig. 1 Raman spectra of molten alkali tetrabromoaluminates



Fig. 2 Raman spectra of molten alkali tetrabromoindates



Fig. 3 Raman spectra of molten alkali tetrabromomagnesates



Fig. 4 Raman spectra of molten cesium tetraiodomagnesate



Fig. 5 Raman spectra of the melt CaI_2 · 2 CsI

THEORETICAL STUDY OF THE REACTION OF AIF_4^- AND $AICI_4^-$ WITH OXIDE AND SULFIDE IONS

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ABSTRACT

Ab initio quantum mechanical calculations were performed, using the 3-21G extended basis set, on reactions of molecules and ions containing Al-F or Al-Cl bonds with oxygen or sulfur containing species to form products with Al-O or Al-S bonds; from these we deduce the structures of the species and the energetics of the reactions. The results provide evidence for the stability of Al-O and Al-S bonds in molten salts. In addition, this study shows that (1) it may be possible to create simple ionic pair potentials to simulate Al-O and Al-S bonds in a molecular dynamics calculation and (2) that quantum mechanical calculations can provide useful information on the structures and energetics of species in molten salt solutions.

INTRODUCTION

The formation of complex species involving Al^{3+} and O^{2-} or S^{2-} in molten salts is of fundamental scientific significance as well as of importance technologically in current and advanced aluminum smelting processes and batteries. Such species have been extensively studied experimentally in fluoride and chloride solvents.¹⁻¹⁰ Little experimental work^{4,6} and no theoretical studies of the energetics of bonding have been published. In this paper, quantum mechanical calculations are reported on the structures and energetics of gaseous molecules involved in reactions of Al^{3+} with O^{2-} and S^{2-} . Insofar as it is possible, the gaseous molecules are chosen to correspond to species which are expected or possible in molten halide melts. The aims of this calculation are (1) to determine the structures of known moieties in molten salt solutions and (2) to determine the energetics of reactions for the formation of species containing Al-O and Al-S bonds. From a knowledge of the energetics of vapor molecules it is hoped that we can deduce pair potentials for the $Al^{3+}-O^{2-}$ and $Al^{3+}-S^{2-}$ pairs which can be used to realistically simulate the behavior of molten salt solutions of these ions in a molecular dynamics calculation.

QUANTUM MECHANICAL CALCULATIONS

Ab initio molecular orbital LCAO-SCF calculations¹¹ were carried out to determine the structure and energetics of a number of metal halide and metal halide oxide molecules. The extended 3-21G basis set ¹² was used and the structures of the chosen species were optimized subject only to imposed symmetries. Two sets of molecules were optimized: one involving anions and the other involving neutral species.

The following set of reactions involving anions was studied:

$$AlCl_4^- + S^{2-} \to AlCl_3S^{2-} + Cl^- \tag{1}$$

$$AlCl_4^- + S^{2-} \to AlCl_2S^- + 2Cl^- \tag{2}$$

$$AlF_4^- + O^{2-} \to AlF_3O^{2-} + F^-$$
 (3)

The structures of $AlCl_4^-$, AlF_4^- , $AlCl_3S^{2-}$, $AlCl_2S^-$ and AlF_3O^{2-} were optimized. The structural parameters used in the optimizations are illustrated in Fig. 1. The optimal geometries and total energies of the five anions are given in Table I. Based on previous geometry optimizations of molten salt vapor complexes ¹³ the stuctures of the anions should be relatively accurate with the exception of the Al-Cl bond lengths which are probably about 0.1 - 0.2 Å too long.

The 3-21G energy changes, ΔE_{qm} , for the three reactions are given in Table II. The difficulties of molecular orbital theory at this level in calculating energies of anions are well known.¹⁴ The most significant inaccuracy is probably in the calculation of the energetics of the divalent anions S^{2-} and O^{2-} . Both of these ions are predicted to be very unstable, but since such divalent anions have never been observed there is no way of checking the accuracy of our calculations. In addition, the 3-21G electron affinities of the other anions in the reactions will be in error by varying amounts. To a certain extent the errors in the electron affinities of anions on one side will cancel with those on the other side. Another inaccuracy in the reaction energies comes from neglect of electron correlation in the calculational method. However, in calculations for reactions such as (1) and (3) where there are the same number of bonds on both sides of the reaction, there should be considerable cancellation of correlation energies¹⁵ and the error introduced into values of ΔE_{am} from this source is likely to be small. Despite these uncertainties in the energies of reactions (1)-(3), it is likely that, as mentioned previously, the calculated structures of the anions are reliable.

In order to improve the reliability of the results for ΔE_{qm} we performed further calculations for the following reaction involving only neutral species:

$$LiAlF_4 + Li_2O \rightarrow Li_2AlF_3O + LiF$$
 (4)

Reaction (4) eliminates the problems with the anions in reactions (1)-(3). We assumed C_{3v} structures for the LiAlF₄ and Li₂AlF₃O species. They should be only slightly less stable than the most stable configuration.¹³ The C_{3v} structures give the same number and types of bonds on both sides of the reaction which allows for cancellation of correlation energy errors. The energies and geometries of the individual species are given in Table I, the value of ΔE_{qm} is given in Table II, and the structures are exhibited in Figure 2. Comparisons of 3-21G reaction energies for several related reactions with experimental values in the JANAF tables¹⁶ indicate that the ΔE_{qm} for reaction (4) is probably accurate to within about 20^c. The ΔE_{qm} for reaction (4) is considerably less negative than those for the three reactions involving anions.

CLASSICAL ELECTROSTATIC CALCULATIONS

The quantum mechanical results are now compared to energy changes, ΔE_{es} , calculated from the electrostatic energies of interactions of the ions in the species involved in all four reactions. This comparison provides a test of the efficacy of coulomb models for predicting the energetics of bonding in solution^{4,6}. The electrostatic calculation is only for reference and is used to gauge the manner in which one might construct pair potentials for effective molecular dynamics simulations. We chose to perform a simple calculation based on coulomb interactions, $z_i z_j e^2/r$, where $z_i e$ and $z_j e$ are charges on spherical ions separated by a distance r, and the ions are Al³⁺, F⁻, Cl⁻, O²⁻, S²⁻ and Li⁺. In addition, a soft r^{-9} repulsion was assumed. The method of calculation was simply to calculate all of the coulomb energies for the ions involved using the distances deduced from the quantum mechanical calculations given in Table I. These coulomb energies were multiplied by 8/9 to take into account the soft repulsions. The results for ΔE_{es} are given in Table II. For reactions (1), (2), and (3) this simple electrostatic calculation is close to the results of the quantum mechanical calculation, being especially close for reaction (1). However, this correspondence should be considered fortuitous in view of the large uncertainties in ΔE_{qm} for the reactions involving anions. For reaction (4), ΔE_{es} is much more negative than ΔE_{qm} . Since ΔE_{es} is a small difference between the much larger values of E_{es} , moderate changes in the pair potentials can lead to such relatively large differences in ΔE_{es} . For example, softening the repulsive potential between Al³⁺ and O²⁻ ions to r^{-n} where n<9 will lower the stability of the Li₂AlF₃O species and make the calculated value of ΔE_{es} much less negative. Thus, it is possible to create a pair potential which leads to a reliable value of ΔE_{es} for reaction (4) and which is likely to provide realistic

results for the formation of Al-O near neighbor pairs in a molecular dynamics calculation for molten salts.

CONCLUSIONS

The theoretical study presented here provides evidence for the stability of Al-O and Al-S bonds in molten salts. The evidence is twofold. First, in all of the reactions considered the replacement of an aluminum halide bond by an aluminum oxide or sulfide bond is favored energetically. Secondly, the Al-O (and Al-S) bonds are in all cases shorter than the Al-F (and Al-Cl) bonds. This occurs despite the fact that the the Pauling radius of O^{-2} is 0.04 Å larger than that of isoelectronic F^- and the radius of S^{-2} is 0.03 Å larger than that of isoelectronic Cl⁻.

This study also shows that (1) it may be possible to create simple ionic pair potentials to simulate Al-O (and Al-S) bonds in a molecular dynamics calculation and (2) that quantum mechanical calculations can provide significant information on the structures and energetics of species in molten salt solutions.

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REFERENCES

- 1. K. Grjotheim et al., Aluminium Electrolysis, Aluminium Verlag GmbH, Duesseldorf (1977) pps. 103-106
- 2. S. H. K. Ratkje, Complex Formation in Alkali-Aluminium Fluoride Melts, Dissertation, The University of Trondheim, Norway (1974)
- B. Gilbert, G. Mamantov and G. Begun, Inorg. Nucl. Chem. Letters, <u>12</u>. 415 (1976)
- 4. Z. Nagy, J. L. Settle, J. Padova and M. Blander, J. Electrochem. Soc., <u>129</u>, 2034 (1982)
- 5. R.W. Berg, S. von Winbush and N.J. Bjerrum, Inorg. Chem., 19. 2688 (1980)
- 6. M. Blander and Z. Nagy, Z. Naturforsch., <u>A38</u>, 116 (1983)
- 7. K. A. Paulsen and R. A. Osteryoung, J. Am. Chem. Soc., <u>98</u>, 6866 (1976).

- 8. J. Robinson, B. Gilbert, and R. A. Osteryoung, Inorg. Chem., 16 3040 (1977)
- 9. B. Gilbert and R. A. Osteryoung, J. Am. Chem. Soc., 100 2725 (1978)
- 10. R. A. Osteryoung, Proc. Int'l. Symp. Molten Salts, ed. J. Pemsler et al., Electrochemical Society, Pennington, N.J. pps. 240-53
- P. N. van Kampen, G. F. Smits, F. A. A. M. de Leeuw, and C. Altona, Quantum Chemistry Program Exchange, Indiana University, Program No. 437.
- J. S. Binkley, J. A. Pople, and W. J. Hehre, J. Am. Chem. Soc., <u>102</u> 939 (1980); M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro, and W. J. Hehre, J. Am. Chem. Soc., <u>104</u> 2797 (1982).
- 13. L. A. Curtiss, Chem. Phys. Let., <u>68</u> 225 (1979).
- 14. L. Radom, In "Methods of Electronic Structure Theory"; H. F. Schaefer III, Ed.; Plenum Publishing Company: 1977; Vol pp 333-356.
- R. Ditchfield, W. J. Hehre, J. A. Pople, and L. Radom, Chem. Phys. Let. <u>5</u> 13 (1970).
- D. R. Stull and H. Prophet, eds., JANAF Thermochemical Tables, 2nd Ed., NSRDS-NBS37(1971).

Structure ^a	Geometry ^b	Energy, a.u. ^c
$AlCl_4^-(T_d)$	$\mathbf{r}(Al-Cl) = 2.24$	-2070.20141
$\operatorname{AlF}_4^-(\operatorname{T}_d)$	$r(Al-F) = 1.67[1.69^d]$	-636.59205
$\mathrm{AlCl}_3\mathrm{S}^{2-}(\mathrm{C}_{3v})$	r(Al-Cl) = 2.35, r(Al-S) = 2.17, $\theta = 118$	-2008.35595
$AlCl_2S^-(C_{2v})$	r(Al-Cl) = 2.25, r(Al-S) = 2.11, $\theta = 128$	-1551.03530
$\mathrm{AlF_3O^{2-}(C_{3v})}$	r(Al-F) = 1.72, $r(Al-O) = 1.65$, $\theta = 118$	-611.82848
$LiAlF_4(C_{3v})$	r(Al-F) = 1.71, r(Al-F') = 1.63, $r(Al-Li) = 2.26, \theta = 125$	-644.04689
$Li_2AlF_3O(C_{3v})$	r(Al-F) = 1.74, $r(Al-Li) = 2.25$, r(Al-O) = 1.65, $r(Al-Li') = 3.24$, $\theta = 127$	-627.02952
LiF ^e	r(Li-F) = 1.52[1.564]	-106.35419
$\operatorname{Li}_2\operatorname{O}(\operatorname{C}_{2v})^f$	$\mathbf{r}(\text{Li-O}) = 1.58[1.59, 1.55],$ $\boldsymbol{\theta} = 180 \ [180]$	-89.28714

Table I. Calculated 3-21G geometries and total energies

^a Assumed symmetries in parentheses.

- ^b Bond lengths in \hat{A} , bond angles in degrees. Experimental values in square brackets.
- ^c 1 a.u. = 627.5 kcal mol⁻¹.
- ^d JANAF Thermochemical Tables 1978 Supplement, M. W. Chase, Jr., et al., J. Phys. Chem. Ref. Data, 7, 826 (1978).

^e Ref. 12.

^f K. Raghavachari, J. Chem. Phys., <u>76</u>, 5421 (1982).

ΔE_{qm}	ΔE_{es}
-147	-145
-168	-143
-242	-194
-31	-97
	ΔE_{qm} -147 -168 -242 -31

Table II.Reaction energies (in kcal mol⁻¹)

^a See text for reactions.









Influence of Redox and Lewis Acid Functions of SbCl₃-Rich Molten Salt Catalysts on the Reactions of Coal Model Compounds

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Abstract

Recent studies of the chemistry of coal model compounds in SbCl₃-based molten salt catalysts have shown that both the redox and Lewis acid functions of these media can play principal roles in catalyzing reactions for organic substrates. These two catalytic functions are discussed in relation to two reaction types that have been recently discovered in highly purified, anhydrous SbCl₃-rich melts. The redox function of the melt is shown to play the dominant catalytic role in a transfer hydrogenation reaction for oxidizable arenes that are selectively hydrogenated by tetralin at only 80°C. The arene radical cation is found to serve as the key organic reactive intermediate. The Lewis acid function of the melt is shown to catalyze selective transalkylation chemistry for the α,ω -diphenylalkanes, C₆H₅(CH₂)_n C₆H₅ [n = 1-4] with the catalyst generating a benzylic carbenium ion as the key reactive intermediate.

Introduction

Molten SbCl₃ is one of the metal halide melts that has been reported to be an effective, selective catalyst for hydrocracking coal (1). From our extensive fundamental studies of the chemistry of coal model compounds (e.g. aromatics, hydroaromatics, and α,ω -diphenylalkanes) (2-7), the SbCl₃-based molten salt catalysts have exhibited substantial flexibility particularly with regard to tuning the strength of the catalytic functions. This ability to alter the strength of the catalytic functions in a reproducible manner results in a catalyst system in which not only reaction rates can be controlled but also product selectivities.

Earlier research concentrated on the chemistry of individual polycyclic aromatic hydrocarbons (arenes) in the $SbCl_3$ -based melts (2-4). These arenes were activated by the redox function of the catalytic medium, and arene radical cations were found to be key intermediates. Tuning the strength of the redox function of the melt was found to dramatically alter reaction rates and product selectivities.

In the present description of the melt catalyzed transfer hydrogenation reaction, the versatility of these SbCl3-based melts is further illustrated by the ability to activate one organic substrate (a polycyclic arene) in the melt in the presence of a second unactivated substrate (tetralin) and observe the resulting reaction.

The α, ω -diphenylalkanes, on the other hand, are not capable of being oxidized to radical cations in the SbCl3-based melts, and the transalkylation chemistry observed results from activation by the Lewis acid function of the melt. Tuning the strength of this catalytic function leads not only to a control over reaction rates, but also provides a valuable means for the investigation and discovery of a novel mechanism for this important organic reaction.

Catalytic Functions of SbCl₃

Molecular SbCl₃ is a notoriously weak Lewis acid. However, in the molten state SbCl₃ is weakly ionized, as modeled in eq. 1, with

$$SbCl_3 \neq SbCl_2^+(solv.) + Cl^-(solv.)$$
 (1)

a reported ionization constant, K_i, at 99°C ranging from 3 × 10⁻¹¹ to 2×10^{-8} M² (8,9). The modest Lewis acid function of the melt resides in the chloride deficient antimony cation, SbCl₂⁺. As indicated in eq. 1 the ions are not present in the melt as discrete entities, but instead are strongly solvated to neutral SbCl₃ molecules (or chains) through chlorine bridge bonds as indicated from Raman and electrical conductivity studies (10,11). However, for the purposes of discussing the organic chemistry, it will be sufficient to use SbCl₂⁺ to model the chloride deficient antimony species that is acting as the Lewis acid in the melts.

The Lewis acidity of the melt is tuned by controlling the concentration of $SbCl_2^+$ in the melts by adding chloride donors or acceptors. Basic melts are formed by adding a few mol % of a strong chloride donor such as CsCl (eq. 2), while acidic melts are generated by adding a strong chloride acceptor such as AlCl₃ (eq. 3). The degree to which the Lewis acidity can be

$$CsC1 \xrightarrow{SbC1_3} Cs^+ + C1^-$$
(2)

$$SbC1_3 + AlC1_3 \xrightarrow{SbC1_3} SbC1_2^+ + AlC1_4^-$$
 (3)

altered is indicated from the calculation that in an SbCl₃-10 mol %

AlCl₃ melt the concentration of SbCl₂⁺ is increased by a factor of 10^4 - 10^5 compared to that in a neat SbCl₃ melt (as estimated from the range of K₁ values at 99°C).

We have also found that SbCl₃ melts have a redox function in which Sb³⁺ can act as an oxidant. The concomitant reduction of Sb³⁺ in the melt liberates chloride and, thus, the oxidizing power of the

$$1/3 \text{ SbCl}_3 + e \neq 1/3 \text{ Sb} + \text{Cl}^-$$
 (4)

melt will depend on the melt acidity. The effect of added chloride donor or acceptor on the formal potential of the Sb^{3+}/Sb couple was measured by electrochemical methods (12). As expected the addition of a few mol % of a strong chloride donor (KCl) decreased the oxidizing power of SbCl₃, while the addition of a few mol % of a strong chloride acceptor (AlCl₃) increased its oxidizing power. In going from an SbCl₃-5 mol % KCl melt to an SbCl₃-5 mol % AlCl₃ melt, the formal potential of the Sb³⁺/Sb couple and the resulting oxidizing strength can be tuned over ~0.5 V (9,12).

We have reported that antimony has lower oxidation states between 3+ and the metal, the nature of these species depending on the melt acidity (13). Thus, the single electron oxidation of organic compounds by $5b^{3+}$ can take place homogeneously in the melt with the soluble lower oxidation state species acting as electron carriers. When SbCl₃ is reduced in significant quantities, Sb metal may be isolated from the reaction products upon hydrolysis of the melt as a consequence of a disproportionation reaction of the lower oxidation state species (4).

Redox Catalyzed Transfer Hydrogenation (6)

Certain arenes can be oxidized to radical cations by Sb^{3+} in SbCl_3 -based melts with the degree of oxidation depending on melt acidity as shown in eq. 5. This oxidation process has been studied for

$$ArH + 1/3 SbCl_3 \neq ArH^+ + 1/3 Sb + Cl^-$$
 (5)

many arenes by ESR spectroscopy (14) and, for the case of perylene, by UV-VIS spectroscopy (15). If no other substrates are present to react with the arene radical cations, they will react with themselves, or perhaps with unoxidized arene, leading to condensed products with new aryl-aryl bonds. These radical cation reactions produced some unusual hydrogen transfer chemistry in the melts, which we have previously reported (2-4).

We have initiated a study of the chemistry of these arene radical cations with other organic substrates that are not reactive, alone, in the melt. In this current investigation, tetralin (1,2,3,4-tetrahydronaphthalene) was chosen as the second reagent. Tetralin is a well known hydrogen donor for thermally generated neutral radicals, and we wished to see if tetralin could react with arene radical cations.

The arenes that were examined cover a wide range of oxidizability in the melt, and they are shown in Fig. 1 along with the corresponding anodic E1/2 values measured in a basic SbCl₃ melt at 99°C (16). The oxidative E1/2 of phenanthrene lies beyond the anodic limit of the melt ($Sb^{3+} + Sb^{5+}$), but it has been estimated from the excellent correlation with arene E1/2 values measured in acetonitrile (17). Of these arenes, phenanthrene is the most difficult to oxidize while naphthacene is the most easily oxidized.

Phenanthrene and pyrene are not capable of being oxidized to radical cations by neat SbCl₃. Equimolar solutions of either of these arenes with tetralin in SbCl₃ produces no reaction even at temperatures up to 150°C. The 200 MHz ¹H NMR of these melts gives well-resolved spectra of the molecular components with no indication of any complexation of the organics with the solvent.

The more oxidizable arenes, anthracene, perylene, and naphthacene, are capable of being oxidized to radical cations in neat SbCl3, as we have previously observed in dilute solutions by ESR (14). Anthracene is observed by NMR to react readily with tetralin at 80°C. Analysis of the product mixture following hydrolysis of the melt shows that a very selective transfer hydrogenation reaction has taken place as shown in Fig. 2 with 9,10-dihydroanthracene (DHA) the only hydroanthracene produced. The anthracene radical cation is apparently efficiently trapped by the tetralin, and no bianthracenes are detected that would result from coupling reactions of the radical cation (2,4). Product analysis further shows that no naphthalene is generated, and that the only other major products are 1,2,3,4,5,6,7,8,-octahydro-1,2,-binaphthalene (1) and 2-(1,2,3,4-tetrahydro-1-naphthyl)anthracene (2). The yield of DHA, 1, and 2 depend on the initial concentration of tetralin present, and this dependence is illustrated in Table 1. Anthracene conversions are in the range of 35 to 45% after the 30 min reaction period at 80°C. The yield of DHA is maximized at a tetralin/anthracene ratio of 2.0. Note that it is critical to maintain SbCl₃ as a concentrated melt in order to have catalytic activity. As the last entry in the table indicates, if tetralin is present in large excess such that it is actually the solvent and SbCl3 is present as a homogeneous catalyst (with the same SbCl₃/anthracene ratios), no reaction occurs. The $\frac{1}{2}$ product ratio is also found to increase with increasing tetralin/anthracene ratio. The formation of these particular compounds and the dependence of their yields on the initial

tetralin/anthracene ratio will be discussed later in relation to the proposed mechanism.

Naphthacene also undergoes the transfer hydrogenation reaction with tetralin in SbCl₃. The reaction is even more rapid than that for anthracene with a 97% naphthacene conversion after a 30 min reaction period at 80°C. This reaction is also very selective as shown in Fig. 3 with 5,12-dihydronaphthacene the only hydronaphthacene formed. The byproducts are analogous to those produced in the anthracene reaction with the tetralyl-substituted naphthacene ($\underline{3}$) product being a mixture of two isomers as indicated.

Perylene is also partially oxidized to a radical cation by Sb^{3+} in the melt. However, the radical cation is very persistent and undergoes no further reaction even in the presence of tetralin and at temperatures up to $130^{\circ}C$. This results in a ¹H NMR spectrum of the melt that exhibits signals due only to the tetralin, while the perylene signals are not observed because of rapid electron exchange between the perylene.

The proposed mechanism for the catalytic transfer hydrogenation of arenes by tetralin in SbCl₃ is shown in Fig. 4 using anthracene as The first step is the oxidation of the arene to the radian example. cal cation. Phenanthrene and pyrene do not undergo this electron transfer step and, thus, do not react. Perylene on the other hand undergoes the electron transfer reaction, but as described earlier the resulting radical cation is very persistent and undergoes no further Anthracene and naphthacene are also oxidized in the melt, reaction. and the radical cations react with tetralin by hydride transfer to the cationic center of the radical cation rather than hydrogen transfer to the radical center. The resulting 1-tetralyl cation, 5, then undergoes competitive electrophilic attack on unreacted tetralin and arene as shown in the third and fourth steps. The formation of the particular positional isomers shown is consistent with the known Friedel-Crafts alkylation chemistry of tetralin (18) and anthracene (19) when sterically bulky electrophiles are employed. Since the reaction is catalytic in SbCl3, there must be a reoxidation step as shown in the last two equations. The detailed nature of the reoxidation step is not known, and it has been combined with the hydrogen transfer step that lead to the formation of the hydroarene.

Altering the oxidizing power of the melt has dramatic effects on the transfer hydrogenation reaction. If anthracene and tetralin (1:2 mole ratio) are reacted in a weakly oxidizing SbCl₃ - 8 mol % KCl melt, the reaction rate is substantially reduced with only a 2%. DHA yield (rather than 39%) after 30 min at 80°C. On the other hand, if the reaction is run in the highly oxidizing SbCl₃-10 mol % AlCl₃ melt, not only are the rates enhanced but the product selectivity is completely altered. The transfer hydrogenation reaction is no longer observed and, instead, coupling reactions of the radical cations are

observed exclusively, which produce condensed anthracenes in a reaction that has been previously characterized (4).

The transfer hydrogenation chemistry has produced the first evidence that solution phase hydrocarbon radical cations can react by hydride abstraction. The research also points out the versatility of the SbCl₃-based molten salt catalyst resulting from the ability to reproducibly tune the strength of the redox function, which leads to control over reaction rates and product selectivities. Furthermore, the facility with which arene radical cations can be produced in the presence of a second unactivated organic substrate should allow for substantial advancement in the understanding of reactions of arene radical cations.

Lewis Acid Catalyzed Transalkylation (7)

The α,ω -diphenylalkanes $C_{6H_5}(CH_2)_nC_{6H_5}$ [n = 1-4] have first ionization potentials from photoelectron spectroscopy that are comparable to that of toluene (20). The high oxidation potentials of these compounds, compared to those of polycyclic arenes, places them beyond the range of the oxidizing power of SbCl₃ even in acidic melts. However, these compounds react readily in SbCl₃-rich melts in a reaction that is catalyzed by the Lewis acid function of the melt.

Diphenylmethane (DPM) is the most reactive of the diphenylalkanes with about a 60% conversion in SbCl₃ after 2 hrs at 130°C. The overall reaction is a transalkylation (Fig. 5) that produces, at low conversions (<10%), only benzene and the o-, m-, and p-isomers of benzyldiphenylmethane. At higher conversions, larger polybenzyl oligomers are observed.

1,2-Diphenylethane (DPE) is much less reactive than DPM. At 130°C in SbCl₃, the DPE reaction rate is measured to be 1×10^3 slower than that of DPM. However, rapid reaction rates may be obtained if the more acidic SbCl₃-10 mol % AlCl₃ melt is employed as catalyst. At 100°C, nearly 60% of the DPE reacts within the first 10 min and produces the same product mixture (Fig. 6) as observed in neat SbCl₃. Again a transalkylation reaction has occurred producing benzene, the o-, m-, and p- isomers of (2-phenylethyl)-1,2-diphenylethane, and also the higher oligomers at higher conversions. The observed cleavage of the benzylic sp²-sp³ bond for DPE is very selective, and no products are detected resulting from the cleavage of the central sp³-sp³ bond.

1,3-Diphenylpropane (DPP) and 1,4-diphenylbutane (DPB) react at very similar rates compared to DPE and require the $SbCl_3-10$ mol % AlCl₃ melt for rapid reaction rates. However, neither DPP or DPB undergoes an intermolecular transalkylation reaction. Instead, as shown in Fig. 7, they exclusively undergo an analogous intramolecular reaction to produce benzene and either indan (from DPP) or tetralin

(from DPB). These extremely selective reactions have been monitored by in situ $^{1}\mathrm{H}$ NMR spectroscopy to near quantitative conversions of the DPP and DPB, and the only products observed are those described in Fig. 7. As before, only cleavage of the benzylic $\mathrm{sp}^{2}-\mathrm{sp}^{3}$ bond of these diphenylalkanes is observed.

The transalkylation chemistry of alkylbenzenes has been extensively studied and, normally, protons are invoked as key catalytic agents. In fact the reaction is typically performed in strong protonic acid media such as AlBr₃-HBr, GaBr₃-HBr, and BF₃-HF (21-25). We have examined the least reactive of the alkylbenzenes, toluene, and found it to undergo typical transalkylation chemistry (Fig. 8) in the aprotic SbCl₃-10% AlCl₃ melt, although at a much slower rate (-4×10^2 slower than DPE in SbCl₃-10% AlCl₃ at 100°C).

The transalkylation chemistry for the diphenylalkanes and toluene in aprotic SbCl₃-based melts can be explained by a mechanism in which the rate determining step involves the abstraction of a benzylic hydride by the Lewis acid species in the melt, $SbCl_2^+$ (in its solvated form), as shown for the diphenylalkanes in eq. 6.

PhCH₂(CH₂)_xPh + SbCl₂⁺
$$≇$$
 Ph⁺CH(CH₂)_xPh + HSbCl₂ (6)

The relative reaction rates in SbCl₃ melts,

PhCH₂Ph >> Ph(CH₂)₂Ph ~ Ph(CH₂)₃Ph ~ Ph(CH₂)₄Ph >> PhCH₃,

are exactly those predicted based on the stabilities of the corresponding benzylic cations, namely

PhcHPh >> PhcHCH2Ph ~ PhcH(CH2)2Ph ~ PhcH(CH2)3Ph >> PhcH2

Additional evidence supporting eq. 6 as the key mechanistic step includes:

(1) For DPM the initial reaction rate has a first order dependence on the initial DPM concentration, which was varied from 0.028 to 1.02 M.

(2) For DPE the rate in SbCl₃-10% AlCl₃ at 100°C is greater than that in SbCl₃ at 130°C by 1×10^4 . The rate enhancement at a common temperature, e.g. 100°C, should be greater than 10⁴. This rate enhancement corresponds roughly to the calculated increase in SbCl₂⁺ concentration of 10^4 - 10^5 .

(3) We have also previously reported stoichiometric hydride abstractions for 9,10-dihydroanthracene and 5,12-dihdyronaphthacene in

SbCl₃-10% AlCl₃ melts. For these substrates, the benzylic cation formed is stable in the melt and can be characterized by $^{1}\mathrm{H}$ NMR (5).

Once the benzylic cation is formed in the rate determining step, the product distributions can be readily understood as shown for the case of DPP in Fig. 9. For DPM and DPE stable cyclic products cannot be produced, and the incipient benzylic cation instead undergoes an electrophilic attack on unreacted starting material resulting in the intermolecular transalkylation chemistry observed.

The Lewis acid function of SbCl₃ melts is capable, therefore, of catalyzing a selective bond cleavage reaction for the α,ω -diphenylalkanes by generating a benzylic carbenium ion as the key organic reactive intermediate. The ability to tune the strength of this Lewis acid function allows for control of the reaction rates and provides kinetic information concerning the role of the catalyst.

Experimental

The reactions described above were studied by 1 H NMR spectroscopy at 200 MHz and by product analysis following quench and separation procedures. Detailed experimental procedures have been previously reported (6,7). Both NMR and large scale experiments were performed with highly purified reagents in tubes that were sealed on a vacuum line under purified argon. Material transfers were performed in a controlled atmosphere drybox whose argon atmosphere was continuously purified and monitored for moisture and oxygen content, which amounted to <1 ppm each. Products were analyzed by GC, GC-MS, HPLC, and, where applicable, by 1 H and 13 C NMR. Quantitative results were obtained by GC using internal standards and by HPLC separation with subsequent analysis by UV spectroscopy.

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REFERENCES

- 1. Wald, M. M. U. S. Patent 3 542 665, 1970.
- Dworkin, A. S.; Poutsma, M. L.; Brynestad, J.; Brown, L. L.; Gilpatrick, L. O.; Smith, G. P. J. Am. Chem. Soc. 1979, 101, 5299.
- 3. Buchanan, A. C., III,; Dworkin, A. S.; Smith, G. P.;
- Buchanan, M. V.; Olerich, G. <u>Fuel 1981</u>, <u>60</u>, 694.
- Buchanan, A. C., III,; Dworkin, A. S.; Smith, G. P. <u>J. Am. Chem.</u> <u>Soc.</u> <u>1980</u>, <u>102</u>, 5262.
- Buchanan, A. C., III,; Dworkin, A. S.; Smith, G. P. J. Org. Chem. 1981, 46, 471.
- Buchanan, A. C., III,; Dworkin, A. S.; Smith, G. P. J. Org. Chem. 1982, 47, 603.
- Buchanan, A. C., III; Dworkin, A. S.; Smith, G. P. J. Am. Chem. Soc. 1983, 105, 2843.
 Baughan, E. C. in "The Chemistry of Nonaqueous Solvents",
- Baughan, E. C. in "The Chemistry of Nonaqueous Solvents", Lagowski, J. J. Ed.; Academic Press: New York, 1976; Vol. IV, pp. 145-146.
- 9. Bauer, D.; Texier, P. <u>C. R. Hebd. Seances Acad. Sci., Ser. C</u> 1968, 266, 602.
- (a) Huglen, R.; Mamantov, G.; Begun, G. M.; Smith, G. P. J. Raman Spectrosc. 1980, 9, 188. (b) Aliotta, F.; Maisano, G.; Micali, N.; Migliardo, P.; Vasi, C.; Wanderlingh, F.; Triolo, R.; Smith, G. P. J. Chem. Phys. 1982, 76, 3987.
- Petrovic, C.; Mamantov, G.; Sorlie, M.; Lietzke, M. H.; Smith, G. P. J. Phys. Chem. 1982, 86, 4598.
- 12. Texier, P. Bull Soc. Chim. Fr. 1968, 4716.
- 13. Sorlie, M.; Smith, G. P. J. Inorg. Nucl. Chem. 1981, 43, 931.
- Buchanan, A. C., III; Livingston, R.; Dworkin, A. S.; Smith, G. P. J. Phys. Chem. 1980, 84, 423.
- Sorlie, M.; Smith, G. P.; Norvell, V. E.; Mamantov, G.; Klatt, L. N. <u>J. Electrochem. Soc</u>. <u>1981</u>, <u>128</u>, 333.
- 16. E_{1/2} vs. Sb⁰/SbCl₃ (KSbCl₄, saturated); from Bauer, D.; Beck, J. P.; Texier, P. <u>Collect. Czech. Chem. Commun. 1971</u>, <u>36</u>, 940.
- 17. Pysh, E. S.; Yang, N. C. J. Am. Chem. Soc. 1963, 85, 2124.
- Patinkin, S. H.; Friedman, B. S. in "Friedel-Crafts and Related Reactions"; G. A. Olah, Ed.; Interscience: New York, 1964; Vol. 2, Part 1, pp. 68-74.
- Saidova, F. M.; Sidorova, N. G. Dokl. Akad. Nauk. Uzb. SSR 1968, 25, 37; Chem. Abstr. 1969, 70, 57512t.
- Pignataro, S.; Mancini, V.; Ridyard, J. N. A.; Lempka, H. J. J. Chem. Soc., Chem. Commun. 1971, 142.
- 21. Brown, H. C.; Smoot, C. R. J. Am. Chem. Soc. 1955, 78, 2176.
- 22. McCaulay, D. A.; Lien, A. P. J. Am. Chem. Soc. 1957, 79, 5953.
- 23. Schriesheim, A. J. Org. Chem. 1961, 26, 3530.
- (a) Streitwieser, A.; Reif, L. J. Am. Chem. Soc. 1960, 82, 5003.
 (b) <u>Ibid.</u> 1964, 86, 1988.
- 25. Roberts, R. M.; Roengsumran, S. J. Org. Chem. 1981, 46, 3689.

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Anthracene (mmol)	Tetralin (mmol)	SbC13 (mmo1)	DHA Yield ^b	1/2 Yield (mole ratio)
1.40	0	34.2	_	
1.40	0,70	34.2	20	0.15
1.40	1.40	34.2	30	0.50
1.40	2,80	34.2	39	1.5
1.40	5,60	34.2	38	3.5
0.39	37,8	9.52	_	

Table 1. Influence of Tetralin Concentration on the ${\rm Anthracene-Tetralin-SbCl}_3$ Reaction

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^bBased on original anthracene ($\pm 2\%$).



Figure 1. Anodic E₁/2 values for selected arenes in²a basic SbCl₃ melt at 99°C. Value for phenanthrene (0.9 V) is estimated.









0.21

E_{1/2} (V)

0.9





Figure 3. Transfer hydrogenation reaction for naphthacene with tetralin in molten SbCl₃.





Figure 4. Proposed redox mechanism for the transfer hydrogenation reaction of an arene catalyzed by molten SbCl_3 (illustrated for anthracene).



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Figure 6. Transalkylation reaction for DPE in molten $$\rm SbCl_3\mathchar`-10\%\ AlCl_3\mathchar`-$

Figure 7. Intramolecular transalkylation reactions for DPP and DPB in molten $SbCl_3$ -10% AlCl_3.



Figure 8. Transalkylation reaction for toluene in molten SbCl₃-10% AlCl₃.



Figure 9. Proposed mechanism for the SbCl₃-AlCl₃ catalyzed intramolecular transalkylation reaction for DPP following the initial hydride abstraction by $SbCl_2^+$.



REACTIVITY OF ANTHRACENE IN LIQUID SbCl₃-AlCl₃-N-(1-BUTYL)PYRIDINIUM CHLORIDE MIXTURES

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Abstract

Mixtures of SbCl3 and N-(1-buty1)pyridinium chloride (BPC1) containing 75-87 mol % SbCl3 and SbCl3-AlCl3-BPC1 mixtures containing 60 mol % SbCl3 and 17-24 mol % BPCl were found to be liquid at 25°C. Dilute solutions of anthracene were stable in ternary mixtures containing 18 mol % AlCl₃, but in mixtures containing 22-24 mol % AlCl₃, anthracene reacted under the influence of the solvent, which behaved as both oxidant and H-transfer catalyst. The oxidized product was protonated anthracene, which was stable in this melt. The source of protons was provided by hydrogen-liberating Scholl condensations combined with the reduction of Sb(III). A part of the hydrogen from Scholl reactions reacted with anthracene to form 9,10-dihydroanthracene. By contrast, a liquid mixture without SbCl₃, AlCl₃-BPCl (2:1 mole ratio), proved to be a much less active H-transfer catalyst than the SbCl3-rich liquids even though it is a stronger Lewis acid, and it did not induce protonation beyond a trace attributable to protic impurities.

Introduction

Studies of polycyclic aromatic hydrocarbons and hydroaromatics in anhydrous $SbCl_3$ -based melts have shown these melts to be extremely active catalysts for a variety of hydrogen redistribution reactions at surprisingly low temperatures, $80-130^{\circ}C$ (1-5). This research has revealed that liquid $SbCl_3$ (m.p., 73°C) possesses a previously unrecognized redox functionality and reactions have been observed which involve $SbCl_3$ as an oxidant in both a catalytic (1-3) and stoichiometric (4,5) fashion. The melts investigated previously

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have either been pure SbCl₃ or SbCl₃ with 1-10 mol % of added chloride ion donor such as KCl or chloride ion acceptor such as AlCl₃. The added chloride ion donor reduces the oxidizing power of the melt while the added acceptor increases it.

The development by Osteryoung, et al. (6) of binary roomtemperature melts consisting of N-(1-butyl)pyridinium chloride (BPC1) and AlCl₃ led us to investigate the possibility of preparing SbCl₃-rich mixtures that are molten at ambient temperatures. We felt these mixtures might retain the useful properties of the higher melting salts and, at the same time, have the advantage of being liquid under ambient conditions. We found that SbCl₃-BPCl mixtures containing 75-87 mol % SbCl3 and SbCl3-AlCl3-BPCl mixtures containing 60 mole % SbCl3 and 17-24 mol % BPC1 are liquid at 25°C. The ternary mixtures were of particular interest to us because of the possibility of varying the melt acidity and oxidizing power over substantial ranges by making relatively small changes in the AlCl3:BPCl ratio in the neighborhood of the 1:1 value. Consequently, we undertook investigations of the physical and electrochemical properties of these liquids and of the behavior of organics dissolved in them. The results of the first phases of our study are described in this and the following paper (7). In this paper we describe the reactions of anthracene in liquid SbCl₃-AlCl₃-BPCl mixtures at ambient temperatures. Anthracene was chosen for this investigation because of the extensive research (1,3-5) on its reactivity in SbCl3-rich, high-melting mixtures.

Experimental Section

<u>Materials.</u> — Antimony(III) chloride (Alfa, 99% minimum) was purified by the following procedure. It was first melted under argon and mixed with Sb metal in order to reduce any Sb(V) and with Sb_2O_3 to remove volatile chloride impurities. This was followed by two sublimations under dynamic vacuum and, then, by zone refining a minimum of thirty passes. The resultant colorless crystals melted to give a clear, colorless liquid.

Aluminum chloride (Fluka, puriss), to which 1 wt % purified NaCl was added, was refluxed over high-purity aluminum (Alfa, M6N) for 3 days in sealed quartz ampoules, and then distilled away from the NaAlCl₄ phase. This procedure was repeated twice and the resulting AlCl₃ crystals were then vacuum sublimed through a fine porosity Pyrex frit. The purified AlCl₃ crystals were colorless and melted to form a colorless liquid. The NaCl used in this procedure was prepared from reagent grade material, purified by vacuum drying in the solid state followed by melting and bubbling first HCl and then argon (both high-purity grades) through the melt.

BPC1 was prepared from pyridine (Fisher, certified ACS) and 1-butylchloride (Matheson, Coleman and Bell, >98%). The starting materials were further purified by distillation from P205 under argon. The synthetic procedure given by Robinson and Ōsteryoung (8) was followed. As an added precaution, each step was carried out under argon because BPC1 is exceedingly hygroscopic. The product was recrystallized five times under argon from acetonitrile (Fisher, certified ACS) which had been distilled under argon from P_20_5 . In the original procedure (8) ethylacetate was used in recrystallizing the final product but we omitted this material because we were unable to remove it completely from crystalline BPC1 even after prolonged heating under vacuum at 110°C. The BPC1 was dried under vacuum in the presence of P205 in a drying pistol at 110°C and the drying pistol was transferred to the glovebox while still under vacuum. During preparation and all subsequent handling, BPCl was shielded from exposure to light. The water content of the final product was determined by Karl Fischer analysis (Galbraith Laboratories) to be \leq 0.2%. The elemental analysis (Galbraith Laboratories) showed 62.75% C, 8.06% H, 8.34% N, 20.59% Cl and 0.14% 0 (calculated values: C 62.97; H 8.22; N 8.16; Cl 20.65). The BPC1 was further analyzed for organic impurities by dissolving a 1-g sample in a small amount of water and then extracting with three 30-ml aliquots of methylene chloride. After drying with CaSO4 and reducing the volume to 5 ml the methylene chloride was analyzed using a Hewlett Packard model 5880 gas chromatograph equipped with a flame ionization detector and an OV-101, 12-m capillary column. No measurable levels of organic impurities were found in BPC1 that had been purified without the use of ethylacetate. The melting point of the final product was 132.3-133.1°C (corr.).

Anthracene (Eastman, scintillation grade) was recrystallized from acetic acid and then toluene before sublimation. Analysis by HPLC and GC showed less than 0.1% impurities.

9H-anthracenium heptachlorodialuminate $(C_{14}H_{11}Al_{2}Cl_{7})$ 1 was prepared in Schlenk-ware according to the procedure of Koptyug (9). Thereafter it was stored and handled in a glovebox. The 200-MHz ¹H-NMR spectrum of a solution of this compound in molten SbCl₃-10 mol % AlCl₃ was that of the 9H-anthracenium 2 (the cation of 1, shown in Fig. 2) ion without extraneous peaks.

2-Ethylanthracene (Aldrich, 98%) was recrystallized twice from ethanol. No impurities were detected by GC or HPLC analysis.

<u>Preparation of Solvents and Solutions</u>. — All handling of salts (including weighing on an analytical balance) was carried out in an argon-atmosphere glovebox in which both water vapor and oxygen were monitored instrumentally and kept below 1 ppm by continuous circulation of the atmosphere through a purification train. In preparing the ternary SbCl₃-AlCl₃-BPCl melts, SbCl₃ and BPCl were mixed to form a binary liquid to which $AlCl_3$ was slowly added. This procedure allowed dissipation of the heat generated by the $AlCl_3$ -BPCl reaction so that the rise in temperature was only slight. In the preparation of $AlCl_3$ -BPCl melts a substantial temperature rise could not be avoided.

The formal compositions of ternary melts are specified here in terms of mole percentages of the three constituents in the order $SbCl_3-AlCl_3-BPCl$. Melts for which the mole ratio $AlCl_3:BPCl$ exceeded unity are referred to as acidic while those for which this ratio was less than unity are termed basic.

For the preparation of solutions, anthracene and 2-ethylanthracene were weighed on a microbalance outside of the glovebox while 1 was weighed on an analytical balance in the glovebox. The quantity of solvent (SbCl₃-AlCl₃-BPCl) was determined by analytical weighing in the glovebox. Solvent volume was calculated from the density values reported below.

<u>Density.</u> — The densities of selected ternary compositions were measured by pycnometric weighing in the glovebox at 28°C (60:16:24, 1.998 ± 0.002 g/cm³; 60:19:21, 2.025 ± 0.002 g/cm³; 60:21:19, 2.042 ± 0.002 g/cm³). Values for other compositions were determined by linear extrapolation.

<u>Decomposition Reactions.</u> — The decomposition of anthracene in acidic ternary melts was initiated by mixing a solution of anthracene in a basic 60:19:21 melt with an appropriate amount of an acidic melt. For anthracene solutions at the 150-mM concentration level the extent of reaction was measured by quench and separation at the end of a given reaction period. The same quench and separation procedures were followed as those used previously to study the decomposition of anthracene in SbCl₃-rich melts at elevated temperatures (1). These solutions contained 160-200 mg of solute. Product analysis included antimony metal as well as organics.

Studies of solutions at the 30-mM level included in situ optical spectroscopy (see below) in addition to quench and separation. Product analysis did not include antimony metal because of the small amounts of material involved. After a solution had been prepared, it was divided into two portions. One portion was weighed and left in the glovebox for quench and separation at the end of the reaction period. This portion contained 10 mg or more of solute. The other portion (~1 ml) was loaded into an optical cell (see below) which was then sealed, removed from the glovebox and placed in the spectrophotometer. In several runs, a second 1-ml spectroscopy sample was withdrawn from the quench-and-separation portion after 23 h. The spectrum of this second sample was the same as the 23-h spectrum of the sample that had been removed at the beginning of the run.

Optical Spectroscopy. - Optical absorption spectra were measured either with a Cary 14 or a Cary 219 spectrophotometer. The optical cell, shown in Fig. 1, consisted of a 1-cm pathlength quartz glass cuvette attached by means of a graded seal to a 100-cm long Pyrex glass neck with a #15 Ace threaded glass joint at the top. A quartz glass insert, to which an eyelet was attached, could be lowered into the cell by means of a glass rod with a hook on the end. A Teflon bushing and O-ring provided an air-tight seal. The guartz insert could be rotated so that two different optical pathlengths of about 60 and 110 µm were obtainable. The sample compartments of both spectrophotometers were modified to accommodate these cells. Pathlengths of cells with inserts in place were calibrated using the 373-nm band of K2CrO4 solutions in aqueous 0.05 N KOH [ϵ = 4842 M⁻¹ cm⁻² (10)]. Measurements were made with at least four independently prepared concentrations of dichromate for each calibration and the results were reproducible to within 0.5%.

<u>ESR Spectroscopy.</u> — The spectrometer, sample tubes and experimental procedures have been described previously (11). All material transfers were performed in a drybox. The loaded sample tubes were sealed under argon on a vacuum line. Concentration of anthracene in the melts was ~ 5 mM. ESR spectra were obtained at ambient temperatures (22-23°C).

Results and Discussion

<u>Reactions Among Solvent Components</u>. — The SbCl₃-AlCl₃-BPCl mixtures considered here have formal compositions with the following mole fractions: 0.60 SbCl₃, $(0.20+\underline{a})$ AlCl₃ and $(0.20-\underline{a})$ BPCl, where $-0.04 \le \underline{a} \le 0.03$. Since these components vary enormously in chloride donor/acceptor strength, extensive chloride-exchange chemistry occurs on mixing. Aluminum trichloride is a strong chloride ion acceptor while SbCl₃ is a much weaker chloride ion acceptor and BPCl is a chloride ion donor. Therefore the dominant chloride exchange reaction is

$$BPC1 + AlCl_3 \rightarrow BP^+ + AlCl_4$$
[1]

Since the AlCl₃:BPCl ratio is close to unity for all melts, the liquid may be regarded as consisting of the binary mixture SbCl₃-25 mol % BP(AlCl₄) with relatively small additions of AlCl₃ or BPCl. Pure, molten SbCl₃ is very slightly ionized as shown in Eq. [2] (12).

It is plausible to suppose that the same equilibrium occurs in our low-melting mixtures and is displaced strongly to the left. Likewise, it has been shown that in liquid BPC1-AlCl₃ mixtures at ambient temperatures the AlCl₄ ion is in equilibrium with Al₂Cl₇

and Cl⁻ ions (13). In our ternary mixtures a similar equilibrium must occur as shown in Eq. [3]

$$2A1C1_4 \neq A1_2C1_7 + C1^{-1}(solvated)$$
 [3]

where Cl⁻ is solvated by SbCl₃ molecules. Since Al₂Cl₇⁻ is a much stronger chloride ion acceptor than SbCl₃, the equilibrium in Eq. [3] is strongly displaced to the left. The Al₂Cl₇⁻ anion should also be a stronger chloride ion acceptor than SbCl₂⁺(solvated) so that the equilibrium in Eq. [4]

$$Al_2Cl_7 + SbCl_3 \neq SbCl_2^+(solvated) + 2AlCl_4 [4]$$

should be displaced to the right. This also appears to be the case in SbCl₃-AlCl₃ mixtures at elevated temperatures (12). Thus, when AlCl₃ is added to liquid SbCl₃-BP(AlCl₄), the dominant acidic species should be SbCl₂+(solvated) rather than Al₂Cl₇. On the other hand, BPCl is expected to dissolve in SbCl₃-BPCl to form BP⁺ cations and Cl (solvated) anions with the concomitant suppression of the formation of SbCl₂+(solvated), according to Eq. [2].

In summary, for all of the SbCl₃-AlCl₃-BPCl compositions considered here, the primary consitutents are SbCl₃ molecules, BP⁺ cations and AlCl₄ anions. Secondary constituents are SbCl₂⁺(solvated) and Cl⁻(solvated). When the formal mole ratio AlCl₃:BPCl exceeds unity to a significant degree, the concentration of SbCl₂⁺(solvated) is correspondingly increased while that of Cl⁻(solvated) is greatly suppressed. This situation is reversed when the AlCl₃:BPCl ratio is significantly less than unity. The Al₂Cl₇ anion is probably no more than a minor constituent in all of the ternary melts considered here.

Optical Spectra. — During the decomposition of anthracene the principal species observed by optical spectroscopy are unreacted anthracene and the anthracenium ion. Therefore, for purposes of both identification and quantification the spectra of these species were measured in SbCl₃-AlCl₃-BPCl melts under non-reactive conditions.

Fig. 2 shows the spectrum of a 31.1-mM solution of anthracene in a basic 60:18:22 melt and that of a 9.75-mM solution of 9H-anthracenium heptachlorodialuminate 1 in an acidic 60:22:18 melt. The positions and molar absorptivities of the three maxima in the anthracene spectrum are 347 nm, 4130 M⁻¹ cm⁻¹; 366 nm, 4660 M⁻¹ cm⁻¹; 384 nm, 3830 M⁻¹ cm⁻¹. We attribute these bands to vibronic components of the $l_{La} \leftarrow lA$ electronic transition (14). By comparison we found that the corresponding bands for anthracene in methanol have as coordinates 339 nm, 5447 M⁻¹ cm⁻¹; 356 nm, 8130 M⁻¹ cm⁻¹; 375 nm, 7967 M⁻¹ cm⁻¹. Other bands in this group that we

shall make use of later have maxima at 309 and 323 nm. The vibrational spacing for all 5 bands is close to 0.14 μ m⁻¹. The bands of anthracene in the molten salt are much broader than those of anthracene in methanol so that the band areas and oscillator strengths are more nearly comparable than are the molar absorptivities.

The spectrum of the solution of 1 in Fig. 2 consists of an intense band with maximum at 424 nm and molar absorptivity of 34,500 M⁻¹ cm⁻¹. This is plausibly attributed to the 9H-anthracenium cation 2, the structure of which is shown in the figure. The spectrum of this ion in anhydrous HF at 25°C (15) has a similar band at 408 nm (37,400 M⁻¹ cm⁻¹) while in concentrated H₂SO₄ at 25°C (16) the band maximum is at 424 nm (ca. 30,000 M⁻¹ cm⁻¹).

Spectral data and the results of analysis by hydrolysis and separation show that both the solution of anthracene in the basic melt and that of 1 in the acidic melt are stable. Their spectra remained unchanged after 24 hr. Following hydrolysis of the anthracene solution, the starting material was recovered and no decomposition products were found. Hydrolysis of the solution of 1 resulted principally in the deprotonation of 1 and led to recovery of anthracene equivalent to 85% of the starting material. A similar recovery factor was found when solutions of 1 in SbCl₃-10 mol % AlCl₃ were hydrolyzed by the procedure used here.

Anthracene Decomposition Reaction. — We found that the reactions by which anthracene decomposes in acidic SbCl₃-AlCl₃-BPCl mixtures at 28-40°C are closely related to those that occur in SbCl₃-rich melts at 80-175°C. These elevated-temperature reactions are of two types. First, in SbCl₃-10 mol % AlCl₃, anthracene reacts rapidly and completely with the solvent in a redox process that is schematically illustrated in Eq. [5]* (4). The oxidized product is the 9H-anthracenium ion 2, produced in 55-65% yields. The source of protons for this product is a combination of Scholl-type condensation-dehydrogenation reactions and the reduction of Sb(III). The dominant condensed product is anthra[2,1-a]aceanthrylene 3, produced in yields of ~20 wt % of the starting anthracene. The remaining organic material (~15-25 wt %) consists of a variety of condensed compounds. The accompanying reduction reaction converts Sb(III) into a lower oxidation state, which, when hydrolyzed, disproportionates into Sb metal and Sb(III) (17). Stoichiometry requires that the mole ratio 2:Sb(metal) be 3:1.

The second type of reaction occurs when anthracene is dissolved in SbCl₃ without AlCl₃. This reaction is a relatively slow catalytic hydrogen-transfer with the melt serving as solvent/catalyst (1).

*This equation is at the end, with the figures.

Part of the anthracene is hydrogenated to form mostly 9,10-dihydroanthracene 4^* and the source of hydrogen is Scholl-type condensation-dehydrogenation reactions. A wide variety of condensed products is formed, including 3, but no single product predominates.

In the present study we find that both of the above types of reactions occur simultaneously for anthracene in acidic $SbCl_3-AlCl_3-BPCl$ mixtures at 28-40°C. Evidence regarding the formation of 2 comes from the optical spectroscopic measurements. As noted earlier, this cation is destroyed by hydrolysis so that its presence in the melt cannot be established by quench and separation. The spectra in Fig. 3 are typical of those obtained when ~30 mM anthracene reacts in the acidic melt during a 23-h run at 28-30°C. These spectra are referenced to air and can be converted to absorbance by subtracting the curve labelled <u>solvent</u>. The solvent melt was quite transparent except at the shortest wavelengths so that over most of the wavelength-range in Fig. 3 the apparent absorption of the solvent consists of light losses due to reflections at cell windows.

After 20 min reaction time, the concentration of anthracene fell to $\sim 95\%$ of its starting value of 34.4 mM. A shoulder at ~ 420 nm is attributed to 2 at a concentration estimated to be 1-2 mM. Bands at 510 and 530 nm are due to unidentified reaction products. With increasing time absorption due to anthracene slowly decreased while that due to 2 slowly increased along with bands due to other reaction products at longer wavelengths. At the end of 1380 min (23 h) some anthracene remained but the concentration could not be evaluated accurately because of interference from the band of 2. The concentration of 2 reached ~ 7.5 mM, which is 22% of the initial anthracene concentration.

Identified substances obtained from quench and separation were the following: anthracene (partly unreacted starting material and partly from the hydrolysis of 2); 3; 4; 4 isomers of bianthracene, grouped together here as 5 (2,9'-isomer produced in highest yield); a dihydroanthraaceanthrylene §, (not identified as to isomer); and antimony metal (recovered only for runs at the 150 mM-concentration level). In addition small quantities of unidentified products (usually ~5 wt % of the initial anthracene) were obtained and when the HPLC column was washed with CH₂Cl₂, some highly condensed material came off.

Quench and separation was performed for 8 runs, each terminated after 23 h. Five of these runs were made with 60:22:18 melts at

*Structure displayed at the end, with the figures.

28-30°C and used initial anthracene concentrations of 31, 34, 34, 141 and 157 mM. One run was made with a 60:22:18 melt at 40°C and an initial concentration of 31 mM, while 2 runs were made with slightly more acidic 60:23:17 melts at 28-30°C and initial concentrations of 28 and 139 mM. The only substantial differences in the relative amounts of substances recovered from these runs was between those with initial concentrations of 28-34 mM and those with initial concentrations of 139-157 mM. Table 1 summarizes the 5 runs made with 60:22:18 melts at 28-30°C. In this table the amounts of substances are given as wt % of the initial weight of anthracene. Results for the three runs with initial concentrations of 31, 34 and 34 mM are averaged under the column headed ~30 mM and those with initial concentrations of 141 and 157 mM are averaged under ~150 mM. Typical of deviations about the average values were those for anthracene, namely: 57-67% and 27-30%, respectively. The amounts of anthracenium ion for runs with initial concentrations of ~30 mM were obtained from optical spectra and those for the other runs were calculated from the amounts of Sb metal recovered from quench and separation (moles of anthracenium = $3 \times \text{moles}$ of Sb).

Table 1. Substances recovered from anthracene	
decomposition in liquid SbCl ₃ -AlCl ₃ -BPCl(60:22:18)	
after 23 h at 28-30°C.	

	Amount(wt %)	
Substance	~30 mM	~150 mM
Anthracene Dihydroanthracene 4 Bianthracenes 5 Anthra[2,1-a]aceanthrylene 3 Dihydroanthraaceanthrylene 6 Anthracenium ion 2 Highly condensed material	63 4 11 3 2 20 trace	29 10 11 4 13 14 large

The anthracene recovered from quench and separation consisted of unreacted starting material plus that regenerated from hydrolysis of the anthracenium ion. We estimate a recovery factor of 85% for hydrolysis, hence the amounts of unreacted anthracene were on the order of 43-47% and 15-18% for initial concentrations of ~30 mM and ~150 mM, respectively. Identified products typically accounted for $\sim 80\%$ of the starting material for the former and $\sim 70\%$ for the latter concentration. In both cases an additional amount of material (~5%) consisted of small amounts of various unidentified products observed during chromatography. The highly condensed material accounted for an appreciable part of the remainder in runs with initial concentrations of ~ 150 mM, but very little of this material was found for runs with initial concentrations of ~ 30 mM.

These results show that a part of the hydrogen lost in forming condensed products was consumed in forming hydroarenes while the rest was consumed in protonating anthracene. The same reactions occurred in melts with initial anthracene concentrations of 31-157 mM. At the higher concentrations the conversion of anthracene was greater and relatively less protonated product 2 formed than at the lower initial concentration. Thus, the decomposition of anthracene in acidic SbCl₃-AlCl₃-BPCl melts proceeded by a combination of the same types of reactions found at elevated temperatures in SbCl₃-10 mol % AlCl3 and in SbCl3 alone. It is as though the low-melting mixtures were intermediate in oxidizing power to SbCl3 with and without 10 mol % AlCl3. Further evidence that this is, in fact, the case is provided by the ESR studies described below and the EMF studies in the following paper (7). The reactions in the lowmelting mixtures at 28-40° were very much slower than those at higher temperatures in SbCl3 and SbCl3-10% AlCl3.

ESR Spectra. - The fact that Sb(III) in acidic SbCl₃-AlCl₃-BPCl melts acts as a mild oxidizing agent toward anthracene was established by the recovery of Sb metal. It is interesting, therefore, that we were also able to identify the presence of the anthracene radical cation in these solutions by means of ESR spectroscopy. Dilute solutions (~5 mM) of anthracene in two acidic melts, 60:22:18 and 60:21:19, were examined by ESR at ambient temperatures (22-23°C). In both cases the ESR spectrum of the anthracene radical cation was observed, and the measured proton hyperfine coupling constants ($a_1 = 3.05$, $a_2 = 1.37$, and $a_9 = 6.47$ G) were similar to those measured in SbCl3-8 mol % AlCl3 at elevated temperatures (11). However, these spectra were much less intense than the corresponding anthracene radical cation spectrum observed in SbCl3-8 mol % AlCl3 suggesting that the SbCl3-AlCl3-BPCl melts are weaker oxidants. **ĚМ**Е studies presented in the following paper support this conclusion (7). Thus, the acidic SbCl₃-AlCl₃-BPCl melts can act as oxidants toward anthracene producing radical cations that may be key reactive intermediates in the protonation-condensation reaction as previously proposed for arenes in SbCl3-10 mol % AlCl3 (4).

Anthracene in AlCl₃-BPCl (2:1). - The important role that SbCl₃ played in the anthracene decomposition reactions in acidic SbCl₃-AlCl₃-BPCl melts is emphasized by comparison with the behavior of this solute in a solvent containing only AlCl₃ and BPCl. For this comparison we chose the formal composition AlCl₃-BPCl (2:1), which is, in fact, the liquid compound N-(1-butyl)pyridinium heptachlorodialuminate BPAl₂Cl₇ (13). This is a very strong Lewis acid and if Lewis acidity in combination with such protonic impurities as our melts may contain is sufficient to catalyze the decomposition of anthracene, then the 2:1 melt should be a very active catalyst.

Studies using optical spectroscopy and quench and separation were carried out on a 35-mM solution of anthracene in the 2:1 melt and followed the same general procedures used with acidic SbCl₃-AlCl₃-BPCl melts in so far as possible. The calculation of concentrations was based on the value 1.33 g cm⁻³ for the density of the melt (19). The reaction temperature was 30°C, the time to quench was 24 h, and optical spectra were measured at intervals from 0.5 h to 29 h after mixing and included a spectrum taken at the time of quench.

After quench and separation the only substances found in more than trace amounts were anthracene (78 wt %), 4 (2 wt %) and 5 (6 wt %). No more than a trace of highly condensed material was found when the HPLC column was washed with CH₂Cl₂.

Spectra measured after 0.5 h and 24 h are shown in Fig. 4. These are referenced to air and can be converted to solute absorbance by subtracting the curve labelled <u>solvent</u>. In between 0.5 and 24 h the spectra changed slowly and progressively, never exceeding the extremes shown in the figure. The spectrum measured at 29 h was almost indistinguishable from that measured at 24 h.

The AlCl_3-BPCl solvent melt transmitted further into the ultraviolet than did SbCl_3-AlCl_3-BPCl mixtures so that for the anthracene solution 5 vibronic bands of the $^{1}L_{a} + ^{1}A$ electronic transition were exposed at 312 (sh), 328, 344, 362 and 381 nm with a 0.14 μ m⁻¹ vibrational spacing. These are slightly red shifted with respect to the corresponding bands of anthracene in methanol (see above), and the 344, 362 and 381-nm bands are very close to the corresponding bands for anthracene in SbCl_3-AlCl_3-BPCl. Assuming the concentration of anthracene after 0.5 h to be 35 mM or slightly less, the molar absorptivity of the 362-nm band is calculated to be about 6×10^3 M⁻¹ cm⁻¹. This value is intermediate to those for anthracene in methanol and in SbCl_3-AlCl_3-BPCl, respectively, which is in keeping with the fact that the band widths for anthracene in the 2:1 melt are likewise intermediate.

The only absorption in the 0.5-h spectrum not attributable to anthracene was a band at \sim 420 nm that we attribute to 2. Assuming that the molar absorptivity of 2 has a value similar to that for 2 in SbCl₃-AlCl₃-BPCl, we estimate that its concentration in AlCl₃-BPCl was \sim 1 mM. This small amount of 2 probably came from impurity proton sources. With increasing time the concentration of 2 diminished although a small amount persisted after 24 h.

The only product absorption (other than 2) found after 24 h was a very broad band centered near 640 nm. This does not correspond to either of the major products found on quench and separation; the bands of 4 should lie well out of range in the UV and those of 5 should lie in the same general region as the anthracene bands. The most reasonable source of the 640-nm absorption is a trace of a highly condensed arene in a protonated or oxidized form. Such cations usually have intense absorptions in the visible range and the parent arenes are usually more easily protonated and oxidized than anthracene, 4 or 5.

The long-wavelength absorption bands of bianthracenes in methanol were found to be very similar to those of anthracene in the same solvent. Among other small differences, they were somewhat red shifted. Assuming that a similar state of affairs holds in the 2:1 melt, the absorption in the 300-400 nm region of the spectrum after 24 h was what one would expect for a mixture of anthracene and 5 in the ratio found on quench and separation with an anthracene concentration reduced to roughly 80% of its initial value.

Thus we find that the 2:1 melt, unlike the acidic $SbCl_3-AlCl_3-BPCl$ melt, did not promote the oxidative protonation of anthracene to an appreciable extent. It did catalyze the Scholl condensation-dehydrogenation reaction (to form 5) accompanied by a partial hydrogenation of the substrate (to form 4), but even for these reactions the 2:1 melt was not nearly as active a catalyst as the less acidic melts containing $SbCl_3$.

Effects of Impurities. — Because of the low concentration of anthracene used in the spectrometric studies, we found it necessary to pay close attention to the effects of impurities. Thus, it was not until water and ethylacetate were identified and eliminated as impurities in BPC1 that we obtained consistently reproducible results. Since BPC1 is a widely used constituent in low-melting salt mixtures and since studies of the spectroscopy and electrochemistry of solutes in these melts is commonly done at low concentrations, we describe what we learned about impurity effects.

We found that when BPCl was dried by a less rigorous procedure than that described above and then used to prepare acidic SbCl₃-AlCl₃-BPCl melts, solute anthracene was protonated at a much faster rate and the concentration of 2 reached a much higher level than it did in the reactions described above. When BPCl was dried under vacuum over P₂O₅ at 110°C for progressively longer times, the amounts of 2 diminished. The concentration level for promptly formed 2 achieved after prolonged drying was about 1-2 mM and this we attribute to impurities (not necessarily water).

In the literature procedure (8) for the preparation of BPC1, ethylacetate is used as a cosolvent along with acetonitrile in the

recrystallization of the product. In our initial experiments, which followed this procedure, an unknown product was observed in 16% yield from the reaction in an acidic room temperature melt containing 11 mM anthracene. This product was identified by GC-MS as three isomeric ethylanthracenes. The ethyl group could not have come from the fragmentation of anthracene since no other fragments of the parent arene were found. It is well known (18) that esters will alkylate arenes in organic solvents with a Lewis acid present as catalyst. Analysis of the BPC1 showed that the small ethylacetate content of the sample could account for all of the ethylanthracene found in the reaction of anthracene in the acidic SbCl₃-AlCl₃-BPCl mixture. Vacuum drying of the BPCl crystals resulted in a decrease in the ethylacetate content and thus in the yield of ethylanthracene. However, traces of ethylacetate remained even after a week of drying. To determine whether the presence of ethylacetate and thus ethylanthracene would significantly effect our results, the reaction of 2-ethylanthracene was followed spectroscopically in the acidic, room temperature melts under the same conditions utilized for the reaction of anthracene. Protonated ethylanthracene was formed and found to absorb at 424 nm (the same wavelength observed for the anthracenium ion). In addition ethylanthracene reacted more rapidly than anthracene, probably because ethylanthracene is more easily oxidized and protonated than anthracene. Since the presence of ethylanthracene would obviously interfere with the investigation of the anthracene reaction, all subsequent purifications of BPC1 excluded the use of ethylacetate.

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REFERENCES

- 1. A. S. Dworkin, M. L. Poutsma, J. Brynestad, L. L. Brown, L. O. Gilpatrick, and G. P. Smith, J. Am. Chem. Soc. 101, 5299 (1979).
- A. C. Buchanan, III, A. S. Dworkin, G. P. Smith, M. V. 2.
- Buchanan, and G. Olerich, <u>Fuel</u> 60, 694 (1981).
 A. C. Buchanan, III, A. S. Dworkin, and G. P. Smith, <u>J. Org.</u> <u>Chem.</u> 47, 603 (1982).
 A. C. Buchanan, III, A. S. Dworkin, and G. P. Smith, <u>J. Am.</u> <u>Chem. Soc.</u> 102, 5262 (1980).
 A. C. Buchanan, III, A. S. Dworkin, and G. P. Smith, <u>J. Org.</u> <u>Chem. 46</u>, 471 (1981). 3.
- 4.
- 5. Chem. 46, 471 (1981).
- C. Nanjundiah, K. Smimizu, and R. A. Osteryoung, J. 6. Electrochem. Soc. 129, 2474 (1982). D. M. Chapman, M. Sørlie, G. P. Smith, C. Petrovic, and G.
- 7. Mamantov, "Electrochemical Properties of the Solvent SbCl₃-AlCl₃-N-(1-butyl)pyridinium Chloride and Electrochemical and Spectroelectrochemical Studies of the Solute 9,10-Dimethylanthracene," This Symposium.
- J. Robinson and R. A. Osteryoung, J. Am. Chem. Soc. 101, 323 8. (1979)
- V. A. Koptyug, J. S. Isaev, and A. I. Rezvukhin, Tetrahedron 9.
- 10.
- V. A. Roping, C. C. Link, J. Livingston, A. S. Dworkin, and G. P. Smith, J. Phys. Chem. 84, 423 (1980).
 C. Petrovic, G. Mamantov, M. Sorlie, M. H. Lietzke, and C. Petrovic, I. Phys. Chem. 86, 4598 (1982). 11.
- 12. G. P. Smith, <u>J. Phys. Chem.</u> <u>86</u>, 4598 (1982).
 J. Schoebrechts and B. Gilbert, <u>J. Electrochem.</u> <u>Soc</u>. <u>128</u>, 2679
- 13. (1981).
- 14. H. B. Klevens and J. R. Platt, <u>J. Chem. Phys</u>. <u>17</u>, 470 (1949).
- G. Dallinga, E. L. Makor, and A. A. Verrijn Stuart, Mol. Phys. 15. 1, 123 (1958).
- V. Gold and F. L. Tye, <u>J. Chem. Soc</u>. 2172 (1952). 16.
- M. Sørlie and G. P. Smith, J. Inorg. Nucl. Chem. 43, 931 17. (1981).
- 18. G. A. Olah, in "Friedel-Crafts and Related Reactions", G. A. Olah, Ed., Interscience, New York, 1963, Vol. 1, p. 49.
- J. Robinson, R. C. Bugle, D. Koran, and R. A. Osteryoung, J. 19. Am. Chem. Soc. 101, 3776 (1979).











Fig. 1. Optical cell. A, Pyrex glass rod with hook; B, threaded Teflon bushing; C, threaded Pyrex glass joint; D, FETFE O-ring; E, quartz glass insert; F, quartz glass optical cell.



Fig. 2. Spectra of anthracene and the 9H-anthracenium ion in SbCl₃-AlCl₃-BPC1 melts with compositions of 60:18:22 and 60:22:18, respectively.





Fig. 4. Spectra measured during the decomposition of anthracene in an AlCl₃-BPCl (2:1) melt at 30°C together with the spectrum of the solvent. All spectra referenced against air.

KINETICS OF ORGANIC SUBSTITUTION REACTIONS IN MOLTEN ACETATE AND THIOCYANATE SALTS

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Methyl 3,5-dihydroxybenzoate, like many polyhydroxy compounds, is soluble in molten potassium thiocyanate and in the eutectic $Na^+K^+SCN^-$, and reacts by nucleophilic attack of thiocyanate ion on the methyl group. The rate of this solvolysis for the ethyl ester is only 0.02 times that of the methyl at $150^{\circ}C$. Methyl 2,4-dihydroxybenzoate decarboxylates subsequently to displacement but the kinetics show no catalysis by the neighboring hydroxyl group.

Alkyl p-hydroxybenzoates undergo similar nucleophilic displacements in molten acetates such as Li⁺,Na⁺,K⁺OAc⁻. In contrast to the thiocyanate melt, the fused acetate is basic as well as nucleophilic. In this medium at 181-250°C, methyl, ethyl, propyl, isopropyl, 2-butyl and neopentyl p-hydroxybenzoates show the progressively decreasing rates typical of SN2 reactions. The 2-butyl ester undergoes elimination as well as displacement; optically active substrate is 58% inverted, 42% racemized. Neopentyl p-hydroxybenzoate yields neopentyl acetate without rearrangement.

The rate of isomerization of phenylammonium thiocyanate has been determined over the entire concentration range, from dilute solution to fused thiocyanate eutectic.

Nucleophilic substitutions comprise a class of reactions very important in, though not limited to, organic chemistry. In the general case (1) and the example (2), the nucleophile X and the leaving group Y are bases:

$X: + R-Y \rightarrow R-X + Y$	(1)
OH ⁻ + CH ₃ C1 → CH ₃ OH + C1 ⁻	(2)

Thiocyanate ion is a more reactive nucleophile than hydroxide (3). Potassium thiocyanate moreover is a low-melting salt (mp 177° C). These facts suggested to us the possibility of carrying out nucleophilic displacement reactions in molten KSCN at temperatures compatible with organic substrates. Heterogeneous reactions of the the vapor of simple alkyl halides bubbled through such melts had already been noted (4). This paper reports results obtained with homogeneous solutions in fused thiocyanate salts and extension of the research to fused Group I acetates.

Molten Sodium-Potassium Thiocyanate

The working temperature was lowered by making use of the binary eutectic (5) Na⁺,K⁺SCN⁻, 25-75%, mp 133⁰ which we designate M⁺SCN⁻. Most substrates for conventional substitution reactions in common organic solvents--alkyl halides, for example--are insoluble in this ionic, aprotic liquid. We found, however, that compounds having at least two hydroxyl groups per molecule for hydrogen bonding to thio-cyanate ion were generally soluble in M⁺SCN⁻, just as in ammonium nitrate melts (6). Ethylene glycol, pentaerythritol, hydroquinone and glucose are all quite soluble, for example (7). Some monohydroxy compounds such as water, methanol and benzoic acid are very soluble while higher alcohols and phenols are not. Although quantitative acid-base studies are precluded by the instability of HSCN, simple indicator experiments show that the hydroxyl groups of the soluble alcohols are unionized in the fused salt. The NMR spectrum of pentaerythritol in M⁻SCN⁻ at 150°C shows singlets for CH₂ and OH separated by 0.4 ppm at 60 MHZ. The freezing point-composition curve of the hydroquinone (mp 171°C)-KSCN (mp 177°C) system shows a minimum, 140°C at about 60 mol % hydroquinone, and complete miscibility above 177°C (7).

In a search for suitable substrates, sodium chloroacetate proved insoluble in anhydrous M^+SCN^- (8) and 1-chloro-2,3-propanediol underwent undesirable cyclizations. Alkyl dihydroxybenzoates, however, were soluble and reacted at a convenient rate at 140-160°C, by attack of thiocyanate ion on the α -carbon atom of the alkyl group (9):



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Though recognized early by Ingold (10) as a possible mechanism of hydrolysis, nucleophilic attack at this position is atypical of esters and occurs only when carbonyl attack is impossible. In one striking demonstration, methyl benzoate with sodium methoxide slowly yielded dimethyl ether (11):

$$C_{H_{S}}COOCH_{3} + CH_{3}O^{-} \rightarrow C_{H_{S}}COO^{-} + CH_{3}OCH_{3}$$

In our case, the affinity of thiocyanate ion for Sp^3 carbon is apparently much higher than for Sp^2 .

The kinetics of reaction 3 were followed by trapping the volatile products, methyl thiocyanate and methyl isothiocyanate. (One of the few convenient properties of molten salts is low volatility.) An air pressure of 20 Torr was maintained in the vacuum system to prevent volatilization of the substrate S_1 . The products were redistilled through calcium chloride and weighed. Since methyl 2,4-dihydroxy-benzoate (S_2) undergoes decarboxylation as in equation 4, this reaction could easily be followed by measuring the volume of carbon dioxide evolved. But unlike the first-order reaction of S_1 , the substrate S_2 proceeded only 50% to completion with kinetics according to equation 5:

$$1/2 \ln \frac{a}{a-2x} = kt$$
 (5)

This observation is consistent with the fact that resorcinol distils out of the solution, leaving S_2 as an unreactive and probably insoluble anion, effectively removing one mol of S_2 for each mole undergoing displacement.

The rate constants for reactions 3 and 4 at $150.5^{\circ}C$ are respectively 3.2 x 10° S⁻¹ and 4.7 x $10^{\circ}5$ S⁻¹. The fact that the 2,4-dihydroxy ester reacts more slowly than the 3,5 shows that acid catalysis by the hydroxyl group adjoining the reaction center is absent. It also strongly suggests that decarboxylation occurs subsequently to displacement rather than concurrently, since extra driving force (or lowering of free energy of activation) of concerted fragmentation reactions is usual.

Further evidence for non-participation of the ortho hydroxy group in S₂ is the lack of any appreciable kinetic_isotope effect when both OH groups were replaced by OD ($k = 4.8 \times 10^{-5} \text{ s}^{-1}$).

The product from both substrates was 96% CH₃SCN and 4% CH₃NCS, C-S bond formation predominating as in SN2 reactions at room temperature. Ethyl 3,5-dihydroxybenzoate is 1/50as reactive as the methyl ester S₁. This is typical of bimolecular displacements. Nearly 50% of the product is C₂H₅NCS, an unexpected result indicating some ionic character in the transition state or some other structural effect on its interaction with the nucleophilic solvent. Esters higher than ethyl are not sufficiently soluble in M^+SCN^- for further studies of the effect of structure on reactivity.

Molten Lithium-Sodium-Potassium Acetate

The second fused salt used as a solvent was a eutectic (M^+OAc^-) of three Group I acetates: Li',Na',K'/OAc' (32, 30, 38 mol %) mp 162°C (12). Like the MSCN melt discussed above, M^+OAc^- dissolves organic alcohols and phenols, which however include many monohydroxy compounds. The acetate melt is much more basic than the thiocyanate, as expected from the 10^7 -fold greater basicity of acetate compared with thiocyanate ion in aqueous solution at 25°C. 2,4-dinitroaniline (pK_a 15.00) but not p-nitroaniline (pK_a 18.37) is ionized to ArNH⁻ in M^+OAc^- at 200°C (13).

Acetic acid is soluble in the fused salt; its tendency to associate with the solvent anion to form the hydrogen-bonded species $CH_3COO^-\ldots.HOOCCH_3$ ("homoconjugation") (14) is shown by large deviations of the vapor pressure of the solutions from ideality (15). The presence of acetic acid is required for ready solubility of phenoxides and certain carboxylates such as sodium benzoate, which are likely associated with the acid molecules. The fused salt, M⁺OAc⁻, if it could be freed initially of all traces of water and acetic acid, would seem to be an aprotic solvent though the observed exchange of alpha hydrogen atoms between acetate ions shows that this is not strictly true (13). Clearly, however, the presence of ionized phenols in all our experiments and of acetic acid itself in most, introduced the possibility of acid-base interactions and catalysis in our reactions.

The nucleophilic displacements we chose to study in the acetate melt were analogous to reactions 3 and 4, but since alkyl p-hydroxybenzoates were soluble, it was unnecessary to employ dihydroxy compounds:

 $CH_{3}COO^{-} + C_{2}H_{5}OCOC_{6}H_{4}O^{-} + CH_{3}COOH$ S_{3}^{-} (6) $\rightarrow CH_{3}COOC_{2}H_{5} + CO_{2} + C_{6}H_{5}O^{-} + CH_{3}COO^{-}$

The above example shows the attack of acetate ion on the ethyl group of ethyl p-hydroxybenzoate to give ethyl acetate. The substrate and the phenol formed by decarboxylation are both ionized and hydrogenbonded to acetic acid. p-Hydroxybenzoic acid, like 2,4-dihydroxybenzoic acid (eq. 4) is known to decarboxylate at this temperature; the ring position vacated by carbon dioxide is filled by a proton from acetic acid, if available, or from another substrate molecule. In all kinetic studies, a constant concentration of acetic acid was maintained in the M⁺OAc⁻ solvent, by saturating a stream of nitrogen with acetic acid at 24° C and passing it through the molten salt. The gas served to sweep out carbon dioxide into absorption tubes for following the kinetics.

Reactions were first order in the substrate ester under these conditions, while in the absence of added acetic acid, equation 5 described the kinetics. These observations might be explained by the necessity of one mol of acetic acid in the melt to solvate the phenoxide ion, S_3^- . If the acid is consumed as it donates a proton in the decarboxylation, S_3^- is insoluble and is effectively removed analogously to the removal of the unionized substrates S_1 and S_2 , used in the molten salt M⁺SCN⁻.

In one experiment, however, acetic acid vapor was introduced only after the reaction had proceeded 36% to completion and the plot of ln a/(a-x) vs time had begun to taper off. The presence of acetic acid then caused the reaction to accelerate to a rate higher than normal, the last point falling on the linear plot expected in the presence of acetic acid. This "catching up" would not have been caused by the redissolving of S₃⁻ temporarily removed from solution; it suggests the accumulation of an intermediate such as the primary displacement product $^{-}OC_{6}H_{4}COO^{-}$ which cannot decarboxylate in the absence of a proton donor.

The rate constants (15) for reaction of several alkyl p-hydroxy-benzoates in M^+OAc^- at $200^{\rm O}C$ are shown in Table I.

M'OAc-	at 200°Cª		• •	
R	k,s ⁻¹	no. of runs	av dev, %	k calcd 25°CC
снз	9.5 x 10 ⁻⁵	3	0.8	30
сн _з сн ₂	1.65 x 10 ⁻⁵	2	0.6	(1)
CH3CH2CH2	8.1 x 10 ⁻⁶	2	1.8	0.4
(CH ₃); ₂ CH	4.8 x 10 ⁻⁶	2	3.3	0.025
сн ₃ сн ₂ (сн ₃)сн	2.63 x 10 ⁻⁶	2		
CH3	9.1 x 10 ⁻⁵	۱p		

Table I. Rate Constants for Reaction of $p-HOC_6H_4COOR$ with Molten

^aContaining CH₃COOH from nitrogen stream saturated at 24^oC.

^bNitrogen stream saturated with CH₃COOD.

^CRelative to the ethyl ester.

The decrease in rate with increasing α or β substitution at the reaction center is again characteristic of SN2 reactions.

An Arrhenius plot for the methyl ester over the temperature range $181-220^{\circ}$ C is given by k(S⁻¹) = $1.49 \times 105e^{-19900/RT}$. Using this activation energy for methyl and adding average increments for the other groups in displacement reactions (16) we calculated the hypothetical relative rates at 25° C shown in the last column of Table I which are more closely comparable with known reactions than the 200° data.

We used two additional experimental probes which are obligatory in the study of nucleophilic solvolytic reactions. The first was to employ an optically active substrate, 2-butyl p-hydroxybenzoate, the fifth entry in Table I. The product was 58% inverted, 42% racemized 2-butyl acetate. A one-step bimolecular displacement would cause 100% inversion, but our result is more typical of solvolytic reactions of secondary substrates.

The second experimental variation was to introduce a second nucleophile into the solvent to determine the effect of its concentration on the rate and product composition. Potassium thiocyanate, which is miscible with the molten acetate, M^+OAc^- , indeed accelerated the displacement in concentrations up to 4M or about 25 mol per cent. The acceleration moreover appeared to be greater than would be expected on the basis of the thiocyanate consumed; in other words, thiocyanate ion not only reacted to form RSCN but catalyzed the formation of ROAc. While this suggests an ion-pair intermediate, such a postulate should be supported by correlation of the product ratio with the rates.

One further classical experiment was carried out in the molten salt M^+OAc^- . Neopentyl p-hydroxybenzoate (R = $(CH_3)_3CCH_2$ -) was used as the substrate in eq. 6. If the reaction proceeded via a free neopentyl cation in this ionic, high-temperature medium, the rearranged product, 2-methyl-2-butyl acetate would be expected. Only the unrearranged product, neopentyl acetate, was obtained, proof that the alkyl group does not exist as a carbonium ion and confirmation of the proposed SN2 mechanism.

From Dilute Solution to Fused Salt

One of the original goals of this research was to determine the rate of an organic reaction as a function of ionic strength "from dilute solution to fused salt (17)." We now report the first such study, utilizing the Wöhler isomerization of anilinium thiocyanate to phenyl thiourea in M^+SCN^- :

$$C_6H_5NH_3^+ + SCN^- \rightarrow C_6H_5NHCSNH_2$$

The reaction was followed by acid-base titration. Anilinium chloride was used in the aqueous solutions, with increasing concentrations of sodium and/or potassium thiocyanate. In molten M^+SCN^- , anilinium thiocyanate was used as the substrate. This compound, prepared by precipitating potassium chloride from anilinium chloride and potassium thiocyanate in absolute ethanol, was more soluble in M⁺SCN⁻ than was anilinium chloride.

Figure 1 is a plot of log k (second-order) vs (ionic strength) $^{1/2}$ at 106^OC. The Debye-Hückel limiting slope for the cation-anion reaction is shown by the dotted line. The increase in rate constant with ionic strength at higher concentrations may be related to the decreasing dielectric constant of the medium: the triangle shows the similar effect of ethanol.

At 138° C, just above the melting point of the molten salt eutectic, the reaction was too fast to obtain accurate rate constants; values of k_2 ranged from 1.1 x 10⁻³ to 2.6 x 10⁻³ 1/mol-s for the rearrangement in molten M⁺SCN⁻, which is 17 M. A series of rate measurements with 15.2 M solutions was made at 100°C, 106°C and 113°C, giving an Arrhenius plot from which an extrapolated value of 1.0 x 10^{-3} 1/mol-s was calculated for $138^{\circ}C$. We conclude that the increase in k from 15.2 M solution to the molten salt is probably not more than about 2 to 3-fold.

References

- (1) University of Virginia.
- (2) Pennsylvania State University.
- (3) C. G. Swain and C. B. Scott, J. Am. Chem. Soc., 75, 141 (153).
- D. L. Packham and F. A. Rackley, <u>Chem. Ind. (London)</u>, 899 (1966).
 J. B. Wrzenewsky, <u>Z. Anorg. Chem.</u>, <u>74</u>, 99 (1912).
 O. K. Khaishbasher, <u>Bull. Acad. Sci. URSS</u>, <u>Cl. Sci. Chim.</u>, (4)
- (5)
- (6)587 (1945).
- T. I. Crowell and P. Hillery, <u>J. Org. Chem.</u>, <u>30</u>, 1339 (1965). T. I. Crowell, J. L. Hicks and C. C. Lai, <u>J. Phys. Chem</u>., <u>70</u>, (7)(8)
- 2116 (1966).
- E. W. Thomas and T. I. Crowell, <u>J. Org. Chem</u>., <u>37</u>, 744 (1972). (9)
- C. K. Ingold, "Structure and Mechanism in Organic Chemistry, (10)2nd ed, Cornell University Press, Ithaca, N. Y., 1969, p. 1142.
- (11)J. F. Bunnett, M. M. Robison and F. C. Pennington, J. Am. Chem. <u>Soc</u>., 72, 2378 (1950). E. I. Pochtakova, <u>Russ. J. Inorg. Chem. (Engl. Transl.), 10</u>,
- (12)1268 (1965).
- (13)T. I. Crowell and L. L. Burton, J. Am. Chem. Soc., 90, 5940 (1968).
- Hammett, L. P., "Physical Organic Chemistry,"2nd ed, McGraw-Hill, (14)New York, N. Y., 1970, p. 229.
- E. H. Braue, Jr., V. T. Alexander, L. L. Burton, T. I. Crowell and C. P. Devlin, <u>J. Am. Chem. Soc</u>., <u>101</u>, 5303 (1979). (15)

 (16) A. Streitwieser, Jr., <u>Chem. Rev.</u>, <u>56</u>, 571 (1956).
 (17) C. A. Kraus, <u>J. Phys. Chem.</u>, <u>58</u>, 673 (1954); K. S. Pitzer, <u>J.</u> <u>Am. Chem. Soc</u>., <u>102</u>, 2902 (1980).





REACTIONS OF ETHANE, CHLOROETHANE, AND CHLOROETHENE WITH CHLORINE IN MOLTEN SALTS

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Reactions of chlorine with C_2H_6 , C_2H_5Cl , or C_2H_3Cl were studied in a molten salt bath of LiCl-KCl eutectic or CuCl₂-KCl mixtures. The variables in the experiments were Cl_2 /organic feed composition, molten salt composition, and bath temperature. The analysis of the product gases showed chlorinated ethanes and ethenes as well as ethene and ethyne.

Mass balance calculations have been performed. When C_2H_3Cl became an important species, data showed a decrease in amount of chlorinated products believed to be caused by polymer formation. The extent of chlorination correlated very well with the amount of Cl_2 in the reactant mixture and with the pressure of Cl_2 from the presence of $CuCl_2$ in the melts.

The experimental results were analyzed for the fractional achievement of chemical equilibrium. The equilibrium between cis- and trans- $1,2-C_2H_2Cl_2$ was well established in all melts. In the case of other isomer equilibria, the amounts of 1,1 substitution products were favored to those of 1,2 substitution products. However, melts containing CuCl₂ catalyzed the species associated with 1,2 substitution reactions.

INTRODUCTION

Reactions of organic species in molten salts have been reviewed by Kenney(1). Reactions of hydrocarbons with chlorine have many practical applications. Large amounts of chloroethene are manufactured for the production of polymers. Chloroethene can be made by addition of HCl to ethyne or by chlorine addition to ethene followed by a dehydrochlorination reaction. Both of these reactions have the disadvantage of using expensive reactants. The Lummus Corp. has patented the Transcat process in which ethane or ethene are reacted with chlorine and oxygen in the presence of a molten salt of KCl, $CuCl_2$, and CuCl. Kenney(l) points out that several reactions are occurring at the same time. Three distinct steps are postulated: (l) chlorination of organic feed, (2) catalyst regeneration, and (3) dehydrochlorination.

Reactions of chlorine with ethane, chloroethane, and chloroethene have been performed with molten salt baths of LiCl-KCl eutectic and KCl-CuCl₂ mixtures. The reactions have been performed in a batch process using a bubble reactor at temperatures <u>ca</u>. 400°C. Multiple products have been observed including chlorinated ethanes and ethenes, ethene, and ethyne. The detailed results can be found in a paper by Sørlie, Wahlbeck, and øye(2). Experimental data are given in Figure 1. A summary of the results are given as:

1) With increasing chlorine in the gaseous reactant mixture, more chlorinated products both in quantity and in the number of chlorine atoms added to the organic molecules occurred, and the amount of unsaturated products increased.

2) With the LiCl-KCl eutectic molten salt bath, if no chlorine was in the reactant mixture, no reaction was observed.

3) With $CuCl_2$ as a component of the molten bath, if no chlorine was present in the reactant mixture, the bath would provide chlorine for the chlorination reaction.

4) An increase in the activity of chlorine in the salt bath increased the extent of the production of chlorinated and unsaturated compounds.

5) With the LiCl-KCl eutectic molten salt bath, a change in temperature did not change the product distribution by a large amount.

6) With $CuCl_2$ as a component of the molten salt bath, chlorination increased with increasing temperature.

7) No carbon-carbon bond breakage or formation was observed from detected species (the only products which were observed were C_2 molecules). A small amount of polymeric species may have occurred in some experiments in which the concentration of C_2H_3Cl was large.

ANALYSIS OF THE RESULTS

The data from the chlorination experiments were product distributions as a function of reactant composition, bath composition, and bath temperature. Time was not a variable in the experiments, and chemical kinetic data were not available from these results.

The following model for the reaction was considered. The bubble containing the reactants is a sphere with constant radius where the boundary is the molten salt. The chemical reaction occurs on the molten salt surface. In the case of baths containing $CuCl_2$, the bath may be a source of chlorine. The reaction occurs until the bubble bursts

at the surface of the molten salt bath at which time the reactants and products are diluted with helium.

The reactants and products observed in these experiments consists of 16 species. It would be possible to calculate the amounts of these species if one assumed that chemical equilibrium existed among the species. Thirteen chemical equilibria and three mass balance equations would be required for these calculations. They are:

$C_{2}H_{6} + Cl_{2} = C_{2}H_{5}Cl + HCl$	(1)
$C_2H_5C1 + C1_2 = 1, 1-C_2H_4C1_2 + HC1$	(2)
$C_2H_5C1 + Cl_2 = 1,2-C_2H_4Cl_2 + HC1$	(3)
$1,1-c_2H_4Cl_2 + Cl_2 = 1,1,1-c_2H_3Cl_3 + HCl$	(4)
$1,1-C_2H_4Cl_2 + Cl_2 = 1,1,2-C_2H_3Cl_3 + HCl$	(5)
$C_2H_4 + Cl_2 = C_2H_3C1 + HC1$	(6)
$C_2H_3C1 + Cl_2 = 1, 1-C_2H_2Cl_2 + HC1$	(7)
$C_{2}H_{3}C1 + Cl_{2} = cis-1, 2-C_{2}H_{2}Cl_{2} + HC1$	(8)
$C_{2H_{3}Cl} + Cl_{2} = trans - 1, 2 - C_{2H_{2}Cl_{2}} + HCl$	(9)
$1, 1-c_2H_2Cl_2 + Cl_2 = c_2HCl_3 + HCl$	(10)
$C_2H_2 + H_2 = C_2H_4$	(11)
$C_2H_4 + H_2 = C_2H_6$	(12)
$H_2 + Cl_2 = 2$ HCl	(13)

and mass balance equations for C, H, and Cl. The mass balance equation for Cl is

$$\begin{split} \text{N<Cl>(excess)} &= \text{N<Cl>(reactants)} + \text{Y} \text{N<C}_{2}\text{H}_{6}^{>} - (2-\text{Y}) \text{N<C}_{2}\text{H}_{5}\text{Cl>} \\ &- (4-\text{Y}) \text{N<l}, 1-\text{C}_{2}\text{H}_{4}\text{Cl}_{2}^{>} - (4-\text{Y}) \text{N<l}, 2-\text{C}_{2}\text{H}_{4}\text{Cl}_{2}^{>} \\ &- (6-\text{Y}) \text{N<l}, 1, 1-\text{C}_{2}\text{H}_{3}\text{Cl}_{3}^{>} - (6-\text{Y}) \text{N<l}, 1, 2-\text{C}_{2}\text{H}_{3}\text{Cl}_{3}^{>} \\ &- (4-\text{Y}) \text{N<C}_{2}\text{H}_{3}\text{Cl>} - (6-\text{Y}) \text{N<l}, 1, 2-\text{C}_{2}\text{H}_{3}\text{Cl}_{3}^{>} \\ &- (4-\text{Y}) \text{N<C}_{2}\text{H}_{3}\text{Cl>} - (6-\text{Y}) \text{N<l}, 1, 1-\text{C}_{2}\text{H}_{2}\text{Cl}_{2}^{>} \\ &- (6-\text{Y}) \text{N<C}_{2}\text{H}_{3}\text{Cl>} - (6-\text{Y}) \text{N<l}, 1-\text{C}_{2}\text{H}_{2}\text{Cl}_{2}^{>} \\ &- (6-\text{Y}) \text{N<c}_{1}, 2-\text{C}_{2}\text{H}_{2}\text{Cl}_{2}^{>} - (6-\text{Y}) \text{N<trans-1}, 2-\text{C}_{2}\text{H}_{2}\text{Cl}_{2}^{>} \\ &- (8-\text{Y}) \text{N<C}_{2}\text{HCl}_{3}^{>} - (2-\text{Y}) \text{N<C}_{2}\text{H}_{4}^{>} - (4-\text{Y}) \text{N<C}_{2}\text{H}_{2}^{>} , \end{split}$$

where Y = 0 for C_2H_6 as a reactant, Y = 2 for C_2H_5Cl , and Y = 4 for C_2H_3Cl . The chemical analysis procedures require a mass balance on C. Since Cl_2 and HCl are not directly determined in the experiment, HCl is calculated by assuming a H balance. The chemical reactions (1) through (10) are written conveniently as isomolecular reactions in which Cl_2 is a reactant and HCl is a product. Equilibrium constants for these reactions have been calculated from thermodynamic data given by Stull et al.(3,4) and by Zwolinski et al.(5).

MASS BALANCE CONSIDERATIONS

Calculations of the mass balance of chlorine by adding together the amounts of Cl in products and the Cl in HCl (calculated by using a balance on H) gave results which are plotted in Figure 2.

The upper three curves on Figure 2 are for experiments using LiCl-KCl eutectic baths with the reactants being chlorine with $C_{2}H_{6}$, $C_{2}H_{5}Cl$, and $C_{2}H_{3}Cl$. These data all pass through the origin of the plot showing that if no chlorine is in the reactant gas mixture no chemical reactions occur. In all cases with Cl_{2} in the reactant mixture, not all Cl_{2} reacts, but an excess of Cl_{2} is noted through the mass balance. Chlorine and HCl will not dissolve in the LiCl-KCl bath(6). Thus, the bubbles breaking at the surface have Cl_{2} , HCl, and organic species present.

The lower two curves on Figure 2 are for experiments using baths containing $CuCl_2$ with the reactants being chlorine and C_2H_6 . These data indicate that even with no Cl_2 in the reactant mixture chlorination reactions are occurring. The source of Cl_2 is the molten salt bath. For cases in which excess chlorine is negative, chlorine is being removed from the molten salt bath. At the reactant composition at which excess Cl goes through zero, the reactant mixture is such that all Cl_2 in the reactant mixture is consumed. However, since Cl_2 is not being directly measured, Cl_2 may be lost from the molten salt bath.

The intercepts on Figure 2 show a correlation with the equilibrium pressure of Cl_2 associated with the salt bath. The pressure of Cl_2 is a function of salt bath composition and temperature. Correlation of the intercepts with these two variables are shown in Figures 3 and 4 using equilibrium pressure of Cl_2 data by Sørlie and Øye(7). This correlation shows that the baths containing $CuCl_2$ provided a source of Cl_2 .

CHEMICAL EQUILIBRIUM

Does chemical equilibrium occur within these small bubbles? Calculations were performed using the SOLGASMIX(8-10) computer program. This program used a data base for possible organic species through C_{12} including many of the possible chlorinated species. Up to 15 reactants at a specified temperature and pressure may be entered. Equilibrium concentrations are computed. In the case of reactants being C_{2H_6} and Cl_2 at the experimental temperature and pressure, SOLGASMIX indicates that the products should be C(s) and HCl(g). These products are in agreement with observations when C_{2H_6} and Cl_2 are placed in light in which the products are noted to be "soot" and "vapor". The reaction occurring in light is believed to use a free radical mechanism. Thus, chemical equilibrium was not observed since the number
of C atoms was not changed in the data for products.

Does chemical equilibrium exist among any of the species in the reaction? The following equilibria among isomers are considered:

$1,1-C_{2}H_{4}Cl_{2} = 1,2-C_{2}H_{4}Cl_{2}$	(15)
$1,1,1-C_2H_3C_3 = 1,1,2-C_2H_3C_3$	(16)
$1, 1-C_2H_2C_2 = cis-1, 2-C_2H_2C_2$	(17)
$1, 1-C_{2}H_{2}Cl_{2} = trans - 1, 2-C_{2}H_{2}Cl_{2}$	(18)
$cis-1, 2-C_2H_2Cl_2 = trans-1, 2-C_2H_2Cl_2$	(19)

In Figure 5 are plotted the ratios of K coefficient to K equil, where K coefficient is the ratio of experimental quantities like those of the equilibrium constant. From these data, reaction (19) was noted to be always in equilibrium. Whatever mechanism is producing $1,2-C_{,H_2}Cl_2$ was occurring such that the cis and trans isomers were in equilibrium. The points which are plotted in Figure 5 are averages over data using differing amounts of Cl_2 as a reactant. No strong dependence on amount of Cl_2 was noted in the data. The upturn in K coeff/K equil as the amount of $CuCl_2$ increased in the bath shows that the bath was providing catalytic activity for the reactions also. As the $CuCl_2$ content increased, reactions (15) to (18) proceeded closer to chemical equilibrium.

The reactions proceeded such that 1,1 substitution reactions occurred preferentially to 1,2 substitution reactions as shown by the data for the isomer reactions (15) to (19).

The fractional achievement of chemical equilibrium for reactions (1) through (11) may be evaluated. Since these reactions are all written with Cl_2 as a reactant and HCl as a product, one may compute

$$x[C1_2]/x[HC1] = 1/K \{ x_{product} / x_{reactant} \}.$$
 (20)

Since Cl₂ and HCl are both present in the gas bubbles, the experimental ratio should be close to unity. Data for the above ratios are plotted in Figure 6 for LiCl-KCl eutectic melts and in Figure 7 for CuCl₂ containing baths with no Cl₂ present in the reactant mixture. The figures show that reactions (2) and (4) are closer to equilibrium, and these reactions are ones in which 1,1 substitution reactions occur. Reactions (1), (3), (5), and (6) are grouped together on these figures--this set of reactions contains the 1,2 substitution reactions.

MECHANISM

A free radical mechanism occurs when the reactant mixture is placed in light. This produces C(s) and HCl(g) as products. Since a free radical mechanism is a chain reaction mechanism, the probability that a free radical mechanism is occurring is low.

The reaction mechanism involves reaction steps which are chlorine addition reactions and dehydrochlorination reactions. Products which are formed are dependent upon the order of these two steps. If dehydrochlorination occurs first followed by chlorination,

$$C_2H_5C1 = C_2H_4 + HC1$$
 (21)

$$C_2H_4 + Cl_2 = 1, 2-C_2H_4Cl_2$$
, (22)

1,2 substitution products will be formed. If chlorination occurs first followed by dehydrochlorination,

$$C_{2}H_{5}Cl + Cl_{2} = 1, 1 - C_{2}H_{4}Cl_{2} + HCl$$
, (23)

1,1 substitution products will be formed.

Chlorinated hydrocarbons interacted with molten salt baths containing $CuCl_2$ probably through a Lewis acid-base interaction using electron pairs on the chlorine of the chlorinated hydrocarbon. This interaction would weaken the other bonds in the hydrocarbon facilitating the dehydrochlorination reaction. In this way, $CuCl_2$ would catalyze the 1,2 substitution reactions.

CONCLUSIONS

The experimental results for the chlorination of C_2H_6 , C_2H_5Cl , and C_2H_3Cl using molten salt baths have shown that the products are chlorinated ethanes and ethenes and in addition C_2H_4 and C_2H_2 . Amounts of the products were determined.

Comparison of K coeff with K equil provided a way of determining if chemical equilibrium was achieved and also provided a way of classifying reactions.

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REFERENCES

C. N. Kenney, Catal. Rev. - Sci. Eng. 11, (1975) 197.
Morten Sørlie, Phillip G. Wahlbeck, and Harald A. Øye, Acta Chem.

Scand. (submitted).

- D. R. Stull and H. Prophet, "JANAF Thermochemical Tables," Ed. 2, NSRDS-NBS 37, 1971.
- D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "The Chemical Thermodynamics of Organic Compounds," Wiley, New York, 1969.
- 5. J. Chao, A. S. Rodgers, R. C. Wilhoit, and B. J. Zwolinski, J. Phys. Chem. Ref. Data, 3, (1974) 141.
- S. N. Flengas and A. Block-Bolten, in "Advances in Molten Salt Chemistry, Vol 2, (J. Braunstein, G. Mamantov, and G. P. Smith, ed.), Plenum, New York, 1973, p. 27.
- 7. M. Sørlie and H. A. Øye, unpublished data.
- 8. G. Eriksson, Acta Chem. Scand. 25, (1971) 2651.
- 9. G. Eriksson and E. Rosen, Chemica Scripta, 4, (1973) 193.
- 10. G. Eriksson, Chemica Scripta, 9, (1975) 100.





A) C₂H₃Cl in LiCl-KCl eutectic at 0 400°C. B) C2H5Cl in LiCl-KCl eutectic at 400°C. C) C_2H_6 in 60 mol

15 20 X_{CI2}/X_{C2H6} 05 25 17 30 35 $CuCl_2 - 40 \mod KCI at 397^{\circ}C.$ D) $C_2H_6 \inf 40 \mod CuCl_2 - 60 \mod CuCl_2 - 60$

% KCl at 397°C. E) C₂H₆ in LiCl-KCl eutectic at 400°C. □: single carbon bond; □: double carbon bond; ■: triple carbon bond. Lines from symbols indicate the number and location of Cl atoms on the molecules; e.g. : cis-1,2-C₂H₂Cl₂.







- Fig. 2 (upper left) Mass balance results: g-atoms of Cl in excess in products per mole of C_2 in reactants, vs. composition of reactant mixture. For meaning of squared symbols, see Fig. 1. 0: 40 mol % CuCl₂-KCl; \bullet : 60 mol % CuCl₂-KCl. 400°C.
- Fig. 3 (upper right) Relation between amount of chlorination and equilibrium pressure of Cl₂ for salt bath. Intercepts from Fig. 2. All data at 400°C. Pressures changed by changing salt bath composition.
- Fig. 4 (lower left) Relation between amount of chlorination and equilibrium pressure of Cl₂ for salt bath. Intercepts from Fig. 2 type data. Pressure changed by varying bath temperatures.





- Fig. 5 (upper left) Data for isomer equilibria. Experimental K coefficient/K thermodynamic vs. P(Cl₂) in equilibrium with salt bath. \bullet , reaction 15; \bullet , reaction 16; \blacktriangle , reaction 17; \blacktriangle , reaction 19.
- Fig. 6 (upper right) Data for LiCl-KCl eutectic bath. X_{Cl_2}/X_{HCl} , equ (20), is plotted vs. composition of reactant mixture, \checkmark , reaction 4; \heartsuit , reaction 2; \bigcirc , reaction 1; \circlearrowright , reaction 3; \triangle , reaction 5; \blacktriangle , reaction 6; \diamondsuit , reaction 7; \blacklozenge , reaction 10. Data for reactions 1, 3, 5, 6 form a consistent group.
- Fig. 7 (lower left) Data for salt baths containing CuCl₂. See caption for Fig. 6 for symbols.

THE CHEMISTRY AND STATUS OF RECHARGEABLE MOLTEN-SALT BATTERIES

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ABSTRACT

The chemistry and the state of development of rechargeable molten salt cells and batteries of current interest are reviewed in this chapter.

INTRODUCTION

Molten-salt cells offer the most attractive combination of high specific energy (100-200 Wh/kg), high specific power (50-200 W/kg), and long cycle life (300-1500 cycles) of any rechargeable cells under investigation at this time. It is these important features that justify the development and application of cells that have the disadvantages of operation at elevated temperatures, and difficult materials problems.

There are two major categories of molten-salt cells: those in which the molten salt is the sole electrolyte, and those in which the molten salt serves as a reactant and as an auxiliary electrolyte (the main electrolyte is a solid). In the first category are such cells as LiAk/LiCk-KCk/FeS, LiAk/LiCk-KCk/FeS2, and Li₄Si/LiCk-KCk/FeS2; in the second category are Na/Na₂O•xAk₂O₃/Na₂S_n-S, Na/Na₂O•xAk₂O₃/SCk₃AkCk₄ in NaCk-AkCk₃, and Li/Li₂O/LiNO₃-KNO₃/V₂O₅. These cells have operating temperatures ranging from 150 to 475°C, and all must be sealed from the atmosphere because of the alkali metal reactants and hydrolytic degradation of molten salt electrolytes.

In this chapter, we will review the relevant chemistry of several of the systems mentioned above, and the state of development of rechargeable cells and batteries based on those systems.

CELLS WITH MOLTEN SALTS AS THE SOLE ELECTROLYTE

The LiAl/LiCl-KCl/FeS Cell:

This cell makes use of a solid lithium-aluminum alloy as the negative electrode. It supplies lithium as the reactant; the aluminum serves primarily to immobilize the lithium and store it in a solid form at cell operating temperature $(450-475^{\circ}\text{C})$. The most recent phase diagram of the Li-Al system⁽¹⁾ indicates that at the cell operating temperature $(400-460^{\circ}\text{C})$ the solubility limit of lithium in aluminum is 10 at.%, which is the boundary of the α -Al phase field. The β -Li-Al field has a composition width of 9 at.% lithium (47-56 at.%). The electrode is normally cycled across the two-phase region between 10 and 47 at.% lithium, within which the emf of the electrode at 450°C is constant at 292 mV relative to lithium.^(2,3) As the lithium content is increased above 47 at.% into the β -phase, the potential decreases steeply and approaches that of lithium.^(3,4).

The positive electrode of this cell is iron monosulfide. The chemistry of the FeS electrode has been the subject of considerable research, much of it focused at Argonne National Laboratory (ANL). Recently, Tomczuk et al., $^{(5)}$ published a definitive paper on the phases formed in the electrode, the phase sequence during charge and discharge, and the thermodynamics of the electrochemical and chemical reactions occurring in the electrode, as well as electrolyte effects on such reactions. As much of the earlier work $^{(6-10)}$ was discussed and cited in this paper, it was used as the principal source of information for this review, unless stated otherwise.

Five phases have been identified in the FeS electrode when operated in LiCl-KCl electrolyte: FeS, LiK₆Fe₂₄S₂₆Cl (\equiv J-phase), Li₂FeS₂ (\equiv X-phase), Li₂S and Fe. The FeS phase corresponds to a fully charged cell, the J- and X-phases are present at intermediate states of charge and discharge, and the Fe and Li₂S phases are present in the fully discharged state. Figure 1 shows the ternary Li-Fe-S phase diagram for 450°C, on which all of the phases just mentioned (except J-phase) can be located. Line H-M of Figure 1 represents the pathway of the overall electrode composition as the cell is discharged.

Using the Gibbs phase rule for condensed systems and the fact that all the FeS electrode phases can be prepared from five components: LiCL, KCL, Li₂S, Fe and FeS, it was found that for a given Li^+/K^+ ratio in the electrolyte and a given temperature, only two sulfide phases can be in equilibrium; therefore, six such combinations of four sulfide phases result in six possible electrode discharge reactions. These reactions are as follows:

$26 \text{FeS} + \text{Li}^+ + 6\text{K}^+ + C\text{L}^- + 6\text{e}^- + \text{J} + 2 \text{Fe}$	[1]
$J + 25Li^+ + 20e^- + 13X + 11Fe + 6K^+ + C\ell^-$	[2]
$J + 51Li^+ + 46e^- + 26Li_2S + 24Fe + 6K^+ + C\ell^-$	[3]
$2FeS + 2Li^+ + 2e^- \rightarrow X + Fe$	[4]
FeS + $2Li^+$ + $2e^-$ + Li_2S + Fe	[5]
$X + 2Li^+ + 2e^- + 2Li_2S + Fe$	[6]

In an actual electrode, different regions are not always in equilibrium with one another. For example, it will occasionally be necessary to consider mixtures of three sulfide phases with iron. Such mixtures can be at equilibrium in a given electrolyte at only one temperature. At other temperatures in the same electrolyte, the three sulfide phases are not in equilibrium, and a chemical reaction tends to consume one of them. The four possible chemical reactions are:

$23X + Fe + 6KCl + J + 20Li_2S + 5LiCl$	[7]
$3X + 20FeS + Fe + 6KCl \rightarrow J + 5LiCl$	[8]
23 FeS + $3Li_2S$ + Fe + $6KCl \rightarrow J$ + $5LiCl$	[9]
$FeS + Li_2S \rightarrow X$	[10]

In their work, Tomczuk, <u>et al.</u>, used extensive emf and cyclic voltammetric measurements combined with metallographic examinations of the electrode to determine the electrode phase sequence during charge and discharge.

Metallographic examinations of the electrodes showed that during the first discharge, when large particles of FeS are present, the discharge of the particle proceeds in four successive stages: (1) FeS on the surface discharged to J-phase and iron, (2) FeS in the core discharged to X-phase and iron, (3) X-phase in the core discharged to Li₂S and iron, and (4) J-phase on the surface discharged to Li₂S and iron. Because the formation of J-phase was limited by diffusion and the discharge of J-phase was found to be a slow, lower-voltage reaction, suppressing these reactions and accentuating the X-phase reaction seemed desirable.

One method found and implemented to decrease the stability of J-phase was to increase the Li⁺/K⁺ ratio of the electrolyte, which tends to drive the chemical reactions [7]-[9] to the left.^(6,7) Saboungi, et al., investigated the stability of J-phase and the effect that the Li⁺/K⁺ ratio has on the stability of J-phase, using both an electrochemical titration method.⁽⁶⁾ and a metallographic reaction product-examination method.⁽⁷⁾

A first discharge of FeS in LiCl-saturated (68 mol % LiCl) electrolyte at 425°C indicated the J-phase surface layer generated under these conditions was only one fifth as thick as the surface layers generated under similar conditions in the eutectic (~58 mol % LiCl) electrolyte. (5) Vissers, et al., (9) in tests of small FeS cells found the active material utilization of FeS electrodes improved

markedly as the LiCl content of electrolyte was increased above that of the eutectic. From these cell studies, it was apparent that the LiCl-rich electrolyte (68 mol % LiCl-32 mol % KCl) permitted recharge of the electrode at a low voltage (~1.55 V, IR-included) and discharge of the electrode at high current densities (50-100 mA/cm²). Consequently, this electrolyte composition was taken to be an optimum and it is referred to as LiCl-rich electrolyte. This electrolyte is now routinely used in 300 Ah cells.

To determine the phase sequence in the FeS electrode during charge and discharge, cyclic voltammetric, emf, and metallographic studies were conducted on the FeS electrode both in the eutectic and in the LiCl-rich electrolytes.⁽⁵⁾ These studies were conducted with well-cycled electrodes where the particle size of the active electrode material was $\langle 20\mu m$.

The phase sequence determined for the electrode during charge and discharge in the eutectic and LiC2-rich electrolytes is summarized in Figure 2. In this figure, the Roman numerals indicate the sequence of electrochemical reactions, while the broad arrows indicate the chemical reactions.

In the eutectic electrolyte, the charge sequence found was I_c , $Li_2S + X$; II_c , X + FeS; chemical reactions [7] $X + J + Li_2S$, [8] FeS + X + J and III_c , J + FeS. The $X + J + Li_2S$ chemical reaction is believed to be minimal. On discharge, the sequence was I_D , FeS + J; II_D , FeS + X, III_D , J + X; IV_D , $X + Li_2S$; V_D , $J + Li_2S$ (Note that each phase discharges by multiple pathways). The chemical reactions [7] and [8] or $X + Li_2S$ and J, and FeS + X + J are superimposed on the electrochemical discharge pathways.

In the LiC2-rich electrolyte, the phase sequence during charge is very similar to that in the eutectic electrolyte, except that the chemical reactions forming J-phase are greatly reduced. The result is an electrode that is much more readily charged. On discharge, the electrochemical phase sequence is similar to that found in the eutectic electrolyte, except that J-phase may now react chemically with Li₂S to form X-phase, a material with fast electrochemical kinetic properties.

Phase transition potentials were measured in an investigation on the thermodynamic properties of the FeS electrode system in LiCl-KCl eutectic electrolyte.⁽⁵⁾ For three of the phase transitions: $E_3(J + X)$, E_4 ($J + Li_2S$) and E_7 ($X + Li_2S$), the emf of the FeS electrode was measured at appropriate states of charge and discharge. In making such measurements, an emf value was extracted from such data only when certain reversibility criteria were satisfied. For example, the J + X(E_3) data were obtained at both 20% discharge and 80% charge, which are equivalent states of charge approached from different directions. The agreement in these measurements is an indication of reversibility. To obtain the other three phase-transition potentials, the emf of the FeS + Li₂S transition was calculated from the available free energy values for $(\alpha + \beta)$ -Li-Al, FeS and Li₂S; the FeS + X and FeS + J values were then calculated from the thermodynamic interdependence that exists between the potentials. The potentials E₂, E₃, and E₄, which are dependent on electrolyte composition, were then calculated for the LiCl-rich (67 mol % LiCl) electrolyte from the reaction stoichiometry and the changes in the activity of LiCl and KCl with electrolyte composition. The regions of phase stability and emf values for the respective transitions in the two electrolyte systems (eutectic and LiCl-rich) are summarized in Figures 3 and 4.

Using the emf equations and the activities of LiCl and KCl, Tomczuk, et al., calculated the temperature at which the emf curves intersect in LiCl-saturated electrolyte. The intersection of E_2^* , E5*, and E3, which occurs at 621°C in eutectic electrolyte, was calculated to occur at 481°C in electrolyte saturated with LiC2 [75.2 mol % LiCl(11)]. This temperature is in excellent agreement with the metallographically determined temperature of $481^{\circ} \pm 5^{\circ}C_{\bullet}(7)$ Similar calculations for the intersection of E_3 , E_4 *, and E_7 (which occurs at 473°C in eutectic electrolyte) provided a value of 429°C in LiCl-saturated electrolyte [68.4 mol % LiCl⁽⁵⁾], which is in reasonable agreement with the $419^{\circ} \pm 5^{\circ}$ C temperature determined in the metallographic studies.⁽⁷⁾ The above temperature calculations rely on the reaction stoichiometries and certain emf differences, while the metallographic studies only require the presence or absence of phases. The good agreement between these independent methods tends to confirm the emf equations and the reaction stoichiometries. Therefore, the free energy changes of the chemical reactions can be calculated with a reasonable degree of confidence.

The free energy changes of the four chemical reactions were calculated from the thermodynamic relationships between the six electrochemical transition potentials and the free energies. The free energy changes of the chemical reactions are:(5)

where the temperatures are in °C and free energy changes are in kJ.

In a more recent study, Tomczuk, <u>et al.</u>, (12) determined the phase transition potentials of the FeS electrode from similar studies in LiF-LiC2-LiBr, where the only phase transitions are FeS + X and X + Li2S. The results of these emf measurements were:

*Indicates the emf has been calculated.

E (in mV), FeS \leftrightarrow X = 1338.9 + 0.0133T(K) E (in mV), X \leftrightarrow Li₂S = 1432.11 - 0.147T(K)

These values are in good agreement with their earlier values.⁽⁵⁾

Thermodynamically, one would predict that the principal overcharge reactions of the FeS electrode are as follows:

FeS
$$\neq$$
 Fe_{1-X}S + x Fe⁺² + 2xe⁻ [11]

$$2FeS + FeS_2 + Fe^{+2} + 2e^{-1}$$
 [12]

The calculated voltages for these reactions vs. $(\alpha + \beta)$ -Li-Al at 450°C are 1.84 and 2.17 V, respectively; studies of overcharged FeS electrodes by Tomczuk, et al., confirm the proposed overcharge reactions. (13)

A large number of LiAl/LiCl-KCl/FeS cells of various sizes and designs have been built and operated. A typical cell design is shown in Figure 5. The electrodes are pressed plaques of electrode reactant and powdered electrolyte; the electrolyte between the electrodes is usually held in a boron nitride felt (but sometimes is used in a paste form using MgO powder).⁽¹⁴⁾ Cells of the type shown in Figure 5 having capacities up to about 350 Ah have been tested, and they have demonstrated cycle lives of 250-400, with a few cells surpassing 1000 deep cycles. Specific energy values up to about 100 Wh/kg have been achieved.

A few batteries of LiA&/FeS cells have been tested in sizes up to about 4 kWh. The lifetimes, as is to be expected, have been shorter than for single cells. These batteries have shown cycle lives up to about 275.(15) The main cause of failure is the extrusion of the pasty positive electrode active material out of the positive electrode. This extruded material bridges across to the negative electrode, shorting the cell.

Table 1 summarizes the status of cell performance, lifetime, and other features. The recent cell development activities are also summarized, including work on 10-cell batteries, as are the remaining problem areas.

The Li-Si/LiCl-KCl/FeS₂ Cell:

This cell is closely related to the one discussed just above. It makes use of electrodes that have a much lower equivalent weight, and therefore has a significantly higher specific energy.

The negative electrode of this cell is a solid lithium-silicon alloy, which operates very effectively at practical current densities, and can store up to about four lithium atoms per silicon atom. The Li-Si phase diagram has been subject of several investigations, (16-18) with considerable discrepancy regarding exact phase compositions. According to the most recent work, (19-21) the phases include Li4.4Si, Li3.25Si, Li2.33Si, Li1.71Si, and Si. The emf values (vs. Li) for the corresponding phase transitions are 44, 150, 277 and 326 mV, respectively, at 450° C.(16-18) During normal cell operation, the Li-Si electrode is usually operated between the Li3.25Si and Si° sections of the phase diagram to avoid the corrosion and self-discharge problems associated with the Li4.4Si-Li3.25Si two-phase region.

The positive electrode of this cell is solid FeS₂. This is an attractive material because it is plentiful, has good electronic conductivity, a reasonably low equivalent weight, rapid reaction rates at cell operating temperature (450° C), and has a sulfur activity such that good potentials are achieved (1.6-2.1 V vs. Li).

The most extensive study of the high-temperature phases in the Li-Fe-S system was conducted by $Martin^{(22,23)}$ who employed metallography to establish the number and identity of the phases and X-ray diffraction to support the phase identification. In his work, Martin developed the Li2S-FeS-FeS2 section of the Li-Fe-S phase diagram, which provides an excellent guide for electrochemical investigations. Tomczuk, et al., (24) have subsequently updated this work on the phase relationships of the FeS2 electrodes and elucidated their role in the chemistry of the electrode. The updated phase diagram is shown in Figure 1. The major ternary phases in the diagram are indicated by the point F, which is the compound Li3Fe2S4 (or Li_{1.5}FeS₂), and the field C-D-E, which is a solid solution whose composition can be approximated by $Li_{2+x}Fe_{1-x}S_2$. This field is quite narrow and is best approximated in the diagram by a line, although, of course, it must have some finite width. At X = 0 (point E), this phase has the composition Li_2FeS_2 and it is a major phase in FeS electrodes. At X $\stackrel{\sim}{=}$ 0.2 (point D), the composition is approximately $\text{Li}_{2,2}\text{Fe}_{0,8}\text{S}_2$; this composition is in equilibrium with $\text{Li}_3\text{Fe}_2\text{S}_4$. At X $\stackrel{\sim}{=} 0.33$ (point C), the composition is $Li_{2.33}Fe_{0.67}S_2$, and the material of this composition is in equilibrium with Li2S and FeS2.

The dashed lines A-L and H-M are given in Figure 1 to indicate the equilibrium phase progressions in FeS₂ and FeS electrodes, respectively. [These progressions are only valid, of course, in the absence of phases like LiK₆Fe₂₄S₂₆Cl (which would require a quinary diagram)]. Thus, the dashed line H-M gives FeS * Li₂FeS₂ and Fe * Li₂S and Fe as the predicted phase progression in the FeS electrode, but, as noted before, more complex phase progressions are also known. The dashed line A-L gives as the predicted phase progression in FeS₂ electrodes:

FeS₂ • Li₃Fe₂S₄ • Li_{2+x}Fe_{1-x}S₂ + Fe_{1-x}S • Li₂FeS₂ • Li₂S + Fe

The arrows on the above phase progression are a shorthand notation used by Tomczuk, et al., $(^{24})$ for the cell reactions.

The phases found in the room-temperature examinations of the FeS₂ electrodes were FeS₂, KFeS₂, Li₃Fe₂S₄, Li_{2.33}Fe_{0.67}S₂, Li₂FeS₂, Fe_{1-x}S, LiK₆Fe₂₄S₂₆CL, Li₂S, and Fe. In metallographic examinations, these phases could be readily distinguished from one another by their color, isotropy, and crystal structure. The X-ray diffraction patterns and crystal systems are presented in this work⁽²⁴⁾ for the respective phases. If the two potassium-containing compounds, which were present at low levels, are excluded from consideration, the phases identified by Tomczuk, et al.,⁽²⁴⁾ in the FeS₂ electrodes are in agreement with Martin's phase diagram.

Coulometric discharge data⁽²⁴⁾ obtained on the FeS_2 electrode also support Martin's phase diagram. The breaks in the discharge curve were located at 37.9, 42.6, and 50% of the total capacity. These values compare well with the breaks predicted by the phase diagram, namely 37.5, 41.8, and 50%, and they indicate that the phase sequence during discharge observed in the FeS_2 electrodes agrees with that predicted by the phase diagram if one neglects the potassium-containing compounds.

The phase sequence during charge was found by Tomczuk, et a1., $^{(24)}$ to be slightly different than that observed during discharge for the Li₃Fe₂S₄ ~ FeS₂ phase transition. During discharge, the Li₃Fe₂S₄ formed on the FeS₂; during charge, the FeS₂ formed on the Fe_{1-x}S. The phases formed during charge are shown in Table 2. Cyclic voltammetry studies $^{(25)}$ have shown that the discharge begins very near 1.76 V vs. ($\alpha + \beta$)-Li-Al, but the charge reaction occurs at 1.82 V; these observations are also supported by the cell data. $^{(24)}$ A nonequilibrium soluble electrode species also seemed to be formed in this transition region during charge, $^{(24)}$ which further suggests that the charge and discharge reactions for this transition must be quite different.

The principal overcharge reaction (25) of the FeS₂ electrode occurs at ~2.4 V vs. $(\alpha + \beta)$ -Li-Al and is:

$$FeS_2 + 2Cl^- \neq FeCl_2 + 2S + 2e^-$$
[13]

where the formation of sulfur and ferrous chloride increases the porosity of the electrode and decreases the coulombic efficiency of the cell.

A number of Li-Si/FeS₂ cells of various designs have been built and operated at Argonne National Laboratory, and General Motors Research Laboratories. The GM cell was disk-shaped and had the construction shown in Figure 6. Cells of this type had a capacity of about 70 Ah, and had voltage vs. capacity curves as shown in Figure 7. These cells had lifetimes of up to 16,000 h, and cycle lives of up to about 700 cycles. Only a small amount of work has been performed on batteries of $Li-Si/FeS_2$ cells. This system is in an earlier stage of development than $LiA\ell/FeS$, but offers the possibility of twice the specific energy, as shown in Table 3, which summarizes the status of the $Li-Si/FeS_2$ cell.

CELLS WITH MOLTEN SALTS AS REACTANT AND AUXILIARY ELECTROLYTE

The Na/Na₂O•xAl₂O₃/Na₂S_n-S Cell:

This cell makes use of a molten sodium negative electrode; a solid tubular electrolyte of beta alumina $(Na_20 \cdot xAA_20_3, x = 5 \text{ to } 11)$ which conducts sodium ions; and a molten sulfur-sodium polysulfide positive electrode with graphite felt as the current collector. The operating temperature is 350° C. The overall cell reaction can be represented by

$$2Na + xS \longrightarrow Na_2S_x$$
 (x = 2 to 5) [14]

The reaction at the sulfur electrode

$$(x-1)S_x^{=} + 2e^{-} \implies xS_{x-1}^{=}$$
 (x = 3 to 5) [15]

is followed by equilibration with the free sulfur phase

$$S_{x-1}^{=} + S \xrightarrow{s_x} S_x^{=}$$
 [16]

as long as free sulfur exists.

This overview will discuss the Na₂S₂-S phase diagram, some of the properties of sodium polysulfides and the electrochemical reactions at the electrode interface including diffusion and subsequent chemical reactions. Only highlights can be given of facts that are well established and of important questions that are still open.

The phase diagram (Figure 8) has been investigated numerous times. (26-30) The main difficulty in such investigation is that in this system equilibria are established slowly and that sodium polysulfides tend to undercool and solidify as glasses. (31) If the glass is subsequently crystallized, the resulting crystals are not necessarily in equilibrium with the melt at the liquidus line. The salient features of the phase diagram are the existence of the three polysulfides Na₂S₂, Na₂S₄ and Na₂S₅, and a miscibility gap with liquid sulfur and Na₂S₅ saturated with sulfur in equilibrium. This miscibility gap plays an important role in electrode kinetics and

consequently in cell performance. Na₂S₃ is stable at room temperature, but decomposes above 100°C into Na₂S₂ and Na₂S₄, which of course does not preclude its existence in the melt. $^{(32,33)}$

Attempts have been made to interpret the dependence of the open circuit voltage of the cell on melt composition thermodynamically.(34-36)

One difficulty in analyzing the kinetics in this system is our limited knowledge of the exact composition of the melt, i.e., of the nature of the ions present. However, it has been established that uncharged sulfur is present in the polysulfide melt only in the form of polysulfide ions. (36)

The propensity of polysulfide melts to solidify as glasses was used to advantage in Raman spectroscopy.(33) Investigations at the temperature of the melt gave little insight, because of the coexistence of a series of polysulfides, (37) whereas with glasses interpretable results were obtained. The presence of the ions S_2^- , S_4^- , and S_5^- in melts of the appropriate composition was confirmed, but the existence of S_3^- in the melt is still controversial.

Another difficulty in analyzing the kinetics is the problem of defining diffusion in a pure melt. Earlier approaches used in other systems have been applied here successfully. (38,39) Also, it must be kept in mind that in electrochemical measurements in pure melts without solvent, migration of reactant ions is not negligible, and diffusion coefficients obtained are only effective values. However, these values (around 10^{-6} cm²/s) agree quite well with those determined by tracer studies. (40) Activation energies are in agreement with those found for melt viscosity. (41-43)

The rate of the interfacial reactions at practical current densities is clearly determined by diffusion. Exchange currents are extremely high. Relaxation methods have yielded values of 1 A/cm² with steps up to 400 mV and of more than 10 A/cm² with steps of a few millivolts. This may be understood as measuring one and in the former case both of two consecutive steps in the two electron reaction.(38,39)

Kinetics have been investigated by potential sweep chrono-amperometry, (38, 39) by chronopotentiometry, (44) and by the rotating disk method. (45, 46)

The kinetics of the cell reactions are illustrated by Figure 9 of a cyclic potential sweep with melt resistance measured concurrently. Neither anodically nor cathodically do we see a limiting current. On both sides the reaction peak (A,F) is followed by an abrupt decrease

in current caused by an insoluble reaction product: solid Na_2S_2 on the cathodic side (B) and liquid sulfur on the anodic side. The conductance decreases correspondingly. The formation of insoluble products necessitates the use of expanded electrodes in all but very thin layers of polysulfide electrolyte. The reduction peak A has been identified as a superposition of two consecutive one electron reaction peaks. On the return sweep the current always passes through zero at the potential of a melt saturated with Na_2S_2 .

It has been suggested that the Randles-Sevcik equation cannot be applied because of formation of these blocking surface layers. However careful analysis has shown that the influence of layer formation becomes noticeable only after the peak has been reached, and the consistent results obtained with Randles-Sevcik analysis bear this out.

The formation of solid Na₂S₂ does not pose a problem in cell operation, especially since the layers seem to be crystalline and not very dense; they in fact inhibit overdischarge. The influence of sulfur formation at the anode depends on the nature of the electrode material, i.e., on its preferential wettability. Carbon and many other materials are preferentially wetted by sulfur. When the melt composition reaches Na₂S₅ and becomes saturated with sulfur, there is no longer a mechanism for the removal of the adsorbed insulating sulfur layer. Current flow is blocked, and the cell cannot be recharged beyond this point. Fortunately there are means of modifying the surface so that it becomes preferentially wetted by polysulfide and permits charge into the two phase region of the phase diagram. Certain metal surfaces (e.g., those of chromium steels) will not block anodic current at all. These surfaces (covered by a corrosion layer) are clearly preferentially wetted by polysulfide. Unfortunately they are not stable enough for use in practical cells.

Basic research stimulated by the invention of the sodium/sulfur cell has established many facts that are essential for the development work. But there are still a few important questions to be solved:

- 1) the distribution of ion species $S_X^=$ (x = 2 to 6) in sodium polysulfide melts;
- the actual values of the very high exchange currents at the electrode;
- 3) the role of migration in the transport process.

Even though there are some unanswered questions about the sulfur-sodium polysulfide electrode, there is enough known to allow high-performance, long-lived cells to be built in significant quantities. Cells of various sizes, recently 65-200 Ah, have been operated, and have demonstrated specific energies of 120-160 Wh/kg, peak specific power values of 100-200 W/kg, and cycle lives of 300-1500. A typical cell design is shown in Figure 10.

Difficulty has been encountered in obtaining full recharge of the sulfur electrode because of the formation of an insulating layer of

sulfur at the sites of the electrochemical reaction. Various schemes were devised for maintaining electrolytic and electronic contact between the solid electrolyte, the polysulfide phase, and the graphite current collector. Some useful approaches have included gradedresistance graphite felt current collectors (to distribute the reaction zone more widely), layered current collectors (graphite felt, well wetted by sulfur, in alternating layers with alumina cloth, well wetted by polysulfide), with the planes of the layers perpendicular to the axis of the electrolyte tube, and additives to sulfur, to improve its electronic conductivity.

A number of batteries of Na/Na_2S_n -S cells have been tested. Figure 11 shows typical charge and discharge curves for a parallelconnected module of 25 cells⁽⁴⁷⁾ Most of the batteries have been able to store about 10 kWh, and a recent one has stored 100 kWh. One 25 kWh module of the latter battery has operated for over 600 cycles. This represents the largest and longest-lived high-temperature battery known to these authors.

The status of the work on this system is summarized in Table 4. The remaining problems include corrosion of the metals in contact with the sulfur electrode, the high cost of the electrolyte, seals, and failure of cells during freeze-thaw thermal cycling.

The Na/Na₂O•xAl₂O₃/SCl₃AlCl₄ in AlCl₃-NaCl Cell:

This cell offers an unusually high voltage of 4.2 V, and a theoretical specific energy of 563 Wh/kg, corresponding to the reaction:

$$4Na + SCl_3AlCl_4 + 3AlCl_3 + S + 4NaAlCl_4$$
 [17]

It is also possible to discharge the sulfur to the minus-two valence state. In this case, the reactions are:

$$4Na + SCl_3AlCl_4 + 3AlCl_3 + S + 4NaAlCl_4 \qquad [17]$$

$$2Na + S + AlCl_3 + AlSCl + 2NaCl [18]$$

In addition, the operating temperature is in the range 180-250 $^\circ C$ vs. 350 $^\circ C$ for Na/Na2Sn-S.

As discussed below, Reaction 17 proceeds through several intermediates. The evidence for the reactants, products and the intermediates may be summarized as follows:

1. The Raman spectrum of the melt in the positive electrode compartment of a fully charged cell⁽⁴⁸⁾ is a summation of the spectral features of Al_2Cl_7 , $AlCl_4$ and SCl_3^+ (the presence of Na⁺ ions is, of course, not detected by Raman spectroscopy). The fully charged state may be obtained either by a four electron oxidation of elemental sulfur in the melt or by the addition of the compound SCl_3AlCl_4 ⁽⁴⁹⁾ to an acidic ($AlCl_3/NaCl$ molar ratio > 1) melt. 2. Raman spectra taken at different stages of the first discharge plateau clearly show the disappearance of SCl_3^+ , the increase of $AlCl_4^-$, and the decrease of $Al_2C_7^-$ bands.⁽⁴⁸⁾ In fact, the melt compositions estimated from the intensities of the Raman bands of $Al_2Cl_7^-$ and $AlCl_4^-$ are in reasonable agreement with melt compositions calculated from the stoichiometry of the electrochemical process. Thus, the discharge corresponds to a decrease in the modified Lewis acidity of the melt in the positive electrode compartment, in agreement with Equations 17 and 18. Although no clearcut assignments of intermediate species could be made based on Raman spectra, UV-visible and electron spin resonance spectroelectrochemical and electrochemical studies (50-54) of more dilute melt solutions provide evidence for monovalent sulfur species, present as S_2Cl_2 or possibly S_2Cl^+ , and, in $AlCl_3$ -rich melts, for cations such as S_8^+ , S_5^+ and S_8^+ . (50,51) Thus the overall reduction process of SCl_3^+ involves an increase in S-S bonds and decreasing Cl^- complexation.

3. The end of the first discharge plateau corresponds to the formation of elemental sulfur, present predominantly as S_8 .^(48,55) The solubility of sulfur in the melt increases with the melt acidity⁽⁵⁵⁾ or, in other words, it decreases as the discharge proceeds. Thus, it is likely that in a cell most of the elemental sulfur is present as a suspension.

4. The product formed during the second discharge plateau depends on whether the melt is acidic or basic (this will usually correspond to NaALCL4 saturated with NaCl(⁵⁶)). In acidic melts polymeric (ALSCL)_n is formed, while in basic melt polymeric (ALSCL2)_n is present.^(48,57) The values of n are believed to be ~3-4 in dilute melts.⁽⁵⁷⁾ There is no evidence for the formation of polysulfide ions in ALCL3-NaCL melts, although Raman evidence for the S_3^- ion in basic ALCL3-CSCL melts has been obtained.⁽⁵⁸⁾

The electrochemistry of sulfur oxidation and reduction has been investigated in very acidic (ALCL₃/NaCL, 63/37 mole %) melts, (52) melts of intermediate pCL (where pCL is defined as $-\log [CL^-]$), (54) and in ALCl₃/NaCL melts saturated with NaCL.(53) These investigations, as well as spectroelectrochemical studies in 63/37 ALCL₃/NaCL melts, (51) were performed in more dilute melts than is normally the case for cell studies.

In very acidic melts the oxidation of sulfur to SCl_3^+ involves three voltammetrically distinguishable steps. The first of these steps results in S_8^+ and probably S_8^{2+} and S_5^+ ; (51) the apparent n-value per sulfur atom ranges from 0.13 to 0.22 depending on the temperature (175-250°C) and the concentration of sulfur. The second step results in the formation of monovalent sulfur which is oxidized to SCl_3^+ in the third step. Spectroelectrochemical studies⁽⁵¹⁾ point to the formation of S_4^{2+} and divalent sulfur as intermediates in the second and third oxidation steps. The low oxidation states of sulfur, such as S_8^+ and S_8^{2+} , were found to be unstable in slightly acidic melts (pCl < 3.8);⁽⁵⁴⁾ only two voltammetric steps are observed corresponding to the formation of S_2Cl_2 and SCl_3^+ . In NaCl-saturated melts SCl_3^+ is unstable; the main oxidation product is S_2Cl_2 .⁽⁵³⁾

A number of simple glass laboratory cells of up to twenty ampere hours capacity have been operated, and a few metal-cased cells have been tested.(59,60) Some voltage vs. capacity curves for a cell employing both Reactions 17 and 18 above are shown in Figure 12. The upper plateau corresponds to Reaction 17; the lower plateau corresponds to Reaction 18. This cell used a reticulated vitreous carbon current collector in the positive electrode. Tungsten spirals have also been used.

Recent work with this cell has demonstrated that high power densities (up to 788 mW/cm² at 360 mA/cm² and 2.2 V) can be achieved. Some cells of this type have demonstrated cycle lives in excess of 400 cycles, and one small cell (0.56 Ah) was operated for 1370 cycles (with the positive electrode inside the β "-A&203 tube).

Values for specific energy and specific power of complete cells cannot be quoted because no cells of practical design have been constructed yet. The status of this cell is summarized in Table 5. The problems include: highly corrosive positive electrode material; significant vapor pressure of ALCL₃; seals; poor wetting of the electrolyte by sodium requires special start-up procedures.

CONCLUSIONS

Based upon the material presented in this paper, the following conclusions may be drawn.

1. Molten-salt rechargeable cells are making good progress in their evolution into high-performance, long-lived batteries.

2. The chemistry and electrochemistry of these systems are complex, but are reasonably well understood.

3. Materials problems are significant for these systems, and could well be the pace-setting issues in their development.

4. The field of molten salts offers interesting opportunities for the development of new electrochemical cells. More are sure to follow.

REFERENCES

.

1.	J. L. Settle and K. M. Myles, "The Lithium-Aluminum Phase Diagram," in Argonne National Laboratory Report ANL-76-9 (April
	1976), p. 42.
2.	N.P. Yao, L. A. Heredy, and R. C. Saunders, J. Electrochem. Soc., 118, 1039 (1971).
3.	C. J. Wen, B. A. Boukamp, R. A. Huggins, and W. Weppner, J. Electrochem. Soc., 126, 2258 (1970).
4.	J. R. Selman, D. K. DeNuccio, C. J. Sy, and R. K. Steunenberg, J. Electrochem. Soc., 124, 1160 (1977).
5.	Z. Tomczuk, S. K. Preto, and M. F. Roche, J. Electrochem. Soc., 128, 761 (1981).
6.	M. L. Saboungi, J. J. Marr, and M. Blander, J. Electrochem. Soc., 125, 1567 (1978).
7.	M. L. Saboungi and A. E. Martin, Abs. 339, The Electrochemical
	Society Extended Abstracts, Pittsburgh, PA, October 15-20 (1978), p. 919.
8.	R. A. Sharma, J. Electrochem. Soc., 123, 448 (1976).
9.	D. R. Vissers, K. E. Anderson, C. K. Ho, and H Shimotake,
	"Effects of the LiCL-KCL Electrolyte Composition on the
	Performance of the Positive Electrode in Li-Al/FeS Cells," in
	Proceedings of the Symposium on Battery Design and Optimization,
	Vol. 79-1, S. Gross, ed., The Electrochemical Society, Princeton
	(1979), p. 416.
10.	F. C. Mrazek and J. E. Battles, J. Electrochem. Soc., <u>124</u> , 1556
	(1977).
11.	B. Chu and J. Egan, Ann. NY Acad. Sci., 79, 908 (1960).
12.	Z. Tomczuk, M. F. Roche, and D. R. Vissers, J. Electrochem. Soc., <u>128</u> , 2255 (1981).
13.	Z. Tomczuk, A. E. Martin, and R. K. Steunenberg, Abs. 47, The Electrochemical Society Extended Abstracts, Las Vegas, NV,
	October 1/-22 (1976), p. 131.
14.	D. L. Barney, R. K. Steunenberg, A. A. Chilenskas, E. C. Gay, J.
	E. Battles, R. Hudson, B. A. Askew, and F. C. Tompkins,
	Lithium/fron Sulfide Batteries for Electric-Vehicle Propulsion
	and Other Applications," Argonne National Laboratory Report
15	ANL-81-65 (February 1982).
13.	W. L. Miller, E. C. Gay, and D. Kilsdonk, in Proceedings of the
	Institute of Electrical and Electronic Engineering Conference,
	D 595
14	r. JoJ. E. A. Shumh, Constitution of Bigowy Allows, Const. Currelement
10.	r. A. Shunk, Constitution of Binary Alloys, Second Supplement,
17	D A Charma and D N Confunction I Floatmanham Conc. 122 1762
11.	(1976) (1076)
18.	S_{1} C. Lai I Electrochem Soc 123 1106 (1076)
19.	H. G. von Schnering R. Nesper K F. Tabbe and L. Curda Z.
_,,	Metall., <u>71</u> , 357 (1980).

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- 20. C. J. Wen and R. A. Huggins, J. Solid State Chem., 37, 271 (1981).
- B. A. Boukamp, G. C. Lesh, and R. A. Huggins, J. Electrochem. 21. Soc., 128, 725 (1981).
- A. E. Martin, in "High Performance Batteries for Electric-Vehicle 22. Propulsion and Stationary Energy Storage," Argonne National Laboratory Report ANL-78-94 (1980), p. 167.
- 23. A. E. Martin and Z. Tomczuk, in "High-Performance Batteries for Electric Vehicle Propulsion and Stationary Energy Storage, Argonne National Laboratory Report ANL-79-39 (1979), p. 71.
- Z. Tomczuk, B. Tani, N. C. Otto, M. F. Roche, and D. R. Vissers, 24. J. Electrochem. Soc., 129, 925 (1982).
- S. K. Preto, Z. Tomczuk, S. von Winbush, and M. F. Roche, J. 25. Electrochem. Soc., <u>130</u>, 264 (1983).
- 26. T. G. Pearson and P. L. Robinson, J. Chem. Soc., 132, 1473 (1930).
- 27. N. K. Gupta and R. P. Tischer, J. Electrochem. Soc., 119, 1033 (1972).
- 28. D. G. Oei, Inorg. Chem., 12, 435 (1973).
- 29. E. Rosen and R. Tegman, Chem. Scripta, 2, 221 (1972).
- E. A. Mayorova, N. M. Romanchenko, and A. G. Morachevskii, 30. Electrokhimiya, 17, 523 (1981).
- 31. G. J. Janz and D. J. Rogers, The Electrochemical Society Extended Abstracts, <u>82-2</u>, No. 333.
- 32. D. G. Oei, Inorg. Chem. 12, 438 (1973).
- G. J. Janz, J. R. Downey, G. J. Wasilczyk, J. W. Coutts, and A. 33. Elouard, Inorg. Chem., 15, 1759 (1976).
- A. G. Morachevskii, M. A. Bykova, and L. N. Gerasimenko, Zh. 34 . Fiz. Khim., 45, 2066 (1971).
- H. S. Wroblowa, The Electrochemical Society Extended Abstracts, 35. 82-2, No. 332.
- 36. B. Cleaver and A. J. Davies, Electrochim. Acta, 18, 733 (1973).
- B. Cleaver and S. J. Sime, Electrochim. Acta, 28, 703 (1983). 37.
- 38. R. P. Tischer and F. A. Ludwig, Adv. Electrochem. & Electrochem.
- Eng., <u>10</u>, 391 (1977). D. A. Aikens in <u>The Sulfur Electrode</u>, R. P. Tischer, ed., 39. Academic Press, in press.
- 40. J. Divisek, F. G. Bodewig, J. Mergel, H. Lippert, and B. Kastening, J. Electrochem. Soc., <u>127</u>, 357 (1980). B. Cleaver, A. J. Davies, and M. Hames, Electrochim. Acta, <u>18</u>,
- 41. 719 (1973).
- 42. B. Cleaver and A. J. Davies, Electrochim. Acta, 18, 727 (1973).
- 43. B. Cleaver in The Sulfur Electrode, R. P. Tischer, ed., Academic Press, in press.
- 44. K. D. South, J. L. Sudworth, and J. G. Gibson, J. Electrochem. Soc. 119, 554 (1972).
- R. D. Armstrong, T. Dickinson, and M. Reid, Electrochim. Acta, 45. 20, 709 (1975).
- 46. R. D. Armstrong, T. Dickinson, and M. Reid, Electrochim. Acta, 21, 935 (1976).

- Ford Aerospace & Communications Corporation, Annual DOE Review of the Sodium-Sulfur Battery Program, April 22, 1980.
- K. Tanemoto, A. Katagiri, and G. Mamantov, J. Electrochem. Soc., 130, 890 (1983).
- G. Mamantov, R. Marassi, F. W. Poulsen, S. E. Springer, J. P. Wiaux, R. Huglen, and N. R. Smyrl, J. Inorg. Nucl. Chem., <u>41</u>, 260 (1979).
- 50. G. Mamantov, V. E. Norvell, and L. Klatt, J. Electrochem. Soc., <u>127</u>, 1768 (1980).
- 51. V. E. Norvell, K. Tanemoto, G. Mamantov, and L. Klatt, J. Electrochem. Soc., <u>128</u>, 1254 (1981).
- R. Marassi, G. Mamantov, M. Matsunaga, S. E. Springer, and J. P. Wiaux, J. Electrochem. Soc., <u>126</u>, 231 (1979).
- 53. R. Marassi, G. Mamantov, and J. Q. Chambers, J. Electrochem. Soc., <u>123</u>, 1128 (1976).
- K. Tanemoto, R. Marassi, C. B. Mamantov, Y. Ogata, M. Matsunaga, J. P. Wiaux, and G. Mamantov, J. Electrochem. Soc., <u>129</u>, 2237 (1982).
- R. Huglen, F. W. Poulsen, G. Mamantov, R. Marassi, and G. M. Begun, Inorg. Nucl. Chem. Letters, <u>14</u>, 167 (1978).
- 56. G. Torsi and G. Mamantov, Inorg. Chem., 10, 1900 (1971).
- 57. R. W. Berg, S. von Winbush, and N. J. Bjerrum, Inorg. Chem., <u>19</u>, 2688 (1980).
- R. Fehrmann, S. Von Winbush, G. N. Papatheodorou, R. W. Berg, and N. J. Bjerrum, Inorg. Chem., <u>21</u>, 3396 (1982).
- G. Mamantov, R. Marassi, M. Matsunaga, Y. Ogata, J. P. Wiaux, and E. J. Frazer, J. Electrochem. Soc., <u>127</u>, 2319 (1980).
- 60. G. Mamantov, K. Tanemoto, and Y. Ogata, J. Electrochem. Soc., 130, 1528 (1983).

Table 1. Summary of LiAt/LiCt-KCt/FeS Cell

 $2LiAl + FeS \rightarrow Li_2S + 2Al$ E = 1.33 V; 458 Wh/kg Theoretical T = 450°CStatus 60-100 Wh/kg @ 30 W/kg Specific Energy 60-100 W/kg, peak Specific Power Cycle Life 300+ @ 100% DOD 5000+ h Lifetime >\$100/kWh Cost Recent Work Multielectrode cells LiX-rich electrolyte BN felt separators Wetting agent for separators Powder separators-Mg0 Freeze-thaw cycling Improved current collectors Batteries of 320 Ah cells Problems Low specific energy Low voltage per cell Cell shorting major failure mode Electrode swelling and extrusion Agglomeration of Li-Al with cycling Capacity loss High separator cost Leak-free feedthroughs

Thermal control

Sulfide Phases During Charge of LiAA/FeS2 Cells Operated at 410°C Using Eutectic **Electrolyte^a** Table 2.

			_			-	
Metallographic findings		Li2FeS2 + trace of LiK6Fe24S26C2	Li ₂ FeS ₂ + Fe _{1-x} S + Li ₂ ,33Fe ₀ ,67 ^{S₂}	Li ₃ Fe ₂ S ₄ only	$Li_3Fe_2S_4 + 5\% Fe_{1-x}S$	Not examined	Fe ₂ S + Fe _{1-x} S
indings	Minor phase	LiK ₆ Fe ₂₄ S ₂₆ C&	Fe _{l-x} S	None detected	None detected	FeS ₂ + Fe _{1-x} S	Fe _{1-x} S
X-ray f	Major phase	Li ₂ FeS ₂	Li2.33Fe0.67S2 and Li2FeS2	Li ₃ Fe ₂ Su	Li ₃ Fe ₂ S ₄	Li ₃ Fe ₂ Su	FeS2
Charge potential ^b we (c + c)	LiAC	1.53	1.64	1.72	1.79	1.82	1.85
Cell decignation	חבאדמוומר דחוו	Z-1	Z-9	Z-2	Z-7	Z-3	Z-8

^a The phases Li₂S and Fe are not shown in this table because they react at a much lower potential of 1.33V to yield Li₂FeS₂. ^b Cells were constant-current charged at "18 mA/cm² to this potential and then constant voltage charged at this potential for periods in excess of 18hr. Current densities at the end of this time period were $\langle 2 \text{ mA/cm}^2$.

Table 3. Summary of Li₄Si/LiCl-KCl/FeS₂ Cell

 $Li_4Si + FeS_2 + 2Li_2S + Fe + Si$

E = 1.8, 1.3 V; 944 Wh/kg Theoretical

T = 450°C

Status

Specific Energy

Specific Power Cycle Life Lifetime Cost 120 Wh/kg @ 30 W/kg 180 Wh/kg @ 7.5 W/kg 100 W/kg, peak 700 @ 100% DOD ~15,000 h >\$100/kWh

Recent Work

Bipolar cells Li-Si electrodes BN felt separators 70 Ah cells

Problems

Materials for FeS₂ current collector Leak-free feedthroughs High internal resistance Low-cost separators needed Thermal control Table 4. Summary of Na/Na⁺ Solid/S Cell

 $2Na + 3S \rightarrow Na_2S_3$

E = 2.0 V; 758 Wh/kg Theoretical

T = 350°C

Status

Specific Energy Specific Power Cycle Life Lifetime Cost 90-180 Wh/kg @ 30 W/kg 60-180 W/kg peak 300-1500 3000-15,000 h >\$100/kWh

Recent Work

Batteries, 10-100 kWh $C_6 N_4$ additive to S Ceramic (TiO₂) electronic conductors Shaped current collectors Tailored resistance current collectors Sulfur-core cells Layered current collectors Graphite cladding $Na_{1+x}Zr_2Si_xP_{3-x}O_{12}$ Thermocompression bonded seals

Problems

Low cost electrolyte Corrosion-resistant material for contact with S Thermal cycling Low cost seals Robust electrolyte seals

Table 5

Na/Na₂O•xAl₂O₃/SCl₃AlCl₄ in AlCl₃-NaCl $4Na + SCl_3AlCl_4 + 3AlCl_3 + 4NaAlCl_4 + S$ E = 4.2 V; 563 Wh/kg Theoretical T = 250°CStatus: laboratory cells only (4 Ah) 20 mA/cm² @ 3.5 V 790 mW/cm² max. @ 2.2 V Current Density Power Density Cycle Life 1370 @ 100% DOD 7000 h Lifetime Cost too early Recent Work Larger cells - 20 Ah Less expensive current collectors Reduction to $\ensuremath{\mathsf{S}^{=}}$ Problems Sodium wetting? Vapor pressure of ALCL3 Corrosion of metals and some electrolytes Electrolyte cracking? Seals

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PHASES IN THE LI-Fe-S SYSTEM AT 450°C



XBL 838-10979

Figure 2. Summary of reaction assignments for two general cases (a) lower LiCk concentrations and temperatures and (b) higher LiCk concentrations and temperatures. Peak assignments from cyclic voltammetry (roman numerals) and the directions of chemical reactions $(X \leftrightarrow J + Li_2S)$ and $(X + FeS \leftrightarrow J)$ are shown, where X = Li_2FeS_2 and J = LiKe, Fe_24S_26Ck.

XBL 802-8072

H-M = DISCHARGE PATH OF FeS ELECTRODE



Figure 1. Isothermal section of the Li-Fe-S phase diagram at 450°C.

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XBL 829-11434A

Figure 3. Regions of stability of FeS, LiK₆Fe₂₄S₂₆Cl (djerfischerite or J-phase), Li₂FeS₂ (X-phase), and Li₂S in the LiCl-KCl eutectic. An asterisk indicates a calculated emf.



Figure 4. Regions of stability of FeS, $LiK_6Fe_{24}S_{26}C\ell$ (J-phase), Li_2FeS_2 (X-phase), and Li_2S in LiCl-rich electrolyte (67 m/o LiCl). An asterisk indicates a calculated emf. Note that E_2*' , E_3' , and E_4*' are shifted from their corresponding values in eutectic electrolyte.



Figure 5. Design used for the immobilized electrolyte/powder separator cells.



XBL 802-8075

Figure 6. Cross section of a disk-shaped Li₄Si/FeS₂ cell, having about 70-Ah capacity.





Figure 9. Cyclic sweep and melt conductance in Na₂S₄ at 300°C. Vitreous carbon electrode area is 0.0047 cm². Sweep is IR corrected.⁽³⁷⁾



XBL 802-8070

Figure 10. Exploded view of a 168-Ah sodium/sulfur cell of the sodium-core design.



Figure 11. Charge and discharge curves for a 25-cell parallelconnected Na/S battery.





NITRITE MOLTEN SALT FOR USE IN INTERMEDIATE TEMPERATURE LITHIUM CELLS

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ABSTRACT

The LiN0₂-KNO₂ (40-50 m/o) molten salt, which melts at 120°C, has been employed as an electrolyte in intermediate temperature lithium cells. The behavior of solid lithium in this electrolyte is analogous to the behavior of lithium in the similar intermediate temperature alkali nitrate electrolyte. Lithium reacts with the melt to form a thin, lithium ion conducting, protective layer which is believed to be Li₂O. The electrolyte is electrochemically reduced below 1.9 volts versus Li*/Li, and is oxidized to lithium metal and NO₂ gas above 3.5 volts versus Li*/Li. This electrolyte can be used in secondary cells with lithium or high lithium activity negative electrodes, and lower lithium activity positive electrodes which react reversibly with lithium.

The resistance of the protective layer on lithium increases with time as the thickness increases. Its resistance is of the order of 1-10 ohms after 10 hours at 150° C.

INTRODUCTION

Most lithium batteries presently under development operate either at the high temperatures associated with the LiCl-KCl molten salt (350-450°C), or at ambient temperatures utilizing organic solvent-based electrolytes. Intermediate temperature lithium batteries would be an attractive alternative if the problems associated with high temperature corrosion could be avoided, without sacrificing reasonable kinetic properties. Recently, the lithium chlorate and alkali metal nitrate systems have been proposed as electrolytes in intermediate temperature lithium cells (1,2).

Several battery systems are able to utilize lithium or high lithium activity negative electrodes whose potentials lie below the reduction limit of the electrolyte. This is a result of the formation of a protective layer which acts as a second electrolyte in series with the original electrolyte. A schematic drawing of this arrangement is shown

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in Figure 1. This layer must have an adequate lithium ion conductivity, a relatively small electronic conductivity, and be mechanically and chemically compatible with the original electrolyte. This appears to be the situation with lithium in some organic solventbased cells and in the sulfur dioxide and thionyl chloride systems.

When solid lithium is exposed to the $LiNO_2-KNO_2$ (40-60 m/o) molten salt, which melts at 120°C, it is immediately covered by a thin layer of lithium oxide, as shown in Figure 2. This prevents a massive direct chemical reaction of the solid lithium with the molten nitrite, whilst allowing the ready transport of lithium ions across this newly formed intervening layer. This protective layer allows the use of this electrolyte in primary and secondary lithium cells with promising kinetic and energy storage properties.

THERMODYNAMICS OF THE NITRITE ELECTROLYTE

Solid lithium metal reduces the nitrite electrolyte at 150° C to form a thin lithium oxide layer. The identity of the other reaction product is not known at this time. It is possibly a hyponitrite species or even nitrogen gas.

The stability limits of an electrolyte define the potential range within which the electrolyte is stable to electrochemical reduction or oxidation by a chemically inert electrode. The reduction and oxidation potentials of this nitrite electrolyte were determined by cyclic voltammogram experiments. The voltage of an inert platinum electrode was swept at a constant rate between two voltage limits while the current and voltage with respect to a lithium reference electrode were recorded. Figure 3 shows that a reduction reaction occurs at 1.9 volts versus Li†/Li at 150°C. A maximum in the reduction current was observed when the potential was swept below this value. This occurs because lithium oxide, a relatively insoluble product of the reduction reaction, forms on the inert platinum electrode and prevents the further reduction of the electrolyte by blocking the transport of electronic species. If the lithium oxide is not removed, only a small current will pass until a potential is reached at which lithium (or a lithium-platinum alloy) is formed. If the lithium oxide is removed by oxidation, dissolution or any other process, a substantial reduction current will once again be observed upon lowering the potential below 1.9 volts versus Li⁺/Li. Because the other product of the reduction reaction is not known, no theoretical calculation of the reduction potential can be made at this time.

The half cell electrochemical reaction associated with the oxidation of the nitrite electrolyte is believed to be:

 $NO_2^- = NO_2(g) + e^-$

(1)

This can be combined with the lithium reduction half cell reaction:

Li⁺ + e⁻ = li(s)

The chemical oxidation reaction for the nitrite electrolyte is therefore:

(2)

(3)

 $LiNO_2 = Li(s) + NO_2(q)$

This was observed to occur experimentally at 3.5 volts versus Li⁺/Li at 150° C in a cyclic voltammogram experiment, as shown in Figure 4. Using the free energies of formation of LiNO₂ (3) and NO₂(g) (4) at 150° C, a theoretical potential of 3.4 volts versus Li⁺/Li can be estimated for this reaction, which is in quite good agreement with the experimental results. The stable potential range of this system is therefore 1.9 to 3.5 volts versus Li⁺/Li, similar to some organic solvent-based lithium electrolytes.

SECONDARY CELL APPLICATIONS

Suitable positive electrode materials must be found in order to construct a nitrite secondary lithium cell. The combination of negative and positive electrode materials must provide an adequate specific energy. This requires a maximization of the capacity for lithium and the cell potential and a minimization of the molecular weights of both the negative and positive electrode materials.

Several positive electrode materials which have been used in other lithium cells were tried in the nitrite electrolyte. V_2O_5 , $Na_0.,WO_3$, $Na_0.,SWO_3$, MoO_3 , TiS_2 , FeS and FeS₂ all reacted chemically with the nitrite melt and released a gaseous product. The composition of these gases and the final products of these reactions are not known at this time.

An alternative approach to positive electrode materials in the nitrite electrolyte is the use of lithium-containing binary or ternary alloys. These typically have higher lithium activities than oxides or sulfides, hence lower cell potentials. A capacity of 1/2 of a lithium per metal ion in an oxide is common, while some binary alloys react with up to 3 lithiums per metal ion. Therefore a secondary cell with an alloy positive electrode material may well have a smaller cell potential but a larger capacity than a cell with a typical oxide The specific energy of a secondary cell with an alloy electrode. positive electrode should be similar to that of a cell with an oxide reactant if the molecular weights are comparable. One possible disadvantage of using alloy positive electrodes is that they may be corroded by the nitrite melt because of their high lithium activity. If their potentials are below the reduction limit potential of the electrolyte, they will be oxidized by the nitrite ions. This phenomenon also occurs on the negative electrode, as will be discussed in a later section of this paper.

The lithium-bismuth system has been studied in the LiCl-KCl electrolyte at elevated temperatures (5). The high temperature results indicated that this would be a good system to study in the nitrite

Electrodes were prepared by two different methods. Elemental bismuth was mechanically pressed onto a steel screen and was used directly. Another method of electrode preparation was to melt the bismuth in a molybdenum bucket at approximately 300°C in a heliumfilled dry box. Lithium was then added a little at a time while the temperature was raised to keep the mixture in a molten state. The maximum temperature was a function of the composition of the mixture, as determined by the lithium-bismuth phase diagram. A steel screen was then dipped into the molten alloy and removed. The amount of the alloy which froze onto the screen was then weighed and used as an electrode of that specific composition. The bismuth-containing electrode was then placed in the nitrite electrolyte along with a lithium electrode at 150°C. Electrochemical experiments were performed in order to determine the equilibrium potential versus composition (coulometric titration) curve for this system. Current was passed through the cell with a galvanostat while the amount of charge was monitored with a coulometer. This allowed the calculation of the amount of lithium added to or subtracted from the electrode. The voltage of the electrode was monitored on a chart recorder. When equilibrium was attained, the voltage and composition of the electrode were recorded. This was repeated over the compositional range of interest for this The solid line in Figure 5 shows the equilibrium electrode system. coulometric titration curve for the lithium-bismuth system in the nitrite melt at 150°C. A two-phase mixture of Bi and LiBi exists from x=0 to x=1 at a potential of 0.833 volts versus Li*/Li. This is similar to the results obtained in the LiCl-KCl melt at elevated temperatures, except for the fact that bismuth is molten above 271°C and dissolves an appreciable amount of lithium. The titration curve in the LiCl-KCl melt at 380° C is shown as a dashed line in Figure 5 (5). There is virtually no solubility of lithium in solid bismuth at 150°C. A second two-phase plateau consisting of LiBi and Li₃Bi exists from x=1 to x=2.8. Once again, this is similar to the high temperature data (5). The potential of this plateau was measured as a function of temperature in the LiCl-KCl melt (5). If these data are extrapolated, a value can be predicted at 150°C, as shown in Figure 7. The potential experimentally measured in the nitrite melt, 0.797 volts, agrees well with the extrapolated value of 0.803 volts. The LigBi phase has a width of approximately 0.2 lithiums per bismuth in both the nitrite and chloride melts, as shown in Figure 5. The maximum theoretical specific energy can be calculated from the equilibrium coulometric titration curve obtained using the nitrite electrolyte. A value of 233 watthours/kg is thereby assigned to the lithium-bismuth system at 150° C.

The lithium-antimony system has also been studied at elevated temperatures in the LiCl-KCl melt (5). It should exhibit a greater theoretical specific energy than the lithium-bismuth system because of the smaller molecular weights and higher potentials of the antimony alloys.

Lithium-antimony electrodes were prepared in a similar manner to the lithium-bismuth electrodes. Lithium and antimony were reacted in a helium-filled dry box. The mixture was equilibrated, ground into a fine powder and pressed into small pellets. A pellet was then placed in a molybdenum noose and used as an electrode. The method of dipping a steel screen into the molten mixture could not be used because iron reacts with antimony at the temperatures required to keep the mixture in a molten state. The equilibrium coulometric titration curve was obtained for this system using the nitrite electrolyte and is displayed as the solid line in Figure 6. The corresponding curve in the LiCl-KCl melt is shown as a dashed line in the same figure (5). Both curves show a two-phase plateau from x=0 to x=2, and a two-phase plateau from x=2 to x=3. The temperature dependence of the plateau potentials measured in the chloride melt is shown in Figure 7 (5). If these are extrapolated, they can be compared to the values obtained in the nitrite melt at 150° C. The experimentally obtained potential of the Sb-Li₂Sb plateau in the nitrite melt, 0.958 volts, is slightly higher than the extrapolated value from the chloride melt data, 0.947 volts. Similarly, the Li_2Sb-Li_3Sb plateau potential found in the nitrite, 0.930 volts, is higher than the value obtained from the chloride melt experments, 0.914 volts. The maximum theoretical specific energy calculated from the titration curve utilizing the nitrite melt is 535 watt-hours/kg.

NITRITE CORROSION REACTION

A spontaneous chemical corrosion reaction occurs in all cells which employ an electrode which forms a protective layer. This is a consequence of the electrode potential being below the reduction limit potential of the electrolyte. The electrode is oxidized by the electrolyte while the electrolyte is reduced by the electrode.

Several properties of the protective layer, the dissolution rate, mechanical stability, thickness, ionic and electrical conductivity will control the rate of this corrosion reaction. This is an important property to quantify, since the corrosion reaction decreases the capacity of the electrode.

An experiment was devised to estimate the magnitude of this corrosion current. A constant lithium activity of 0.01 volts versus Li⁺/Li was maintained on an inert nickel electrode in a nitrite melt saturated with lithium oxide. This was done to simulate the high lithium activity present at a lithium electrode, while minimizing the dissolution of the lithium oxide layer. If the potential were below 0.0 volts versus Li⁺/Li, lithium plating would occur. The inert electrode should differ from a lithium electrode only by the morphology of the metal-protective layer interface. The current which passes through this electrode is due to the reduction of nitrite ions, the only species capable of being reduced at this potential. The electrons in the nickel electrode can reduce a nitrite ion only if there is a discontinuity in the protective layer, or an operable electronic

transport mechanism. This may be the result of a break in the layer, as shown in Figure 8. Another possible mechanism could be the local dissolution of the layer resulting in a thinner region, which increases the probability of electron tunnelling.

The measured current density was a constant 20 microamps/cm² of nickel, similar to the corrosion current density measured in the LiNO₃-KNO₃ electrolyte, which also exhibits a lithium oxide protective layer on lithium (6). This experiment was repeated with a Li_3Bi electrode replacing the inert nickel electrode in the nitrite melt. Once again, about 20 microamps/cm² was measured for the corrosion current density. These corrosion current densities are a measure of the rate of loss of the electrode due to corrosion.

PROTECTIVE LAYER RESISTANCE

The impedance of the protective layer on lithium or lithium alloys in the nitrite melt is important because the layer is in series with the molten salt electrolyte and contributes to the total cell impedence. This determines the IR losses, a critical battery parameter.

AC techniques were used to measure the impedance of the protective layer on lithium in the nitrite melt. A small amplitude sine wave was applied between two new lithium electrodes and the response was analyzed at several frequencies. A frequency low enough to obtain a response similar to a DC resistance was chosen, 1000 Hz. The DC resistance was then measured as a function of time at different temperatures. Figure 9 shows a plot of the resistance of two reaction product layers plus the electrolyte versus time at two different temperatures. As one would expect, the resistance is greater at lower temperatures. The resistance increases with time, but it does not obey This is probably a result of simple parabolic oxidation kinetics. complicating phenomena such as electron tunneling, breaking of the protective layer and possibly local dissolution of the protective layer.

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REFERENCES

- (1) S. S. Wang and D. N. Bennion, J. Electrochem. Soc., <u>130</u>, 741 (1983).
- (2) I. D. Raistrick, J. Poris and R. A. Huggins, Proceedings of the Lithium Battery Symposium, Hollywood, Fla., The Electrochemical Society, <u>81-4</u>, 477 (1981).

- (3) L. E. Gastwirt and E. F. Johnson, USAEC Matt-98, U. S. Government Printing Office, (1961).
- (4) I. Barin and O. Knacke, <u>Thermochemical Properties of Inorganic</u> <u>Substances</u>, Springer Verlag, Berlin/Heidelberg, (1973).
- (5) W. Weppner and R. A. Huggins, J. Electrochem. Soc., <u>125</u>, 7 (1978).
- (6) I. D. Raistrick, J. Poris and R. A. Huggins, Proceedings of the 16TH IECEC, <u>1</u>, 774 (1981).

(-) | PROTECTIVE LAYER | ELECTROLYTE | (+)

<u>Figure 1</u> Schematic drawing of an electrode-electrolyte system with a protective layer

Li | Li20 | (Li, K) NO2 | (+)

T=150°

<u>Figure 2</u> Configuration of the lithium electrode in the nitrite melt at 150° C





Thermal Behavior of the Potassium-Sulfur Electrolyte

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ABSTRACT

Enthalpy of fusion and heat capacity data are reported for the compositions: di-, tri-, tetra-, penta-, and hexapolysulfides. Pronounced glass forming tendencies on cooling from the molten state are observed in the region of \sim 62 to \sim 67 wt% sulfur; this composition range is also characterized by inverse crystallization phenomena, much as observed in the closely related sodium-sulfur system. The calorimetric studies were extended to compositions in the region of liquid-liquid immiscibility, and the behavioral aspects are also reported.

Introduction

High-temperature thermodynamic data have recently been reported for the Na₂S-sulfur system as part of investigations of energy-related candidate salt systems for the molten sulfur electrode. In the present communication we report the results of an extension of these studies to the K₂S-sulfur system. Interest in this system has been restimulated through two recent developments in advanced battery concepts, namely the reports by Tsang (1) of potassium permeable hollow glass fibre techniques and by Crosbie and Tennenhouse (2) and Crosbie (3) of potassium beta"-alumina membranes. The potassium-sulfur system differs from the sodium-sulfur system in at least two aspects of practical interest; the open-circuit voltage (OCV) is higher in the potassium system, (2.414 V and 2.08 V, respectively) and the solidus-liquidus fields in the potassium system enable operation of the molten sulfur electrode at temperatures significantly lower than in the corresponding sodium system. For additional information, see ref. 3.

Investigations of the thermal properties appear limited to the work of Bousquet et al. (drop calorimetry; differential thermal analysis) (4). Markedly different values for the enthalpy of fusion were reported for two of the potassium polysulfides, viz: K_2S_4 and K_2S_5 , the technique of DTA leading to values \circ 70-250% larger than from drop calorimetry. Our principle effort, thus, was aimed at obtaining reliable values for the thermal properties. The measurements were extended to the characterization of the melting-crystallization behavior of compositions lying in the liquid-liquid immiscible region of the K_2 S-sulfur system, and these results are also reported.

Experimental

The differential scanning calorimetry facility in this laboratory centers around a Perkin Elmer DSC-Model 2 calorimeter, together with an LMS system of microprocessor components and software (5) for computer-assisted data acquisition, base-line corrections, and data analysis in enthalpy and heat capacity measurements. A Cahn electrobalance for quantitative and accurate small mass measurements completes the assembly. The latter was kept in a dry N₂ atmosphere together with the sample capsules and seal-press so that all steps in the sample transfers and encapsulations were carried out in an inert environment.

Energy calibrations were made with three metals, indium, tin, and lead, and two salt systems, KNO_3 and LiCl-KCl eutectic (6-8). The accuracy limits of the measurements thus established were as follows: temperatures, ± 0.5 °C; heats of fusion, $\pm 2\%$; heat capacities, $\pm 2\%$.

For the enthalpy and heat capacity measurements, the compositions were prepared "in-capsule" i.e, the reactant materials were directly weighed into the DSC sample pans in milligram amounts and in the exact stoichiometries required for the desired compositions. Contamination through trace impurities, such as moisture and oxygen, is thus minimized, if not completely by-passed.

The K_2S_3 was prepared from metallic potassium (Purified Grade; Baker Chemical Co., Inc.) and highly refined sulfur (9) using the ethanolic technique of Pearson and Robinson (10). The analytical procedures of Feher and Berthold (11) were used to establish the exact composition of the K_2S_3 (±2%). The tetra-, penta-, and hexa-sulfide compositions were prepared by the "incapsule" DSC technique using K_2S_3 and the highly refined sulfur in the required (weighed) amounts. For K_2S_2 , the "in-capsule" technique was also used, but with K_2S^2 (99.9% purity; Cerac/Pure Chemicals Co., Inc.) and K_2S_3 as reactant materials. The use of K_2S and sulfur as starting materials for the preparation of the above polysulfides via the "in-capsule" technique was explored but was not successful. The events during the above processes are illustrated in Fig. 1 and the values are given in Table 1. Completion of the reaction was taken as disappearance of the $K_2 S_3$ or the sulfur endotherms (via repetitive scans). The DSC scans for the melting process for the polysulfides thus prepared are also in Figure 1, together with the results for elemental sulfur. Melting temperatures were determined from the leading edge of the melting endotherms (12,13).

The enthalpies of solid-solid transitions and melting, and the heat capacities of the polysulfides as crystalline solids and as glasses and molten liquids are summarized in Tables 2-5. For these measurements, the heating and cooling rates were set at $10^{\circ}/\text{min}$, with a N₂ sweep of ~ 20 cm³/min throughout the assembly. The heat capacity data were acquired in overlapping 50° temperature increments over the total temperature range spanned.

Results and Discussion

The data of the Phase-Rule studies (3,10,15, and present work) are summarized in Figure 1. Inspection shows the existence of five maxima and three eutectics. For the di-, tri-, penta-, and hexa-polysulfides the maxima are well defined; for the tetra- the maximum appears to be slightly hidden (i.e., incongruently melting composition). At compositions of 71.8 wt% sulfur and greater, there is a separation into two layers (3), one consisting of a saturated solution of sulfur in the hexasulfide and the other, a saturated solution of the polysulfides in sulfur. The proposal by Pearson and Robinson (10), that the di- and tri-polysulfides do not melt congruently is not supported by the present meltingcrystallization studies. In a related communication from this laboratory concerning structural studies (14), the macroscopic preparative synthesis and the characterization of this polysulfide series are reported (melting points, elemental analyses, X-ray powder diffraction data). The results from the present DSC measurements (Table 2, mpts) are in close accord with the earlier observations ($^{\pm}3^{\circ}C$); for the disulfide the limits are somewhat larger, ($^{\pm 5}$ °C). The Na₂S-sulfur system is also shown in Figure 1. Inspection shows the lower range of temperature available for the molten sulfur electrode in the K₂S-sulfur system.

Melting-crystallization behaviors are illustrated in Figure 3 for the five stoichiometric compositions, and Figure 4 for the two additional compositions of higher sulfur content. The partial crystallization exhibited by some compositions (e.g., K_2S_5 , Fig. 3), the pronounced supercooling effects, and the onset of the crystallization

exotherms on reheating the materials (i.e., "inverse" crystallization, K_2S_4 ; K_2S_5 ; Fig. 3) indicate clearly the difficulties that would be encountered in obtaining trustworthy transition point data (m.pts., enthalpies, heat capacities) with techniques such as drop calorimetry and/or DTA (differential thermal analyses). It is of interest to examine the enthalpies of fusion from the various calorimetric techniques, viz:

∆H	(k J mol ⁻¹)	κ ₂ s ₂	κ ₂ s ₃	к ₂ s ₄	к ₂ s ₅	к ₂ s ₆
Drop	cal. (4)	11.150	16.150	8.305	7.196	25.941
DTA (4)		14.64	14.23	25.10	26.36
DSC (this work)	18.28	24.94	11.63	26.99	27.61

Inspection shows that the results from all three techniques for K_2S_6 are in close accord and for K_2S_5 the agreement is moderately good from two (for DTA and DSC). For K_2S_5 , the difference between the drop and the differential calorimetric techniques is in the direction predicted for partial crystallization effects.

The differing results from the DTA (4) and the present DSC measurements are not as readily understood. Some of the differences may be due, in part, to the thermal history of the materials prior to the measurements. In the present work an "in-capsule" preparative technique, with K_2S , K_2S_3 , and sulfur as reactants, was used to gain the various polysulfides as polycrystalline materials.

For the two compositions that fall in the region of liquid-liquid immiscibility, the melting behavior is summarized in Table 2 and in Figure 4, respectively. The melting point data (Table 2) indicate very sparing solubilities of the second components. Quantitative solubility estimates, however, were not undertaken in the present work. Relative to the enthalpies of fusion and the heat capacities it is found that these can be predicted quantitatively from the known stoichiometries of these samples, and the data for sulfur (9,12) and for the hexa-sulfide (Tables 2-5), using the principles of mol-fractions and state-functions additivity. Thus using heat capacity as illustration the results are: $K_2S_{7,0,8}$, C_p (J deg⁻¹ mol⁻¹): obsv'd, 169.4; calc'd, 173.0 at 300°C; and for $K_2S_{10,8,4}$, C_p (J deg⁻¹ mol⁻¹): obsv'd, 86.9; calc'd, 84.7 at 250°C. The agreement leaves little to be desired, and offers additional support for this as a region of liquid-liquid immiscibility.

Comparison of the composition ranges over which the glass-forming tendencies are greatest in the Na₂S-sulfur system and in the K₂S-sulfur system is of interest. In the sodium system it was found to be most pronounced in the tri-sulfide composition range (10,12,15,16); by contrast, in the potassium system, the tri-sulfide compo-sition shows sharp crystallization exotherms, with virtually no supercooling (present work), i.e., the same behavioral aspects as shown by well-defined crystalline materials such as NaCl, KCl,...). The tendency to glass formation in the potassium system is greatest in the tetra- to penta-polysulfide composition range. The glass transition temperature (Tg) from the present measurements, for K_2S_4 and K_2S_5 are respectively 46.9°C and 49.4°C. For the tetrasulfide, Cleaver (16) reported a value of 42°C; no value was reported for K_2S_5 .

The melting-crystallization measurements of "aged" melts were limited to two compositions in this glassforming range, namely the tetra- and the penta-polysulfide compositions. Samples of each, after "aging" in the molten state for \sim 800 hrs at 315°C were re-examined by the DSC technique by repeated thermal cycling, much as for the freshly prepared systems. The properties for the penta- were virtually unchanged from those prior to this aging treatment, i.e., the DSC thermal spectra were unchanged from those in Fig. 3, and the m.pts. and ${}^{\rm \Delta H}_{\rm fus}$ were as in Table 2. The tetra- samples, however, showed differences in the melting-crystallization pattern after this "aging" in the molten state. The tendency to formation of amorphous glassy masses on cooling was retained, but on reheating, the on-set of crystallization was no longer reproducible. When crystallization did occur, the on-set of this event now had shifted to higher temperatures (see Fig. 3, K_2S_4). Thus at the tetra-sulfide composition, "aging" in the molten state induces structural changes that favor a complete "loss-of-memory" of crystallinity in the amorphous material gained by cooling the melts. Measurements are in progress to characterize the range of compositions for this, and further discussion is deferred until additional results are on-hand.

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References

1.	Tsang, F. Y., NASA Contract RepNASA-CR-135144
2.	Crosbie, G. M. and Tennenhouse, G. J., J. Amer.
	Ceram. Soc., 65, 187 (1982).
3.	Crosbie, G. M., J. Electrochem. Soc., <u>129</u> , 2707 (1982)
4.	Bousquet, J., LeToffe, J. M., and Diot, M., J. Chim Phys. 71 1180 (1974)
5	Chudzicki M Ishonetery MigneSusters Inc.
5.	D. O. Der 226 There NY 12100 www.hlished.com
	12180, unpublished Work
~	(1980).
6.	"Selected Values of Chemical Thermodynamic Proper-
	ties", National Bureau of Standards, US Department of
	Commerce, Washington, DC, Circular 500, 1960.
7.	Janz, G. J., J. Phys. Chem. Ref. Data, 9, 791 (1980).
8.	Clark, R. P., J. Chem. Eng. Data, 20, 18 (1973).
9.	Janz, G. J., and Rogers, D. J., Proc. 8th Int. Sym.
	Thermophysical Properties, 2, 626 (1981).
10.	Pearson, T. G., and Robinson, P. L., J. Chem. Soc.,
	1304 (1931).
11.	Feher, F., Berthold, H. J., Fresenius Zeit, Anal.
	Chem., 138, 245 (1953).
12.	Janz, G. J., and Rogers, D. J., J. Applied Electro-
	chem., 13, 121 (1982).
13.	Rogers, D. J., and Janz, G. J., J. Chem. Eng. Data,
	27, 424 (1982).
14.	Janz, G. J., Coutts, J. W., Downey, Jr., J. R.,
	Roduner, E., Inorganic Chem., 15, 1755 (1976).
15.	Thomas, J. S., and Rule, S., J. Chem. Soc. (London),
	105, 177 (1914).
16.	Cleaver, B., Davies, A. J., Hames, M. D., Electrochem.
	Acta, <u>18</u> , 719 (1973).

Temperature Range		Event	
(°C)	thermicity	thermicity ΔH (
	$K_2S_3 + K_2S \neq 2K_2$	S ₂	_
265° - 293°	endothermic	2,610	(per mole K_2S_2)
293° - 340°	exothermic	9,880	(per mole K_2S_2)
	$K_2S_3 + S \rightarrow K_2S_3$	5 ₄	_
100° - 121°	endothermic	15,930	(per mole sulfur)
127° - 260°	* * *	6,380	(per mole K_2S_4)
	$K_2S_3 + 2S \rightarrow K_2S$	5 5	
100° - 121°	endothermic	15,590	(per mole sulfur)
129° - 177°	endothermic	1,372	(per mole K ₂ S ₅)
177° - 197°	endothermic	2,778	(per mole K_2S_5)*
177° - 217°	exothermic	1,058	(per mole K_2S_5)*+
	$K_2S_3 + 3S \rightarrow K_2S_3$	5	
100° - 121°	endothermic	15,000	(per mole sulfur)
132° - 177°	endothermic	4,100	(per mole K ₂ S ₆)
177° - 200°	exothermic endothermic	460 2,340	(per mol K ₂ S ₆)* (per mole K ₂ S ₆)*

Table 1. Thermicities of events during preparative reactions

* integrated for all the exotherms and endotherms in this temp. range

⁺prior to enthalpy of fusion

*** integrated over both the endo- and exo- therms

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Composition		t	\land H		
 sulfur (wt %)	formula	(°C)	(J g ⁻¹)	(J mol ⁻¹)	
		solid	state tr	ansition	
45.1	$\mathbf{K}_{2}\mathbf{S}_{2}$	146°	1.05	150	
		solid	🛫 melt (fusion)	
45.1 55.2 62.1 67.2 71.1	K ₂ S ₂ K ₂ S ₃ K ₂ S ₄ K ₂ S ₅ K ₂ S ₆	487° 302° 154° 205° 189°	128 143 56.1 113 102	18,280 24,940 11,630 26,990 27,610	
74.3 81.6	K ₂ S _{7.06} K ₂ S _{10,84}	sulfu and t v 188	r sat'd l he hexasu °C	ayer melts ∿ lfide layer :	118°C, melts

Table 2. Enthalpies of Fusion and Solid-Solid Transitions (a)

(a) for conversion of SI units to other units: 4.184 J = 1 cal.

Composition	t range	C _p = a +	bt + ct ² (J	deg ⁻¹ mol
	(°C)	a	b x 10 ³	c x 10 ⁶
K ₂ S ₂	57°-450°	110.47	64.58	-
K253	57°-252°	158.46	-438.27	1890.29
2 5	327°-492°	709.56	-2859.30	3906.18
K ₂ S ₁	57°-130°	146.90	425.43	-
K ₂ S ₅	57°-177°	176.41	274.32	-
K256	57°-150°	185.04	427.81	-

Table 3. Heat Capacity-Temperature Equations

Table 4. Heat Capacity Data

t (°C)	cp	c _p	(°C) C _p
	κ ₂ s	2	κ ₂ s ₅
60 100 200 400 450 487 507 550 590	0.80 0.82 0.91 0.96 0.98 m.p 1.13 1.13 1.13	114.3 116.9 123.4 129.8 136.3 139.5 t. 160.2 160.2 160.2	60 0.81 192.9 100 0.85 203.8 150 0.91 217.6 170 0.93 223.0 205 m.pt. 225 1.21 290.2 325 1.21 290.2 375 1.21 290.2 K ₂ S ₆
60 100 250 302 330 350 400 450	K ₂ s 0.80 0.77 0.84 0.96 m.p 1.10 1.07 1.09 1.23	139.0 133.6 146.4 167.0 5t. 191.4 186.4 190.6 213.9	60 0.78 210.7 100 0.84 227.8 150 0.92 249.2 160 0.93 253.5 189 m.pt. 215 1.14 308.3 320 1.14 308.3 K ₂ S _{7.06}
490 100 120 130 154 175 300 475	1.41 K 0.83 0.91 0.95 0.97 m.p 1.12 1.12 1.12	246.4 2 ² S ₄ 172.4 189.5 197.9 202.2 t. 233.2 233.2 233.2	118 S melting 189 K_2S_6 melting 260 0.55 169.4 280 0.54 166.5 300 0.55 169.4 310 0.56 172.1 $K_2S_{10.84}$ 118 S melting 189 K_2S_6 melting 200 0.21 91.4 220 0.20 86.9 270 0.20 86.9 280 0.20 86.9

[c_p, J deg⁻¹ g⁻¹; C_p, J deg⁻¹ mol⁻¹]

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(c _p , J deg ⁻¹ g ⁻¹ ; C _p , J deg ⁻¹ mol ⁻¹)						
	t (°C)	cp	Cp	t (°C)	с _р	с _р
		K ₂ S	4		K ₂ S ₅	
	-15°	0.73	151.7	-15°	0.71	170.5
	-10°	0.73	151.4	-10°	0.72	171.5
	- 5°	0.74	152.8	- 5°	0.73	173.2
	0 °	0.75	155.4	0 °	0.74	175.6
	5°	0.76	157.3	5 °	0.73	174.9
	10°	0.76	156.3	10°	0.74	176.6
	20°	0.77	158.4	20°	0.75	178.2
	40°	0.79	162.5	40°	0.78	185.5
	45°	0.93	186.6	45°	0.85	203.1
	50°	1.23	255.2	50°	1.07	254.4
	55°	1.14	234.8	55°	1.27	303.0
	60°	1.14	234.8	60°	1.16	276.5
	70°	1.14	234.8	70°	1.16	276.5
	75°	1.14	234.8	75°	1.16	276.5
	tg	r = 46.9	۶°C	•	^t g = 49.	4°C

Table 5 Heat Capacity Data: Glassy State and Super-Cooled Liquid State



Figure 2.

DSC scans illustrating thermicity of preparative reactions and of melting for a series of potassium polysulfides.

(a) thermicity of reactions observed by the in-situ DSC preparative technique: A: sulfur melting zone; B: chemical reaction zone; (b) fusion endotherms for sulfur and five polysulfides



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Figure 3.

Melting-crystallization behavior on thermal cycling a series of potassium polysulfides.

For the tetra-sulfide, the open circles show the DSC heating scan for a sample that had been "aged" in the molten state (\sim 800 hrs, at 315°C); no crystallization was observed on cooling from the molten state to ambient temperatures.



Figure 4.

The thermal behavior observed for polysulfide compositions greater than 71 wt% sulfur.

The DSC scans for "melting" are shown for two polysulfide compositions, $K_2S_{7,06}$ (74.3% sulfur) and $K_2S_{10,84}$ (81.6% sulfur), respectively. The behavioral pattern is that of the melting of a mixture of sulfur and K_2S_6 to form two immiscible liquid phases.



CANDIDATE MATERIALS FOR THE SULFUR ELECTRODE CONTAINER/CURRENT COLLECTOR CERAMIC OXIDES

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SUMMARY

In the search for materials for the container/current collector of the sulfur electrode in the sodium-sulfur cell, several chromium oxide based candidates for possible use as coatings have been tested. Samples of chromium oxide doped with Li20, MgO, NiO and Ta205 have been produced and characterized. The only n-type oxide - Ta205 - was rejected, a priori, owing to its high initial resistivity. Corrosion tests were carried out at 350°C in small laboratory cells using the bulk oxide samples as test electrodes. The latter were exposed to the extremes of electrochemical conditions to which the container/current-collector might be locally exposed in a practical Na/S cell for periods of time up to ~6 months. Surface attack was found to be negligible. However, an increase of bulk resistivity of the samples and of overpotential was observed in all cases. The increase of resistivity is attributed to the loss of carriers in the p-type semiconductor oxides, caused by equilibration of the latter with the negligible partial pressure of oxygen in the reducing atmosphere of the sulfurpolysulfide melt at 350°C. The increase of overpotential is interpreted in terms of the loss of the electroactive surface area due to, among other reasons, the accumulation of sulfur or solid lower sulfides at the interface and/or changes of its adsorptive properties.

Potential candidate materials are Li20-doped and Mg0-doped Cr203.

I. Introduction

Secondary batteries employing molten sulfur electrodes must operate above the melting point of sulfur (113°C) and of the medium containing the sulfur ions (> 300°C in the case of sodium polysulfides Na_2S_x , where $3 \le x \le 5$). At the upper end, the practical operating temperature is limited to ~400°C by the increasing vapor pressure of sulfur. Material problems, i.e., accelerated corrosion of electrodes, of the container/current collector, and seals also become more severe with increasing temperature. Container corrosion can have diverse effects. Apart from attacking the material and consuming active reactant (thereby reducing capacity), it forms surface layers that increase contact resistance to the felt electrode. Also soluble corrosion products can be redeposited, clogging the felt electrode, obstructing transport of active materials, and causing uneven current distribution. If deposited on the electrode surface, they may change its structure and wettability and therewith the kinetics of reactions occurring at this surface to the point where it may become partially or completely blocked. Corrosion products can also be deposited on the surface of the solid electrolyte partially blocking, damaging or destroying it by causing locally excessive current densities or by direct interaction or penetration.

Few conductive materials can withstand the attack of the polysulfide melt at the operating temperature of the Na/S cell. Metals are thermodynamically unstable. They form sulfides, whose solubility in the polysulfide/sulfur melt is, in most cases, not negligible. Some metals like chromium, molybdenum,' tungsten, and aluminum become covered by protective layers which, however, lose their passivating properties under certain conditions. Among electronically conductive materials which have been reported, or are expected, to resist polysulfide melt attack are various forms of carbon, certain oxides, carbides, nitrides, and conductive glasses.

This part of the ongoing study involves doped chromium oxides.

II. Corrosion in Polysulfide/Sulfur (PS) Melts

Chromium oxide has been chosen as the base for candidate coating materials in view of the prior experience of corrosion stability of Cr_2O_3 under static conditions (1).

III. Required Coating Characteristics

The necessary coating characteristics consist of inherent material properties:

- . Corrosion stability of the doped material interfacing with the polysulfide (PS) melt, when exposed to the wide range of the inter facial potential drops encountered in a practical Na/S cell.
- Sufficient and stable conductivity, such that the resistance of the coating is negligible in comparison with that of the entire Na/S cell. The percentage of the power loss as a function of material resistivity and coating thickness is shown in Fig. 1.



- Fig. 1 Power loss as a function of material resistivity and coating thickness for a 230 cm² container and for 0.02 Ω cell resistance due to all other sources.
- . Preferential wettability for sodium polysulfide rather than sulfur.

In addition to these inherent material properties, coatings must also have the following characteristics:

- Adherence to the substrate under conditions of thermal and electrothermal cycling.
- . Impermeability.

• Cost-viability, involving primarily a cheap production method of deposition on a self-healing substrate, i.e., one which passivates upon exposure to the melt.

IV. Conductivity of Oxides Studies

Doped Chromium Oxides

A reliable value of the resistivity of air-annealed polycrystalline Cr_{2O_3} (97+% dense, total impurity less than 0.01%) at 350°C is reported as 410 Ω cm (5). The interpretation of the electronic resistivity of highly pure Cr_{2O_3} in terms of defects, their concentrations, and mobilities remains incomplete. Lower partial pressures of oxygen (below 1125°C) cause higher resistivities. This, together with the sign of the thermoelectric coefficient, implies p-type conduction.

Impurities of p-type, such as NiO, appear to be charge compensated by electron holes (high $p_{0,2}$) or oxygen vacancies (low $p_{0,2}$). Thus, p-type dopants tend to enhance electronic conductivity after an air anneal.

A substantial increase in the conductivity of air annealed Cr_{203} (above 400°C) by doping with N10 (7,8) and Mg0 (7,9) has been reported. Literature data concerning the conductivity of Li₂O doped Cr_{203} are inconclusive (6,10). Other dopants are reported either to increase the resistivity (Nb₂O₅ (7,9,10) TiO₂ (7,8,11) WO₃ (8)) or to have little or no effect (Al₂O₃ (10), Fe₂O₃ (7), ZnO (8)).

V. Experimental

A. Materials

A separate paper on the preparation and characterization of doped chromium oxides will be published (presented at the April 1983 meeting of the American Ceramic Society).

B. Apparatus

Test Procedure

The corrosion test cell (Fig. 2) consisted of a glass vessel provided with graphite counter and reference electrodes and a graphite rod to which the test sample was dove-tailed and fastened by Dylon graphite cement. The contact resistance of this connection was negligible. The cell had a separate outlet for evacuation.



Fig. 2 Corrosion test cell.

The corrosion tests were preceded and followed by \underline{ex} situ measurements of sample resistivity as a function of temperature, using the AC method at 1.6 and 20 kHz.

The surfaces of the samples were examined before and after the corrosion tests by means of SEM,* EDAX,** and AES.***

The cell was assembled by fitting the electrodes and the thermocouple-well into the silicone stopper. A weighed amount of sodium polysulfide was filled into the cell in the dry box. Before heating in the furnace, the pressure in the cell was reduced to about 60 kPa by a vacuum system filled with prepurified argon to prevent backstreaming of air into the cell. Cells were tested at 350°C.

*** AES -- Auger electron spectroscopy

^{*} SEM -- Scanning electron microscopy

^{**} EDAX -- Energy dispersive analysis of x-rays

The samples were either exposed to cathodic or anodic polarization at various current densities and periods of time, or cycled at the desired current densities with a frequency of 5 cycles/day. The resistive contribution to the sulfur electrode potential was monitored by the AC and/or the interrupt method.

VI. Resistivities of Test Materials

These resistivities at 350° C are shown in Table I. The values given are measured with 20 kHz AC, and they are within 3% of the 1.6 kHz values in all cases. The capacitive contribution (phase shift) was negligible at both frequencies.

TABLE L

RESISTIVITY OF DOPED CHROMIUM OXIDE AT 350°C

AFTER AIR ANNEAL

Mol % dopant	Li ₂ 0	Mg0	NiO	Ta205
Cr ₂ 0 ₃ - CP				
	Ω	cm		
0		170.	<u>.</u>	
0.1	530.	2.5		-
0.2			16.0	
0.5	66.	4.3		
		5.4		
1.0	162.	3.8	3.8	
		4.3	5.0	
			7.8	
2.0			2.5	
			3.6	
Cr ₂ 0 ₃ - HP				
0.5	4.4	2.6ª	3.2	470.
	4.0	152.	4.3	

a) Air-annealed as a 2.5 mm thick bar.

Dopant homogeneity is likely to improve with the exposure of the oxide to an oxidizing environment, and such treatment would be expected to cause a shift of positive defect types from ionic ones (such as oxygen vacancies, which are likely needed for low-oxygen-pressure sintering, or chromium interstitials) to electron holes.

Resistivities considered acceptable (<100 Ω cm) were achieved in all samples (Table I), except CP - Cr₂O₃ without dopant, HP - Cr₂O₃ with Ta₂O₅, and CP - Cr₂O₃ with Li₂O. (CP: chemically pure, HP: high purity)

As an example, the resistivity of the as-oxidized NiO doped series is shown (Fig. 3) to follow a simple pattern in spite of different oxide purity level (HP and CP) and variations in density and grain size: a higher dopant level produces a lower resitivity. The approximate linearity suggests that the solubility limit for NiO is not passed.



Fig. 3 Resistivity of NiO-doped Cr_2O_3 at 350°C. Each symbol denotes bars from one hot pressing.

VII. Method of Testing Material Suitability

The corrosion tests, as a rule, involve bulk samples in order to separate the inherent material suitability from complications arising due to poor adhesion and/or porosity of coatings. Also, the development of an lengthy adequate coating method is a difficult task, and bulk testing allows the elimination of unsuitable materials at an early stage.

The bulk samples are tested as electrodes polarized in sodium polysulfide (PS) melt at 350°C.

The exposure of the sample to the PS melt is accompanied by extremely fast Faradaic redox reactions of the sulfur system. Therefore corrosion currents cannot be observed directly. Electrochemical measurements can only indicate changes in the apparent resistance, which may be due to

 a) changes of the resistance of the part of the circuit comprising the test and reference electrodes, and the PS melt,

and/or

b) changes of overpotential, reflecting the loss of electroactive surface area and/or change of the adsorptive properties of the interface.

Re a): The ohmic component involves primarily the ohmic drop, IR_e , in the oxide electrode. The remaining part (i.e., the resistance of the electrolyte between the test and reference electrodes, as well as that of the current leads) is constant and negligible as compared with R_e .

Re b): The overpotential consists mainly of concentration polarization. Therefore, a change of the melt composition in the immediate vicinity of the test electrode will result in a change of potential at constant current. An increase of activation overpotential may be observed due to the accumulation of reaction products blocking large parts of the surface.

The suitability of the tested sample has to be inferred from a) the observed changes in resistance and overpotential (at constant current) as a function of time and electrochemical treatment; b) comparison of the surface by optical, SEM, and spectroscopic methods before and after the experiment.

It follows that the acquisition of the electrochemical data necessary to evaluate the sample requires

- 1. Separation of the ohmic potential drop from the electrode overpotential. This is accomplished by monitoring the test electrode resistance, R_e ;
- Establishment of the real current density at the tested sample. Owing to the high resistivities of ceramic oxides, the current distribution along the sample may not be uniform, and therefore the apparent average density of the polarizing current does not represent the real situation.

In Fig. 4 the approximate equivalent circuit of the test cell is shown, on which the calculation of the current distribution at the test sample as a function of its resistivity is based (similar calculations have been previously reported (12)).



R, - RESISTANCE OF THE MELT PER UNIT LENGTH OF TESTED SAMPLE , 0/ CM

Rs	-	RESISTANCE OF TESTED SAMPLE PER ITS UNIT LENGTH,	Ω/cm
۷	-	STEADY STATE VOLTAGE,	۷
- I,	-	CURRENT INCREMENT, dī/jā, IN THE ELEMENT "K",	Юсм

Fig. 4 Approximate equivalent circuit of the test cell under current.

Solving (n + 1) Kirchhoff equations one arrives at the equation

$$(\overline{i}_{n+1} - \overline{i}_n) - (\overline{i}_n - \overline{i}_{n-1}) = (R_S/R_P) \overline{i}_n$$
(1)

where $i_k = i_k/I_T = dI(x)/dx$, $I_x = I_x/I_T$, x = x/L,

R_S = resistance per unit test-sample length,

- Rp = effective melt resistance per unit length of test sample,
- L = length of the immersed electrode,

 $I_T = total current.$

The solution of eq. (1), rewritten in the form

$$\overline{\mathbf{i}}''' - (\mathbf{R}_{\mathbf{S}}/\mathbf{R}_{\mathbf{P}}) \ \overline{\mathbf{i}}' = 0 \tag{2}$$

is given by

.

$$\overline{I}_{x} = \sinh \left(x \sqrt{R_{S}/R_{P}} \right) / \sinh \sqrt{R_{S}/R_{P}}$$
(3)

which represents the current profile along the electrode. The task is to find the part of the electrode length x, which practically carries no current, e.g. $I_X < 0.1$. Introducing the latter condition into eq.(3) and solving for x, one obtains

$$\overline{\mathbf{x}} = \sqrt{R_{\rm P}/R_{\rm S}} \sinh^{-1} \left[0.1 \sinh \sqrt{R_{\rm S}/R_{\rm P}} \right] \tag{4}$$

Then the electrode length which has to be taken into account in evaluating the current density is given by

$$1 - \overline{x} = 1 - \sqrt{R_P/R_S} \sinh^{-1} \left[0.1 \sinh \sqrt{R_S/R_P} \right]$$
(5)

The plot of the percentage of the electroactive electrode area as a function of $\sqrt{R_S/R_P}$ (lower scale) is shown in Fig. 5. On the upper non-linear abscissa scale resistivities of the test materials are indicated (which take into account the resistivity of the melt and the geometry of the test cell).

It can be seen that for the doped $Cr_{2}O_{3}$ samples (ρ > 50 $\Omega cm)$ over 90% of the current is carried by only ~6% of the electrode area.



Fig. 5 Percent of the electrode area which carries 80, 90, 95 and 99% of total current as a function of $\sqrt{R_S/R_P}$ (lower scale) and material resistivity (upper scale). R_S resistance of the electrode, R_P resistance of the electrode (Ωcm^{-1}).

VIII. Results and Discussion

Ceramic oxide samples were exposed to polysulfide melt at 350° C for periods of time of up to 6 months. During this time they were polarized anodically, cathodically, and/or cycled at current densities sufficient to expose the sample surface to the entire span of melt compositions between sulfur and Na₂S₃, to which parts of the container (current collector) can be exposed locally.

No signs of corrosion have been observed either by surface examination (SEM, EDAX, AES) (exemplified by Fig. 6) or by analysis of the melt carried out using ICP (inductivelycoupled plasma) atomic emission spectroscopy. Results of the latter analyses showed negligible traces of the elements present in the sample to be dissolved in the melt even after 150 days of exposure (10 - 20 ppm).



before









Fig. 7 Resistivity change with time during test of doped Cr_2O_3 samples.

However, all samples showed changes in their electrochemical behavior in that both the resistive and the other components of overpotential varied with time.

A. Resistivity as a Function of Time

The resistivity of all materials changed with time, as shown in Fig. 7 for doped $Cr_{2}O_{3}$. This behavior seems to be independent of polarization, since the resistivity of a non-polarized MgO doped $Cr_{2}O_{3}$ sample also increased upon exposure to $Na_{2}S_{5}$ melt (cf. Fig. 7). In the case of Li₂O doped HP-Cr₂O₃ and MgO doped Cr₂O₃, the resistivities eventually stabilized at values about 60 Ω_{cm} , measured <u>in situ</u>.

There was the possibility that the resistance increase was due to surface leaching of the dopant. However, this proved not to be the case. The phenomenon was found to be 1) a bulk effect (abrading the surface layer did not improve the conductivity of the sample as measured <u>ex situ</u> or <u>in situ</u> after reintroduction into a new cell), 2) resulting from exposure to the melt (cf. Table II, AC) as well as from exposure to sulfur vapor only (cf. Table II, AE), or to a low Po₂ in the absence of sulfur (cf. Table II, AF), 3) reversible (ex situ) by a 6 h anneal in air at 1500°C, i.e., by repeating the pretreatment of hot pressed oxides (cf. Table II, AD and ADA, AC and ACA).

This leads to the conclusion that the reducing atmosphere of a sulfur or polysulfide environment (in which the sample tends to equilibrate with an extremely low partial pressure of oxygen) results in an increase of oxygen vacancies and a concurrent decrease in the number of holes (carriers), and therefore of conductivity.

B. Overpotential (at Constant Current) as a Function of Time

The overpotential, remaining after deducting the IR drop from the total polarization, also shows an increase with time, for which there are three possible mechanisms.

- Part of this increase is due indirectly to the rise in sample resistance. This reduces the effective surface area of the sample (cf. Fig. 5) and thereby increases the current density.
- 2) An increase in polarization may also be caused by accumulation of reaction product(s) (S, Na₂S₂) or of Na₂SO₄ (which may result from oxygen diffusion through the porous graphite rods) on the sample surface. Even during cycling, reaction

TABLE II

SUMMARY OF TREATMENTS AND POST-TESTS FOR CHROMIUM OXIDE BARS EXPOSED TO THE SULFUR/POLYSULFIDE MELT

	Key to	treatme	nts: A - init	ial resistivity of	air
			anne:	aled samples, 1500	J°C, 6 h
			B - held	in air, 350°C for	- 20 h
			C - held	in wa255, 350°C,	no current
			350°	C	ide meit at
			E - held	above Na ₂ S ₅ , 350°	°C, with
			curr	ent	
			F - held	above Cu/Cu ₂ 0 at	350°C
		_	Resistivity	E _a (1)	$E_{a}(II)$
		Time	at 350°C	(100 to 350°C)	(300 to 350°C)
1	Treatment	(day)	<u>(Ωcm)</u>	eV	eV
			0.5 mol % Li2	0 – HP	
1	A	0	4.1	0.36	0.32
2	A.	0	3.1(4.0) ^a	0.45	0.35
3	A + B	20	4.4(4.5)a	0.35	0.33
4	A + D	20	10.8b		
5	A + D	183	47.	0.41	0.38
	followed by				
6	A		1.4	0.33	0.27
7	A + F	20	8.9	0.37	0.37
			0.5 mol % Mg	0 - CP	
8	A	0	4.3	0.36	0.31
ğ	A	ŏ	14.2	0.42	0.41
10	A + C	9ñ	86.(97)a	0.46	0.33
	followed by				0000
11	A		1.74	0.33	0.29
12	A + D	210	510.	0.57	0.51
			1.0 mol % Mg	0 - CP	
13	A	0	2.9	0.32	0-32
14	A + D	159	163.	0.45	0.37
15	A + E	159	90.	0.65	0.37
			2.0 mol % Ni	0 - CP	
16	Δ	0	2.5	0.41	0-35
17	A + D	19	170.	0.49	0.47
11	followed by	19	1.0.	0.49	V.47/
18	A		3.6	0.34	0.36

_ _ _ _ _ _

a) (Actual value) at 350°C differed more than 10% from least squared error fitted value.
b) <u>In situ</u> measurement.

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products are not always totally removed by the opposite halfcycle.

3) In some cases there is evidence which implies a change in surface adsorptivity toward more preferential wetting by sulfur. But it may also be argued that the accumulation of sulfur growing with each cycle during the later stages of testing is caused by the higher current density arising from the phenomena described under 1) and 2).

There is no easy way of separating these effects, which will be of minor importance in the practical Na/S cell, where the reaction predominantly proceeds on the graphite felt rather than on the current collector.

IX. Conclusions

- 1) The $Cr_{2}O_{3}$ based materials did not exhibit morphological or chemical surface changes upon prolonged exposure to sodium polysulfide (PS) melt under dynamic conditions.
- Wettability changes toward preferential wetting by sulfur may occur at the surface of these materials. However, the evidence is not conclusive.
- 3) The attainment of high densities for the sintering conditions used here depends on the addition of dopants. Dopants of 1+ and 2+ valence are effective in lowering the resistivity of high purity Cr_2O_3 .
- 4) A high purity of the precursor oxide does not appear to be necessary for either the low resistivity (except in the case Li₂0), nor for high corrosion resistance in sodium pentasulfide at 350°C.
- 5) Bulk resistivity increases during exposure to PS melt of up to 210 days are observed for all samples. This increase is not linked to the leaching of the substituent, but rather to the equilibration with the low oxygen pressure in the polysufide melt.
- 6) Among chromium oxide based materials, the high purity $Cr_{2}O_{3}$ doped with 0.5 mol% Li₂O seems most suitable as a potential coating. After the initial increase (over 30 days) the resistivity of the sample cycled in the PS melt remains constant at ~50 Ω cm for 150 days. In the case of MgO doped $Cr_{2}O_{3}$ the value is ~100 Ω cm after 100 days.
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REFERENCES

 Ford Motor Company, NSF-RANN Program, Contract No. NSF-C805 (AER-73-07199), Annual Reports for period June 30, 1974 to June 1975, July 1975 and for period June 30, 1975 to June 29, 1976, July 1976.

K. R. Kinsman and W. L. Winterbottom, Thin Solid Films <u>83</u>, 417 (1981).

 T. D. Claar, "The Kinetics and Mechanisms of Sulfidation of Chromium Oxide," Ph.D. Thesis, Northwestern Univ., Evanston, Illinois, June 1978.

D. R. Stull, Dir., "JANAF (Joint Army-Navy-Air Force) Thermochemical Tables," Dow Chemical Co., Midland, Michigan. Also, 1975 Supplement.

K. C. Mills, <u>Thermodynamic</u> <u>Data</u> for <u>Inorganic</u> <u>Sulphides</u>, Selenides and <u>Tellurides</u>, <u>Butterworths</u>, <u>London</u>, 1974.

N. K. Gupta and R. P. Tischer, <u>J. Electrochem. Soc.</u>, <u>119</u>, 1033 (1973).

- R. A. Bailey and J. M. Skeaff, <u>J. of Chemical and Engineering</u> Data, 24, 1267 (1979).
- D. S. McClure, in "Physics and Chemistry of Ceramics," C. Klingsberg, Editor, p. 110, Gordon and Breach, New York, 1962.
- D. B. Meadowcroft and F. G. Hicks, (Proc.) Brit. Ceram. Soc., No. 23, 33 (1973).

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- H. V. Anderson and C. A. Sorrell, "Development and Characterization of High Temperature Electrically Conducting Oxides." U.S. Dept. of Energy Report DOE/ER/10598-2, Nov. 1981, Contract #DE-AC02-80ER10598.
- D. de Cogan and G. A. Lonergan, <u>Solid State Comm.</u>, <u>15</u>, 1517 (1974).
- 8. K. Hauffe and J. Block, Z. physik. Chem., 198, 232 (1951).
- W. A. Fischer and H. Dietrich, <u>Z. physik</u>. <u>Chemie</u> (<u>N.F.</u>), <u>41</u>, 205 (1964).
- W. A. Fischer and G. Lorentz, <u>Arch. Eisenhüttenwesen</u>. <u>28</u>, 497 (1957).
- W. A. Fischer and G. Lorentz, <u>Z. physik. Chem. (N.F.)</u> 18, 308 (1958).
- G. Robinson, Current Distribution in Tubular Sulfur Cells, ECRC/M-1008, U.S. Department of Commerce, PB-276512.

SOLUBILITY OF Li₂S IN LiF-LiCl-LiBr ELECTROLYTE: MEASUREMENTS AND CALCULATIONS

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ABSTRACT

The solubility of Li₂S in LiF-LiCl-LiBr electrolyte was determined at 739 and 773 K, by measuring the change in the emf of the Li-Al/Ni₃S₂ couple as the Li₂S concentration was changed in the electrolyte. The measured solubility values were 6840 ± 300 ppm at 739 K and were 8700 ± 300 ppm at 773 K. The Li₂S solubilities in different solvents have been calculated using the conformal ionic solution theory. The computed values are in very good agreement with experiments and confirm the strong dependence of the solubility on the composition.

INTRODUCTION

High performance lithium-alloy/iron sulfide cells have been considered as possible power sources for electric vehicles(1). These cells were operated at high temperatures (703 to 773 K) and utilized Li-Al or Li-Si negative electrodes, FeS positive electrodes, and a molten salt electrolyte. In the early work, LiCl-KCl of eutectic composition (58.2 mol %LiCl-41.8 mol %KCl) was the only candidate but various Li containing electrolytes were also considered, *i.e.*, LiCl-rich LiCl-KCl (typically 67 mole %LiCl), LiF-LiCl-KCl, or LiF-LiCl-LiBr (1). It was shown that, upon cycling, local electrolyte compositional changes occurred resulting from a combination of ion transport processes and chemical reactions in the cells containing LiCl-KCl as electrolyte (2-4). These compositional changes could be avoided if the LiF-LiCl-LiBr electrolyte was used. However, the final discharge products, iron and lithium sulfide, are unaffected by the temperature or the electrolyte. A systematic investigation of the Li₂S solubilities in LiCl containing electrolytes as a function of temperature is technologically significant. From a fundamental point, the solvent dependence of the Li₂S solubility can be examined using available molten salt theories.

The solubility of Li₂S in LiCl-KCl eutectic (58.2 mol %LiCl-42.8 mol %KCl) has been thoroughly investigated in the temperature range 673 to 823 K (5-7) using different experimental techniques. The results indicate a relatively low solubility (e.g., \sim 1000 ppm at 723 K) increasing with temperature (\sim 2000 ppm at 773 K). At a fixed temperature the Li₂S solubility decreases with increasing KCl content and increases with the LiCl content (8). The Li₂S solubility is relatively high in the LiF-LiCl eutectic (5).

In this paper, we report solubility measurements of Li2S in the LiF-LiCl-LiBr electrolyte

(22 mol \Im -31 mol \Im -47 mol \Im) at 739 and 773 K using electromotive force (emf) measurements. The results are compared to those calculated from equations derived by Saboungi et al. (5,9) on the basis of the conformal ionic solution theory.

EXPERIMENTAL

The solubility of Li₂S in the LiF-LiCl-LiBr eutectic mixture was determined using the Nernstian response of the Ni/Ni₃S₂ half-cell to Li₂S activity in the following electrochemical cell:

$Ni/\alpha - Al, \beta - LiAl/LiF - LiCl - LiBr, Li_2S/Ni_3S_2/Ni$

The details of cell construction have been reported elsewhere (10). In this work the ternary solution of eutectic composition was used instead of the LiCl-KCl electrolyte; the Li-Al electrode consisted of a premixed alloy (38 atom %Li, 62 atom %Al). The sulfide concentrations were changed by successive additions of weighed amounts of Li2S. Following each addition, the cell was discharged and held at temperature for ~ 16 Hrs. After this time period, the Ni-200 rod was anodized to produce between three and ten coulombs of Ni₃S₂ (1.6 and 6.2 mg, respectively); the emf of the Li-Al/Ni₃S₂ couple was then measured. The time needed to reach an equilibrium value was typically 20 minutes, and the emf value was stable for periods in excess of 1 hour. Additions of Li2S were continued until at least three consequent compositions yielded the same emf, indicating that the electrolyte was saturated with Li2S. The cell temperatures was measured with a calibrated chromel-alumel thermocouple; the two temperatures, 739 and 773 K, were chosen to correspond to the extreme temperatures of practical interest in the operation of the Li-Al/FeS cells. At the end of each set of experiments, the anodized Ni-200 rod was removed quickly from the electrolyte and examined metallographically and by Xray diffraction. The results of these examinations showed that the only nickel containing sulfide phase formed was Ni₃S₂.

RESULTS

The emf data as a function of Li₂S concentration in the melt are shown in Fig. 1. At each temperature, the data can be fit by two straight lines. The first line shows a dependence on the Li₂S concentration, while the second is independent of the Li₂S concentration and is horizontal. The intersection of these two lines yields the Li₂S saturation solubility. Thus, the measured solubility of Li₂S is 6840 ± 300 ppm ($8.8 \pm 0.4 \times 10^{-3}$ mole fraction) at 739 K and 8700 ± 300 ppm ($1.12 \pm 0.4 \times 10^{-2}$ mole fraction) at 773 K. The experimental Nernstian slope values are 70.1 and 76.4 mV at 739 and 773 K, respectively, and these values agree well with the theoretical values of 73.3 at 76.7 mV calculated for the expected reaction:

$$4LiAl + Ni_3S_2 \rightarrow 3Ni + 2Li_2S + 4Al \tag{1}$$

X-ray diffraction results of the products are consistent with the above cell reaction.

DISCUSSION

Our results confirm the trend noted in the earlier work (5), namely that Li_2S solubility increased with increasing LiCl content of the electrolyte. In what follows, the dependence of the Li_2S solubility on the nature and composition of the solvent is analyzed using theoretical considerations based on the conformal ionic solution theory (5,9).

As mentioned above, the solubility of Li_2S in the LiCl-KCl eutectic has been thorougly investigated so one could use these data as a baseline for the calculations.

The dissolution of Li₂S in LiCl-KCl leads to a ternary reciprocal system (5); at low sulfide concentrations, the activity coefficient of Li₂S, γ_{Li_2S} , can be expressed as:

$$RTln\gamma_{Li_2S} = 2[X_K \Delta G^o + X_K (X_K - X_{Li})\lambda_{Cl} + X_K X_{Li}\lambda_S + X_{Li}\lambda_{Li} + X_K \lambda_K] - \frac{X_K X_{Li} (\Delta G^o)^2}{ZRT}$$
(2)

where ΔG^{o} is the Gibbs free energy change for the reaction:

$$1/2Li_2S(l) + KCl(l) \rightleftharpoons 1/2K_2S(l) + LiCl(l)$$
(3)

In Equation [2], X_{Li} and X_K are the ion fractions of Li and K, respectively, λ_i is an interaction coefficient for the binary subsystem having *i* as the common ion and Z is a parameter, similar to a coordination number and is taken to be 6. Experimental values for λ_{Li} and λ_K for the two common cation subsystems (LiCl-Li₂S and KCl-K₂S, respectively) are not available to our knowledge; they are likely to be small and thus are assumed to be zero. The value of λ_S has not been measured but is likely to be negative and of the same order of magnitude as λ_{Cl} for the LiCl-KCl; we therefore assume that $\lambda_S = \lambda_{Cl} = -3.2$ kcal.mol⁻¹ (11). The calculated value of ΔG^o is equal to 8.32 kcal.mol⁻¹ at 823 K (12,15).

The dissolution of Li₂S in LiF-LiBr-LiBr leads to a quaternary additive system. At low sulfide concentration, the activity coefficient, γ_{Li_2S} , is given to a first approximation (5) by:

$$RTln\gamma'_{Li_2S} = -2(X_{Cl}X_{Br}\lambda_{LiCl-LiBr} + X_{Cl}X_F\lambda_{LiCl-LiF} + X_{Br}X_F\lambda_{LiBr-LiF})$$
(4)

where $\lambda_{LiCl-LiF} = -0.2 \text{ kcal.mol}^{-1}$, $\lambda_{LiCl-LiBr} = 0.1 \text{ kcal.mol}^{-1}$ and $\lambda_{LiBr-LiF} = -0.9 \text{ kcal.mol}^{-1}$ (11). Thus, the solubility of Li₂S in the LiF-LiCl-LiBr eutectic, N'_S, can be calculated from that in LiCl-KCl eutectic by :

$$N'_{S} = N_{S} \left(\frac{X_{Li}^{2}}{X_{Li}^{\prime}}^{2} \right) \left(\frac{\gamma_{Li_{2}S}}{\gamma_{Li_{2}S}^{\prime}} \right)$$
(5)

where N_S is the measured value of Li₂S solubility in LiCl-KCl eutectic at the temperature of interest and X and X' are the ion fractions of lithium in the LiCl-KCl eutectic and LiF-LiCl-LiBr electrolyte, respectively.

From the preceding equations, the calculated values are 6350 ppm $(8.2 \times 10^{-3} \text{ mol} \text{ fraction})$ and 8175 ppm $(1.06 \times 10^{-2} \text{ mol} \text{ fraction})$ at 739 and 773 K, respectively. For comparitive purposes, the measured values were 6840 ± 300 ppm and 8700 ± 300 ppm at these same temperatures. One should be aware, however, that $RT \ln \gamma'_{Li_2S}$ is assumed to remain constant in this temperature range.

The Li₂S solubility calculated for different solvents based upon that for the LiCl-KCl eutectic is sensitive to the values obtained for ΔG^{o} of reaction [3]. These calculations indicate, however, that small changes in temperature or the use of coordination parameter of either four or five as compared to six do not change the computed values significantly. The results of such calculations are shown in Figs. 2-4. Figure 2 shows that the Li₂S solubility relative to that in LiCl-KCl eutectic increases as the LiCl content is increased for a given value of ΔG^{o} , and changes markedly as ΔG^{o} for reaction [3] is changed from 6320 calories by increments of 2000 calories. The major uncertainties in the numerical values of ΔG^{o} stem from the large uncertainties affecting the experimental values assigned to the Gibbs free energy of formation of Li₂S and K₂S (see for example refs. 12, 13,14, 15).

Similar calculations were carried out for LiCl-rich and KCl-rich LiCl-KCl solutions at 673 and 723 K and the results were compared to data reported by Warin *et al.* (8). For these calculations, the solubility in the off-eutectic electrolyte was computed from equation (5). At 723 K, the computed Li₂S solubility is 2.14×10^{-3} mol fraction (1840 ppm) for LiCl-rich (66 mol %LiCl) and agrees well with the measured value of 2.16 $\times 10^{-3}$ mol fraction (1860 ppm). For KCl-rich (54 mol %LiCl) electrolyte at 723 K, the computed value is 1.27×10^{-3} mol fraction (1063 ppm) and the experimental value is $1.06 \pm 0.1 \times 10^{-3}$ mol fraction (840 ppm). At 673 K, the computed solubility becomes 1.29×10^{-3} mol fraction (1104 ppm) for LiCl-rich (65 mol %LiCl) electrolyte, and this value compares well with the measured value of $1.28 \pm 0.13 \times 10^{-3}$ mol fraction (1100 ppm). For KCl-rich electrolyte (55 mol %LiCl), the calculated value is 8.05×10^{-4} mol fraction (664 ppm), a value which agrees well with the measured value of $8.04 \pm 0.8 \times 10^{-4}$ mol fraction (650 ppm).

The excellent agreement between calculated and measured values suggests that the free energy values derived for K_2S and Li_2S from data in Mills (12) are reliable. In fact, the computed values for Li_2S at 673 and 723 K agree within 1 kcal.mol⁻¹ with those which can be derived from the data of Tomczuk *et al.* (13). The values derived for K_2S agree well with those derived using the data of Johnson and Steele (14), but differ significantly from the data in the JANAF tables (15). (Note that there is a difference of ~10 kcal.mol⁻¹ between the JANAF and Johnson and Steele data).

From our results and the calculations reported in Table 1, better agreement between measured and calculated Li₂S solubility values is obtained if the value for the Gibbs free energy of formation of K₂S as derived from the data of Johnson and Steele (14) is used. A similar trend is also obtained if the experimentally derived values for Li₂S (13) are used for such calculations. Thus the results of our calculations suggest that the ΔG values for K₂S over the temperature range considered (673-723 K) in the JANAF tables are too positive, and the correct values should be closer to the results of Johnson and Steele (14).

CONCLUSION

The solubility of Li₂S in LiF-LiCl-LiBr was determined at 739 and 773 K. Calculations using an equation deduced from the conformal ionic theory yield solubility values which are in excellent agreement with experiment and confirm the observed trend in the variation of the solubility. Additional calculations for Li₂S solubility in LiCl- and KCl-rich electrolytes at 673 and 723 K reproduce experimental values reported earlier. These calculations also suggest that the value reported by Johnson and Steele (14) is more consistent with our analysis than that selected by JANAF.

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REFERENCES

- 1. D. L. Barney, et al., Argonne National Laboratory, ANL-81-65 (1982).
- 2. Z. Tomczuk, S. K. Preto, and M. F. Roche, J. Electrochem. Soc., 128, 760 (1981).
- 3. C. E. Vallet and J. Braunstein, ibid, 126, 1193 (1978).
- 4. R. Pollard and J. Newman, ibid, 126, 1713 (1979).
- 5. M. L. Saboungi, J. J. Marr, and M. Blander, Met. Trans. B, <u>10B</u>, 477 (1979).
- 6. M. L. Saboungi, J. J. Marr, and M. Blander, J. Electrochem. Soc., <u>125</u>, 1567 (1978).
- 7. C. H. Liu, A. J. Zielen, and D. M. Gruen, ibid, 120, 67 (193).
- 8. D. Warin, Z. Tomczuk, and D. R. Vissers, ibid, 130, 64 (1983).
- 9. M. L. Saboungi, J. Chem. Phys., 73, 5800 (1980).
- 10. Z. Tomczuk, D. Warin, and D. R. Vissers, Abstract 688, Extended Abstracts of Electrochemical Society, Vol. 82-1, 1982.
- 11. J. Lumsden, <u>Thermodynamics of Molten Salt Mixtures</u>, Academic Press, New York, 1966.
- K. C. Mills, Thermodynamic Data for Inorganic Sulfides, Selenides, and Tellurides, Buttersworth London Publishers, 1974.
- 13. Z. Tomczuk, M. F. Roche, and D. R. Vissers, J. Electrochem. Soc., <u>128</u>, 2255 (1981).
- 14. G. K. Johnson and W. V. Steele, J. Chem. Thermodynamics, 13 985 (1981).
- 15. JANAF Thermochemical Tables, Chemical Co., Midland, Michigan, March 31, 1978.

Electrolyte	T,K	Measured Solubility, ppm (mol fraction)	Predicted Solubility Using K ₂ S Values from Johnson (A) and JANAF (B), ppm (mol fraction)			
			A	B		
65 mol % LiCl, 35 mol % KCl	673	1100 (1.28 × 10 ⁻³)	1261 (1.47 × 10 ⁻³)	1729 ($2.02 imes 10^{-3}$)		
55 mol % LiCl, 45 mol % KCl	673	$650~(8.04 imes10^{-4})$	$617~(7.64 imes10^{-4})$	513 (6.35 $ imes$ 10 ⁻⁴)		
66 mol % LiCl, 34 mol % KCl	723	$1860~(2.16 imes10^{-3})$	$2064~(2.39 imes10^{-3})$	$2891~(3.36\times 10^{-3})$		
54 mol % LiCl, 46 mol % KCl	723	840 (1.06 \times 10 ⁻³)	970 (1.21 × 10 ⁻³)	769 (9.57 $ imes$ 10 ⁻⁴)		
22 mol % LiF, 31 mol % LiCl, 47 mol % LiBr	<pre>{ 739 773</pre>	$6840 \ (8.80 \times 10^{-3})$ 8700 \ (1.12 \ \ 10^{-2})	$10516 (1.36 \times 10^{-2})$ $12415 (1.61 \times 10^{-2})$	$15400 (2.00 \times 10^{-2})$ 19484 (2.50 × 10^{-2})		
				10101(200 × 10)		

 Table 1.
 Comparison of Li₂S Solubility Results With Calculations When Other Values For K₂S Are Used



Fig. 1. Emfs of Li-Al/Ni₃S₂ cell for different sulfide concentrations in LiF-LiCl-LiBr electrolyte at 739 and 773 K. The slanted portion of the solid curves represent the least squares fit of the data before saturation with Li₂S.



Fig. 2. Effect of electrolyte composition and AG* of Reaction 3 on computed Li₂S solubility. Gibbs free energy change values are 6320 cal (---), 8320 cal (---), 10320 cal (-----), and 12320 cal (-----).



Fig. 3. Effect of temperature on predicted Li₂S solubility relative to that in LiCl-KCl eutectic for a given value for ΔG of Reaction 3. Temperatures are 673 K (--), 723 K (---), 773 K (----), and 823 K



Fig. 4. Effect of coordination parameter on Li₂S solubility relative to that in LiCl-KCl eutectic. Coordination parameter values are 4 (---), 5 (---), and 6 (----).

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SPECTROSCOPIC STUDIES OF TRANSITION METAL IONS IN MOLTEN ALKALI METAL CARBOXYLATES^{*}

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Abstract

Electronic absorption and C-13 NMR spectroscopic studies were carried out to investigate the structure of (i) alkali metal formate (Fm) and acetate (Ac) eutectic melts and (ii) solutions of 3d transition metal (TM) cations in these eutectics. Measurements were made over the temperature range $90 \rightarrow 190^{\circ}$ C. The most stable oxidation states of the individual TMs in the Fm and Ac eutectics were: Ti³⁺, V³⁺, VO²⁺, Cr³⁺, Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, and Cu²⁺. The ligand field absorption spectra obtained in these carboxylate melts bore a consistent resemblance to the spectra of these same cations in aqueous media, but the absorptivities were generally higher than are observed for the hexaguo complexes. The results were interpreted in terms of the existence of bidentate coordination in some (if not all) cases, leading to noncentrosymmetric complexation geometries. Key results of the NMR measurements included the apparent observation of two different carboxylate anion environments in Ni²⁺ solutions. C-13 spin-lattice relaxation of the carboxylate anions in the TM-free eutectics was found to be controlled by dipolar coupling to another nucleus. In the TM-containing solutions, the spin-lattice relaxation times were reduced by a factor of 10 to 1000, evidencing the expected shift to electron-nuclear dipolar coupling. Activation energies for viscous flow derived from the spin-lattice relaxation measurements on TM-free melts were in the $10 \rightarrow 11$ kcal/mol range, reflecting the highly ordered. glassy nature of the eutectics studied.

Introduction

Whereas there has been considerable spectroscopic study of inorganic ionic melts, relatively few studies of the spectroscopy of liquid organic anion salts, such as formates and acetates, have been reported. The work that has appeared has consisted mainly of absorption spectrophotometric (1-4) and proton NMR studies (5,6). This paper presents selected results of recent work in our laboratory involving electronic absorption and C-13 NMR measurements on (i) molten alkali metal formates, acetates, formate-thiocyanate mixtures, and acetate-thiocyanate mixtures and (ii) solutions of 3d transition metal ions therein. These studies provide a unique

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opportunity to explore (i) the highly ordered, viscous nature of some alkali carboxylates and carboxylate-thiocyanate mixtures in the molten state, (ii) the ligand field properties of the formate and acetate ions, and (iii) the coordination chemistry of the 3d transition metals in melts containing carboxylate anions.

Experimental Section

To provide the broadest possible temperature range for study and, at the same time, mininize decomposition, low-melting eutectic mixtures of the alkali metal formates, acetates, and thiocyanates were employed. To prepare these eutectic mixtures, reagent grade chemicals were dried in a vacuum oven overnight at ~110°C, weighed to desired proportions, mixed, and loaded into Pyrex filter tubes. All these operations were performed in a helium atmosphere glove box. The loaded filter tubes were capped off with stopcock joints, removed from the glove box, placed in a Marshall furnace, and connected to a glass vacuum line. The salt mixtures were fused under vacuum to remove any remaining moisture and forced through the Pyrex filters (10-20 μ m pore size) by pressurization to ~10⁵ Pa with dry helium.

In the case of samples prepared for C-13 NMR experiments, additions of 5 to 10 mol % of C-13-containing CH₃C^{*}OOK, HC^{*}OOK, and KSC^{*}N were included in the preparation. The C-13 enriched salts (90% C-13 enriched) used in these preparations were obtained from Stohler Isotopic Chemicals. The transition metal (TM) solutions were prepared by adding small measured quantities of the TM acetate or chloride (commercial high-purity grades) to the carboxylate-containing eutectic, fusing under vacuum, and filtering as described above. Since the quantity of TM acetate or chloride added was always a very small fraction of the weight of a sample (<0.5 wt %), the traces of acetate or chloride introduced as a foreign anion (e.g., to formate and formate-thiocyanate melts) was considered inconsequential to the experimental results.

Electronic absorption spectra were recorded using a Cary 17H Absorption Spectrophotometer coupled with a specially designed furnace for elevated-temperature spectrophotometric measurements. The sample to be studied was loaded into an optical assembly consisting of a 1-mm-path-length, UV-grade quartz cell (12.5 mm wide and 45 mm high, from J&S Scientific) fused to the end of a 15 mm diameter quartz tube (~200 mm long) that terminated at the opposite end with a ground joint. After loading in the glove box, the cell assembly was capped off with a stopcock joint, returned to the Marshall furnace, connected to the glass vacuum line, evacuated, and heated to ~150°C. When the sample was completely melted, the cell assembly was backfilled with dry helium, forcing the melted salt to fill the optical path of the cell if it had not already done so. The cell assembly was then rapidly transferred to the preheated spectrophotometer furnace before the sample had a chance to solidify.

C-13 NMR spectra were obtained using a Varian FT-80 Fourier Transform NMR Spectrometer equipped with a variable temperature probe. The spin-lattice relaxation experiments were performed by the inversion-recovery method (7). The NMR cells used in this work were constructed in the following way: A 100 mm

long, 5 mm OD, thin-walled Pyrex tube was fused to a 60 mm length of 8 mm OD, thin-walled Pyrex tubing using a glass lathe. The open end of the 8 mm OD tube was sealed off and a ground joint was fused to the open end of the 5 mm OD tube to finish the cell. A "lock tube" was prepared by sealing a 20 mm depth of (CD₃)₂SO into a 70 mm long, 3 mm OD, thin-walled Pyrex tube (closed at one end). The seal was made near the middle of the tube, with care taken to preserve its straightness. (The deutero-dimethyl sulfoxide in the "lock tube" provides the field lock for the NMR spectrometer during pulsing.) First the carboxylate sample and then a "lock tube" were loaded into an NMR cell, and the cell was sealed off under slightly reduced pressure at a point just below the ground joint. The sample was then melted (using a heat gun) and placed in the preheated probe of the NMR spectrometer. The amount of sample placed in each tube was adjusted so that the height of liquid in the tube during NMR measurements was 2 to 2.5 cm (i.e., enough to just slightly overfill the receiver coil volume). This type of cell was found to be well suited for NMR studies using the FT-80 with sample spinning and operation to $\sim 200^{\circ}$ C, provided the gross cell weight did not exceed ~ 8 g.

To provide an approximate reference point for the C-13 chemical shifts, a small quantity of methyl benzoate having 90% C-13 substitution in the carboxyl position (obtained from Prochem/Isotopes) was included in some of the "lock tubes." Chemical shifts relative to tetramethyl silane (TMS) were then determined by adding the known chemical shift difference between the methyl benzoate carboxyl carbon (MBCC) and TMS (166.8 ppm) to the chemical shifts observed in the carboxylate melts relative to the MBCC.

Results and Discussion

The experimental results of the electronic absorption and C-13 NMR studies and their interpretation are presented and discussed below in two separate sections. In the case of the electronic absorption measurements, comparisons are made with the prior related work of Ingram and co-workers (1, 2) and Bailey et al. (3). The authors are not aware of any previous C-13 NMR studies of molten carboxylates.

Electronic Absorption Studies. — Attempts were made to obtain the ligand field spectra of a variety of 3d TM cations dissolved in the eutectic salts listed in Table I. Spectra were recorded for molten samples and, in some cases, for the transparent glasses formed from these melts after cooling to room temperature. Beyond mentioning that the spectrum of each glass was very much the same as that of its corresponding melt, the remainder of this paper will focus on the analysis and interpretation of the data for the molten state, with the understanding that the findings most probably apply to the glasses as well.

The cations of *titanium* are only marginally stable in acetate media even at the lowest liquidus temperatures (i.e., around 100°C). Spectroscopic evidence of Ti^{2+} and Ti^{3+} has been observed in Ac-02. Ti^{3+} introduced to Ac-02 as $TiCl_3$ appears to react over a period of several hours, producing Ti^{2+} and (presumably) Ti^{4+} . Initially, prior to any significant decomposition, Ti^{3+} solutions in Ac-02 are purple in color. No studies have been made to date on Ti^{3+} in formate- and thiocyanate-

containing melts.

In the case of *vanadium*, the 3+ oxidation state is reasonably stable in Ac-01 and Ac-02, although evidence for VO^{2+} has been seen in the spectra of VCl_3 solutions in both eutectics when they were left standing at elevated temperature (i.e., ~150°C) for a few days or were intentionally exposed to oxygen. Our observations of the spectral characteristics of the vanadyl ion are essentially the same as those of Duffy and Ingram (2). V^{3+} solutions in formate- and thiocyanate-containing melts decompose rapidly. A typical spectrum of the dark green V^{3+} solution in Ac-02 is shown in Fig. 1. (In Fig. 1, and in all subsequent figures presenting absorption spectra, the bands marked with an asterisk are due to vibrational overtones of the formate or acetate ions. With the exception of these overtone bands, the optical transparency of alkali formate and acetate melts is found to be quite good over a wide range of wavelengths.)

For chromium, the 3+ state is extremely stable in all of the eutectics listed in Table I to temperatures as high as 170°C. Cr^{2+} introduced to Ac-02 (as $CrAc_2$) reacted immediately upon fusion to give Cr^{3+} . Cr^{3+} solutions in Ac-02 and Fm-02 are dark green in color and are characterized by the spectrum shown in Fig. 2. The findings for Cr^{3+} are in accord with the results of Duffy and Ingram (2).

Only the 2+ state of manganese was tested. Mn^{2+} solutions formed by introduction of $MnAc_2$ were extremely stable in Ac-02 and Fm-02 to 150 °C. None of the other eutectic salts in Table I were tested with Mn^{2+} . The spectrum of Mn^{2+} in Ac-02 and Fm-02 is very much like the spectrum of $Mn(H_2O)_6^{2+}$ in aqueous solution (8). Molar absorptivities, ϵ , are extremely small ($\epsilon < 0.1$), evidencing a decidedly low-spin ligand field. Solutions of Mn^{2+} in formate and acetate eutectics have a pale pink color. Duffy and Ingram (2) reported that Mn^{2+} solutions in acetate glasses were yellow-brown in color and that their spectra were "uninformative." In our work we have found the formation of brownish melts to be indicative of decomposition.

Solutions of *iron* in the 2+ state are relatively stable in all of the eutectics listed in Table I. These solutions are reddish-orange in color and their spectra typically resemble the one in Fig. 3. Fe^{3+} in Ac-02 (introduced as FeAc₃) appears to be at least partially reduced to Fe^{2+} . This interpretation of the results obtained with iron in the 2+ and 3+ states differs somewhat from the one given by Duffy and Ingram (2), who reported that yellow-brown melts formed, that Fe^{3+} was the stable oxidation state, and that the absorption spectra were "uninformative."

In the case of *cobalt*, Co^{3+} reacts to form Co^{2+} , the only stable oxidation state found for cobalt solutions in the eutectics in Table I. Co^{2+} solutions in Ac-01, Ac-02, and Fm-02 are a beautiful bluish purple color. The absorption spectra of these solutions are typified by the one shown in Fig. 4. Our absorption spectral data for Co^{2+} in molten acetate media are in accord with earlier work (1-3).

Only the 2+ state of *nickel* has been investigated in the eutectics listed in Table I. Solutions in Ac-01 and Ac-02 are a yellow-green color and are reasonably stable

over periods of several hours to a day. However, on prolonged standing at elevated temperature (i.e., $\sim 150^{\circ}$ C) evidence of gradual decomposition can be seen. The spectrum of Ni²⁺ in Ac-02 is shown in Fig. 5. Our spectral results for solutions of Ni²⁺ in molten acetate media are in good agreement with prior work (2,3). Solutions of Ni²⁺ in formate-containing eutectics were found to decompose rapidly just after melting occurred.

Efforts to prepare Ac-02 and Fm-02 solutions of *copper* in both the 1+ and 2+ oxidation states were generally unsuccessful. Slowly decomposing solutions (blue in color) of Cu^{2+} were prepared in Ac-02 on a number of occasions, but the rate of decomposition was such that appreciable deterioration of the sample occurred during the time span of a typical spectral run (around 20 to 30 minutes). The best spectra obtained for these Cu^{2+} solutions showed a broad absorption band centered near 13,900 cm⁻¹, but having appreciable Jahn-Teller distortion of the long-wavelength side. This experience with Cu^{2+} in alkali acetate media is consistent with that reported by Duffy and Ingram (2).

The most conclusive results obtained to date in this work have been those for formate and acetate solutions of V^{3+} , Cr^{3+} , Fe^{2+} , Co^{2+} , and Ni^{2+} ; hence, the remainder of the present discussion will focus on these solutions. Work on Ti^{3+}/Ti^{2+} , the vanadyl ion (VO²⁺), Mn²⁺, and Cu²⁺ is either incomplete or inconclusive and will be left for a future paper, as will be the results for thiocyanatecontaining melts.

The absorption spectrophotometric data for V³⁺, Cr³⁺, Fe²⁺, Co²⁺, and Ni²⁺ are summarized in Table II. In appearance, the ligand field spectra of these cations (see Figs. $1 \rightarrow 5$) in molten carboxylate media are very much like the corresponding spectra in aqueous solution (8), where octahedral hexaquo cations, $M(H_2O)_6^{n+}$, are known to exist. However, in several cases, the molar absorptivities (particularly those for the divalent cations Co^{2+} and Ni^{2+}) are considerably greater in molten carboxylate media than in aqueous media. This finding regarding the absorptivities is consistent with the prior work of Duffy and Ingram (1,2) and Bailey et al. (3) on TM solutions in both molten and glassy alkali carboxylates. A review of these studies and of similar effects in other molten salt systems has been made by Johnson and Dickinson (9). A reasonable interpretation of the seemingly anomalous high molar absorptivities in terms of bidentate coordination can be made based on a structural principle advanced by Cotton and Bergman (10) for polyatomic ligands having two or more chemically equivalent binding sites. In the case of oxo ligands, there are several reported examples of ML_4^{2-} complexes (M = a divalent 3d cation, L = a bidentate coordinated NO_3^- , SO_4^{2-} , or CF_3COO^- ligand), where two oxygen atoms of each L appear to lie within the binding shell of the TM cation, leading to an eight coordinated dodecahedral structure (11-13). To a first order of approximation, the geometric arrangement may be thought of as a distorted cube with oxygen atoms of the ligand occupying the eight corners and the TM cation located in the center of the cube. This principle of Cotton and Bergman has been further elaborated on by Johnson and Dickinson (9) for molten salt systems, wherein they view the eightcoordinated structure as representing a transitive species between octahedral and tetrahedral coordination. This bidentate dodecahedral arrangement has no center of inversion and, thus, provides an explanation of the high molar absorptivities observed for the ML_4^{2-} -type complexes.

It is concluded from the observations of the present work that, to some extent, bidentate coordination interactions (of a type leading to loss of center of inversion of the complex) probably occur for all of the 3d TMs in molten and glassy carboxylates. This would explain the consistently higher molar absorptivities compared to aqueous media (see Table II). In the case of Cr^{3+} , for example, the observed molar absorptivities in carboxylate media are intermediate between those for the purely monodentate $Cr(H_2O)_6^{3+}$ complex and the purely bidentate $Cr(Ox)_3^{3-}$ complex (see Table II). Additional studies of the energetics of these multidentate complexes, through application of ligand field theory and electrostatic formalisms, could shed new light on the details of the complexation interactions.

C-13 NMR Studies. — The C-13 NMR spectra of Fm⁻, Ac⁻, and SCN⁻ in molten alkali metal cation environments are much the same as those found for these same anions in other solvent media, as far as chemical shifts and coupling constants are concerned. Typical spectra recorded at ~150°C are shown in Fig. 6. The values of the coupling constants observed in our work for the Fm⁻ and Ac⁻ ions in molten alkali halide media are:

for Fm⁻:
$$J_{CH} = \sim 185$$
 Hz
for Ac⁻: $J_{CH} = \sim 127$ Hz
 $J_{CC} = \sim 52$ Hz

Spin-lattice relaxation times in the $125 \rightarrow 175^{\circ}$ C temperature interval ranged from 0.5 to 10 seconds for the carboxyl carbons and from 5 to 30 seconds for the thiocyanate carbon. Additions of ~0.1 mol% of Ni²⁺, Co²⁺, or Mn²⁺ reduced these relaxation times by a factor of ~10, ~10, and >1000, respectively. (In the case of Mn²⁺, all resonances were completely broadened out.) The chemical shifts measured for the melts containing Co²⁺ and Ni²⁺ were not significantly different from those for the TM-free melts.

One of the more interesting findings of the C-13 NMR studies of TM-containing melts was evidence for two distinguishable Ac⁻ environments in Ni²⁺/Ac-02 solutions. Spectra of one such solution, showing the two resonances observed in the carboxyl region and the effect of temperature on their chemical shift difference, δ , are presented in Fig. 7. A plot of δ versus reciprocal Kelvin temperature is given in Fig. 8. The slope of the Arrhenius plot yields an activation energy of ~6.6 kcal/mol for the apparent exchange reaction. For Ni²⁺ in weak ligand fields, the d⁸ system tends to have crystal field activation energies that range from 2.0 Dq for S_N1 reactions to 4.26 Dq for S_N2 reactions (14). Typical values of Dq for Ni²⁺ coordinated by oxo ligands are around 850 cm⁻¹; hence, the expected activation energies for S_N1 and S_N2 reactions would be ~4.9 kcal/mol and ~10.4 kcal/mol, respectively (1000 cm⁻¹ = 2.86 kcal/mol). The observation of an activation energy in the range expected for S_N1 or S_N2 reactions suggests that the process giving rise to the results in Figs. 7 and 8 may involve exchange of "free" and "coordinated" Ac⁻ ions around the Ni²⁺ cation.

Further useful insights concerning the structure of molten carboxylates were obtained from C-13 spin-lattice relaxation, T_1 , experiments on the pure (TM-free) eutectics. Results for the Fm⁻ and Ac⁻ carboxyl carbons in Ac-02 and Fm-01 are presented as a semi-log plot of T_1 versus reciprocal Kelvin temperature in Fig. 9. (The corrections for the nuclear Overhauser effect due to the formyl proton in the case of Fm-01 melts is illustrated in the figure.) Literature data for formic and acetic acid (15,16) are also shown in Fig. 9 for purposes of comparison. It is clear from the data in Fig. 9 that spin-lattice relaxation in the formate and acetic acid. The interpretation of the T_1 data for formic and acetic acid (15) has been that at lower temperatures, spin-lattice relaxation of the carboxyl carbon results primarily from dipolar coupling with the methyl protons. At higher temperatures, spin-rotation interaction of the molecule with its own molecular magnetic moment becomes the dominant contributor to relaxation. It is happens (still referring to formic and acetic acid) that both mechanisms play a role throughout the temperature range in Fig. 9.

An attempt has been made to analyze the results for the formate and acetate melts in Fig. 9 on the basis of existing theories and formalisms for C-13 relaxation. The relationship that best fits the data is one based on dipolar coupling of the C-13 nucleus with a second spin system. This second spin system could be (i) the protons present in each anion; (ii) the quadrapolar ²³Na, ³⁹K, and/or ⁴¹K nuclei (all with nuclear spin equal to 3/2); or (iii) a paramagnetic impurity in the melt. Although the latter possibility can not be completely eliminated, it is rather unlikely; hence, the remainder of this discussion will center on the concept of dipolar relaxation due to coupling with another nucleus. As this process is generally controlled by the rotational motion of one nucleus with respect to the other, the equations derived by Abragam (17) for the correlation of relaxation with rotation can be applied. Without including all of the details, T_1 can be related to the rotational correlation time, τ , as follows:

$$\frac{1}{T_1} = C_0 \tau \tag{2}$$

where C_0 is a term that includes geometric and magnetogyric parameters, which are independent of temperature and which may be looked up in Refs. (7) and (17). Several other useful relationships that are somewhat approximate in the context of this analysis are

$$\tau = \tau_0 \exp(Q_\tau/R T) = \frac{4 \pi \eta a^3}{3 k T}$$
(3)

$$\eta = \eta_0 \exp(Q_\eta/R T) = \frac{k T}{8 \pi a D}$$
(4)

$$D = D_0 \exp(-Q_D/R T) = \frac{\langle a^2 \rangle}{6\tau}$$
(5)

where η and D are the viscosity and rotational diffusion coefficient, respectively, the Q_i 's are the corresponding activation energies, a is the radius of the rotating species (assumed for simplicity to be spherically symmetric), and T is the Kelvin temperature. Substitution of Eq. 4 and Eq. 5 into Eq. 2 gives

$$\frac{1}{T_1} = C_1 \frac{\eta_0 \exp(Q_\eta/R \,\mathrm{T})}{k \,\mathrm{T}} \tag{6}$$

$$T_1 = C_2 D_0 \exp(-Q_D/R T) \tag{7}$$

where again C_1 and C_2 are terms incorporating temperature independent parameters. From Eqs. 2, 3, 6, and 7 one sees that a plot of $\ln[T/T_1]$ versus 1/T will yield the approximate activation energy for viscous flow, Q_η , and that a plot of $\ln T_1$ versus 1/T will yield approximate values for $Q_D = Q_\tau$. The latter plot is given in Fig. 9 and the resulting "activation energies" are listed thereon.

A semi-log plot of T/T_1^* versus 1/T for the Ac-03 and Fm-01 data in Fig. 9 is given in Fig. 10. These plots correspond to activation energies for viscous flow that are on the order of 10 to 11 kcal/mol. Similar studies of the SCN⁻ ion in these same melts also gave values of ~10 kcal/mol. This range of values is consistent with studies of mesophasic carboxylate melts (18), but is 2 to 3 times greater than the range for pure acetate melts containing a single alkali cation (19). The interesting feature of these results is that the molten carboxylate-thiocyanate melts present an opportunity to study nearly pure dipolar coupling, free of the perturbing effects of other relaxation mechanisms that crop up in aqueous media and in pure acetic and formic acid (15). This is undoubtedly related to the highly ordered viscous nature of many carboxylate-containing melts, particularly, near their melting points (18,20,21).

Conclusions

With the exception of Cu^{2+} , all of the 3d TMs appear to have at least one oxidation state that is reasonably stable in low-melting alkali metal carboxylate eutectics. The ligand field spectra of the stable 3d TM cations in these eutectics bear a consistent resemblance to their corresponding spectra in aqueous media, but the molar absorptivities are significantly greater than are observed for the hexaquo complexes. The absorption spectrophotometric results are interpreted herein as being indicative of the existence of bidentate coordination by the carboxylate group in some (if not all) cases, leading to noncentrosymmetric complexation geometries.

The apparent existence of distinguishable "coordinated" and "free" Ac^- in Ni²⁺-containing melts over the temperature range from 100 \rightarrow 180°C suggests that the residence time for exchange of "coordinated" and "free" Ac^- is relatively long. In the case of molten formate-thiocyanate and acetate-thiocyanate melts, the finding of (i) rather large activation energies for viscous flow and (ii) a purely dipolar coupling mechanism (as derived from spin-lattice relaxation data) seemingly reflects the persistence into the molten state of a highly ordered, relatively rigid structure.

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References

- 1. M. D. Ingram, G. G. Lewis, and J. A. Duffy, J. Phys. Chem., 76, 1035 (1972).
- 2. J. A. Duffy and M. D. Ingram, J. Chem. Soc. (A), 2398 (1969).
- 3. R. A. Bailey, M. ElGuindy, and J. A. Walden, Inorg. Chem., 8, 2526 (1969).
- 4. T. Suzuki, T. Hatsushika, and Y. Hayakawa, J. Japan Chem. Soc., 1017 (1982).
- V. D. Prisyazhnyi, V. N. Mirnyi, and T. A. Mirnaya, Ukr. Khim. Zh., <u>47</u>, 95 (1981).
- L. L. Burton, S. Sherer, and E. R. Van Artsdalen, J. Chem. Phys., <u>75</u>, 1338 (1971).
- 7. D. Shaw, "Fourier Transform NMR Spectroscopy," Elsevier Scientific Publishing Co., Amsterdam (1976).
- 8. B. N. Figgis, "Introduction to Ligand Fields," John Wiley & Sons, Inc., New York, NY (1966).
- K. E. Johnson and J. R. Dickinson, High Temperature Coordination Chemistry of Group VIII, in "Advances in Molten Salt Chemistry," Vol. 2, J. Braunstein, G. Mamantov, and G. P. Smith, Eds., Plenum Press, New York, NY (1973) pp. 83-198.
- 10. F. A. Cotton and J. G. Bergman, J. Am. Chem. Soc., <u>86</u>, 2941 (1964).
- 11. J. G. Bergman, Jr., and F. A. Cotton, Inorg. Chem., 5, 1420 (1966).
- 12. D. K. Straub, R. S. Drago, and J. T. Donoghue, Inorg. Chem., 1, 848 (1962).
- 13. J. R. Dickinson and M. E. Stone, Can. J. Chem., 50, 2946 (1972).
- 14. F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley & Sons, Inc., New York, New York (1963), p. 109.
- 15. A. Olivson and E. Lippmaa, Chem. Phys. Lett., 11, 241 (1971).
- 16. T. Bjorholm and J. P. Jacobsen, J. Mag. Resonance, <u>39</u>, 237 (1980).
- 17. A. Abragam, "The Principles of Nuclear Magnetism," Clarendon Press, Oxford, UK (1961).
- 18. M. Wolfe, J. Bonekamp, and J. Jonas, J. Chem. Phys., 70, 3993 (1979)
- 19. A. Kisza, B. Walczak, and G. Zabinska, Polish J. of Chem., 54, 2313 (1980).
- 20. A. R. Ubbelohde, Rev. Int. Hautes Temp. Refract., 13, 5 (1976).
- 21. J. Bonekamp, T. Eguchi, and J. Jonas, Chem. Phys. Lett., 75, 360 (1980).

Components ^a	Composition (mol %)	Melting Point (°C)	Designation
LiAc-NaAc-KAc	32-30-38	~160	Ac-01
CsAc-NaAc-KAc	50-25-25	~90	Ac-02
KAc-KSCN	42-58	~130	Ac-03
KFm-KSCN	54-46	~80	Fm-01
LiFm-NaFm-KFm	25-25-50	~110	Fm-02

 Table I.
 Composition, melting point, and designation of eutectic salts used in the electronic absorption and NMR studies.

 $\overline{^{a}\text{Ac}}$ = acetate, Fm = formate.

Table II. Ligand field transition energies (in thousands of cm⁻¹) and molar absorptivities for 3d TM cations in selected molten carboxylates and in aqueous solution.

		Ligand Field	Maximum
3d TM	Ligand	Transition	Molar
Cation	Medium	Energies ^a	Absorptivity ^b
V ³⁺	Ac-01	$(32.8)/23.5^*/15.6$	25
	Ac-02	(31.1)/22.3 [*] /14.9	27
·	H_2O^c	$(36.0)/25.6^*/17.2$	8
Cr ³⁺	Ac-02	$(34.3)/21.8^*/16.3$	70
	Fm-02	(35.9)/23.5*/17.0	45
	$(Ox^{2-})^c_{aq}$	$(37.8)/23.6^*/17.4$	100
	H ₂ O ^c	$(37.0)/24.0^*/17.0$	15
Fe ²⁺	Ac-02	~8.0	9
	Fm-02	~9.2*	16
	H_2O^c	~10.0	2
Co^{2+}	Ac-02	18.8/17.4 [*] /7.3	200
	Fm-02	18.6/17.6*/7.7	50
	H ₂ O ^c	21.6/19.6*/8.0	5
Ni^{2+}	Ac-02	23.1*/14.7/7.7	50
	H ₂ O ^c	25.3*/14.5/8.7	5

^aTransition energies in parentheses were not observed. They were estimated using Tanabe-Sugano diagrams for octahedral complexes (8).

^bMolar absorptivity at the peak marked with an (*) in the column to the left. ^cData taken from reference (8); aq = aqueous media.



Fig. 1. Absorption spectrum of V^{3+} in Ac-02 at ~150°C.



Fig. 2. Absorption spectrum of $\rm Cr^{3+}$ in Ac-02 at ${\sim}150^{o}\rm C.$



Fig. 3. Absorption spectrum of Fe^{2+} in Ac-02 at ~150°C.



Fig. 4. Absorption spectrum of Co^{2+} in Ac-02 at ~150°C.



Fig. 5. Absorption spectrum of Ni²⁺ in Ac-02 at \sim 150°C.



Fig. 6. Selected C-13 NMR spectra of formate-thiocyanate (Fm-01), acetate (Ac-02), and Co^{2+}/Ac -02 melts at ~150°C.



Fig. 7. C-13 NMR spectra of a $Ni^{2+}/Ac-02$ melt showing the frequency region of the carboxyl resonance at two temperatures. The black dots mark signals that are due to spinning side-bands.



Fig. 8. Plot of log δ versus 1/T for the Ni²⁺/Ac-02 melt in Fig. 7, where δ is the chemical shift difference between the two carboxyl resonances.



Fig. 9. Spin-lattice relaxation data for the carboxyl carbon in selected formate (Fm-01) and acetate (Ac-03) melts from Table I. Literature data for formic acid, acetic acid, and aqueous formates are shown for comparison. NOE=nuclear Overhouser effect, N₀/N=the NOE correction factor, and T_1 =the uncorrected spin-lattice relaxation time.



Fig. 10. Semi-log plot of T/T_1^* versus 1/T for the carboxyl carbon in Fm-01 and Ac-03 melts, using data from Fig. 9.

ON THE THERMODYNAMIC CHARACTERISTICS OF WATER IN HYDRATED MELTS OF MAGNESIUM CHLORIDE

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An apparatus for vapour pressure measurements by a static method had been developed, which allows one to examine very corrosive systems up to temperatures of 523 K. The binary system MgCl₂-H₂O containing between 4-8 moles of water per mole MgCl₂ was investigated. The activities and enthalpies of vaporization of water are presented and interpreted in connection with the transition "concentrated electrolyte solution - molten hydrate - molten salt". For treating the data quantitatively the applicability of the B.E.T. equation is tested and discussed.

In recent years greater efforts have been made to study uniformly the thermodynamic properties of salt-watersystems over the entire concentration range, from dilute solutions to molten salts /1/. Within this concentration scale the composition range of the hydrated melts plays a key role in the development of appropriate theories. The concentration range with water contents in which only the strongest hydrating ions can form the first hydration shell is by definition a 'hydrated melt.'' This should be the case for molar water/salt ratios between 4 - 9.

Unfortunately, thermodynamic properties at such water contents are known only for a few salts forming low melting hydrates (e.g. $Ca(NO_3)_2$, LiNO₃, LiCl). In general, for experimental investigations in the composition range of hydrated melts, elevated temperatures are required which complicate precise measurements owing to the elevated vapour pressure and the corrosion problems.

For investigating corrosive salt solutions up to temperatures of 525 K an experimental device for vapour pressure measurements based on the so-called "bithermal method" has been developed.

Experimental

The apparatus (Fig. 1) consists of two identical auto-

claves, one containing the hydrated melt and the other one for distilled, degassed water. The autoclaves are located in aluminium block thermostats controlled independently within \pm 0.01 K. For temperature measurements, shielded platinum resistance thermometers are immersed in the melt and the pure water, respectively. Tubes connect the autoclaves with a third pressure vessel containing a membrane. The tubes and the membrane are thermostrated at a temperature above the dew-point. All parts in contact with the melt, water or vapour phase were made from TiPd alloy. Only the membrane consists of a Cu-Be alloy coated with temperature resistant silicon resin.

The membrane is only used as a zero-point indicator for pressure difference between the two autoclaves. Membrane deformations greater than 0.3 μ m (= 10 Pa sensitivity) could be detected by a differential transformer: By varying the temperature of the water autoclave the membrane is brought into zero position. Equilibrium conditions were assumed to be reached, if for at least two hours the pressure difference Δ p and the drift in temperature Δ T were within the limits of Δ p \pm 100 Pa; Δ T \pm 0.01 K. Under equilibrium conditions the vapour presssure of the solution equals the vapour pressure of pure water. The latter was calculated from the measured equilibrium temperature by means of p-T relations for the saturated vapour pressures.

For temperatures of up to 373 K the relation from GOFF /2/ was used and for higher temperatures the relations proposed by SATOH /3/ and by WUKALOWITSCH /4/ were applied.

Test measurements with 5 molal NaCl solution agreed with LINDSAY'S results /5/ within 1 %. In the binary system MgCl₂-H₂O the vapour pressure was determined up to 513 K. Melts with the following initial compositions were investigated:

I	MgC12	+	8.002	н ₂ 0	IV	MgCl ₂	+	5.500	^H 2 ⁰
II	MgC12	+	7.004	H ₂ 0	v	MgC12	+	5.004	^H 2 ⁰
III	MgC12	+	6.004	н ₂ о	VI	MgCl ₂	+	4.604	H ₂ 0

For the preparation of the melts $MgCl_2.6H_2O$ was dissolved in distilled water and the solution was held at the boiling point for one day before it was filtered. The recrystallized product was slowly dried down to 5.5-4.0 moles H_2O per mole $MgCl_2$, powdered and analyzed for Mg^{2+} , Cl^- and H_2O . The calculated water contents from the different components determined agreed within \pm 0.002 moles $\rm H_2O$ per mole MgCl_. After charging the autoclave with an exactly known amount of magnesium chloride hydrate of between 200-220 g, the amount of water needed was added and then the autoclave was closed.

The ratio of vapour phase to liquid phase volume was about 1:1. Therefore the concentration increase due to heating up to the highest temperatures was smaller than 0.25% for melt I and 0.21% for melt VI.

Results and Discussion

The vapour pressure data, which were not corrected for concentration increase, fulfil the simple relation lnp = (A/T) + B (1) within the maximum experimental error of 2 %. The plots are shown in Fig. 2. By use of Eq. (1) and the wellknown relation

$$\left(\frac{d p}{dT}\right)_{x} = \frac{\Delta_{v} H_{H_{2}0}}{p \cdot \Delta_{v} \overline{v}_{H_{2}0}}$$
(2)

the partial molar enthalpies of vaporization $\Delta_v \overline{H}_{H,O}$ have been calculated. For the computation of the volume difference $\Delta_v \overline{V}_{H,O}$ for the gas phase volume the virial equation was used.

$${}^{\mathbf{X}}_{(\underline{k})} {}^{\mathbf{V}}_{\mathbf{H}_{2}\mathbf{0}} = \frac{\mathbf{RT}}{\mathbf{p}} + \mathbf{B}$$
(3)

$$\mathbf{B} \cdot 10^{3} \left[\frac{\mathbf{kg}}{\mathbf{m}^{3}} \right] = 2.9840763 \cdot 10^{-2} + 2.7108543 \ \mathbf{T}^{-1} -$$

$$4 \cdot 8199159 \cdot 10^{3} \cdot \mathbf{T}^{-2} - 2 \cdot 1080564 \cdot 10^{6} \ \mathbf{T}^{-3} + 1.4117653 \ 10^{8} \ \mathbf{T}^{-4}$$
(4)

The partial molar volume of water in the melt has only a slight influence on the results and was taken as 20 cm³/ mole. The results for $\Delta_v H_{\rm H_20}$ are given in Table 1. In Fig. 3, $\Delta_v H_{\rm H_20}$ is exhibited as a function of the molar water/salt ratio $\rm R_{H^{\bullet}}$. For lower salt concentrations values from the literature were extrapolated from 293-363 K to 474 K /6/. Coming from the pure water side the rapid increase of the curve begins at about $\rm R_{H^{\bullet}}7$ which means, at a water to cation ratio which is near the hydration number of the magnesium cation.

Table 1: The partial molar enthalpies of vaporization of water in system of magnesium chloride-water

$R_{H} \begin{bmatrix} mole H_{2}O \\ mole MgCl_{2} \end{bmatrix}$	$\Delta_{v} \overline{H}_{H_{2}0} \left[\frac{kJ}{mole} \right]$
8.002	43.8
7.004	45•2
6.004	48.5
5.500	51.5
5.000	53.3
4.604	55•7

This clearly demonstrates the transition character of the hydrated melts with respect to the energetics of the water-salt interactions. Similar curves were reported for the systems (LiNO₃, KNO₃ eutec.) - H₂O, LiCl-H₂O, LiNO₃-H₂O, Ca(NO₃)₂-H₂O at temperatures between 298=393 K /³7/². Only for the system (LiNO₃, KNO₃ eutec.)-H₂O the curve could be plotted to the pure molten salt (²Fig. 3). At present, for the MgCl₂-H₂O system, the upper limit of $\Delta_v \ H_{H_2O}$ on the molten salt side cannot be estimated

from the experimental data.

Based on the vapour pressures the activity of water was also calculated taking into account the real gas correction with the second virial coefficient of steam. With values ranging between 0.10 and 0.38 the activities are very low in this system even at high temperatures. The temperature dependence is demonstrated in Fig. 4 in the coordinates $\ln a - \sqrt{T}$.

Using the relation

$$\Delta \overline{S}_{H_20}^{ex} = -R \ln f_{H_20} - RT \left(\frac{\partial \ln a_{H_20}}{\partial T} \right)_{p,x}$$
(5)
with $f = \frac{a_{H_20}}{N_{H_20}}$ and $N_{H_20} = \frac{x_{H_20}}{x_{H_20} + \sqrt[4]{r} \cdot x_{salt}}$; $\sqrt[4]{r} = 3$

the partial molar excess entropies for water $\Delta \overline{S}_{H_0}^{ex}$ were calculated. For the calculation of the temperature slope

 $(\partial \ln a / \partial T)_{n,x}$ the activity data were derived from

$$lna = (A'/T) + B'$$

for exactly isoconcentrated melts by including the evaporation correction. The maximum corrections of the activity were of the order of 2 % and therefore a linear interpolation between neighbouring melt compositions was sufficient.

(6)

A plot of ($\Delta \overline{S}_{H_2O}^{ex}/R$) against R_H at a temperature of 480 K is shown in Ffg. 5.At first we state very high negative values in comparison with for example sodium chloride solution with ($\Delta \overline{S}_{H_2O}^{ex}/R$) =-0.06 at R_H = 7.4 and the same temperature /5/. The sharp drop of the entropy curve is found again at approximately $R_H \approx 7$, which means that the water molecules lose the most entropy in the concentration range of hydrated melts. From the similar behaviour of the enthalpy of vaporization and the partial molar excess entropy of water it can be concluded that the $_{A}H_{-}\Delta S$ compensation effect well-known for aqueous solutions also holds for hydrated melts. To demonstrate this, the partial molar excess enthalpy and entropy of water were plotted against each other at 480 K (Fig. 6). The numbers at the points refer to the number of the melt. Within the concentration range investigated the curve exhibits only a small curvature, which means that the compensation effect exists. This effect may be one reason for the applicability of the simple BRUNAUER-EMMETT-TELLER (B.E.T.) adsorption isotherm to the quantitative description of activity data.

According to a proposal by STOKES and ROBINSON /7/ the original B.E.T. equation was modified for electrolyte solutions and in the mole fraction scale it has the following form:

$$\frac{a_{w}(1-x_{w})}{x_{w}(1-a_{x})} = \frac{1}{c_{v}r} + \frac{(c-1)}{c_{v}r} a_{w}$$
(7)

where a, x are the activity and mole fraction of water and both c and r represent empirical parameters. Derived from this equation the parameter r gets the meaning of a mean hydration number of ions and c is considered as an energetic parameter expressed by

$$c = \exp\left[-\frac{(E_{ad} - E_{L})}{RT}\right]$$

_

with the difference $(E_{ad} - E_L)$, defined E_{ad} is the heat of adsorption for a monolayer around the ion and E_L is the heat of liquefaction of pure water. By a more Figorous derivation it can be shown that the heats should be replaced by the corresponding so that standard free energies It was found that the B.E.T. equation applies well for water activities up to 0.7 /9/. Because our activities determined are below this value, we fitted our data to this equation. In Fig. 7 the activities are plotted against the left hand-side expression of (7) for different temperatures. With a maximum deviation of 2.7 % and mean deviations of 1.5 % the fit is reasonably good. The computed parameters r, c and $(E_{ad} - E_L)$ are listed in Table 2.

Table 2:	The	computed	parameters	r,	С	and	(E	 E _T)	of
	the	B.E.T. ed	Juation				au	LL LL	

т [К]	r	С	$\Delta \mathbb{E}\left[kJ/mole\right]$
393,15	6.1063	42.0656	12.22
403,15	6.0289	42.7944	12.59
413,15	5.8724	39.5740	12.63
423,15	5.7313	41.4269	13.10
433,15 ·	5.6225	39.5826	13.25
443,15	5.5525	34.6848	13.07
453,15	5.4650	31.7281	13.03
463,15	5.3790	28.9843	12.96
473,15	5.2949	26.4210	12.88
483,15	5.2127	24 .0199	12.77
493,15	5.1339	21.7384	12.53

The values of r between 5.1 - 6.1 can be accepted as a mean hydration number of the magnesium cation. The temperature dependence agrees with the findings that the hydration number is lowered at higher temperatures. In Fig. 8 this tendency is illustrated. The curve includes a value of r, which had been estimated from room temperature activity data /10/. Also the range of 12 - 13 kJ/mole for - ($E_{ad} - E_T$) is consistent with its physical meaning. As expected this value is much higher than that reported for the cations T1⁺, Ag⁺, (1,3 kJ), Cd²⁺ (4,0 kJ), and Ca²⁺ (4,6 kJ) in their nitrates at temperatures of about 370 - 400 K /11/.

Another calculation yields the temperature dependence of (1/c.r). It can be shown that the relation

$$\frac{1}{c \cdot r} = \int_{H_20}^{\infty} H_20$$
(8)

is valid, where $\gamma_{\rm H_20}^{\bullet}$ is the limiting activity coefficient of water in ${}^{\rm H_20}$ the pure molten salt, Furthermore, from the temperature dependence of (1/c.r) the enthalpy of vaporization of water at infinite dilution in the molten salt, $\Delta_{\rm v} {}^{\rm H_20}$, is calculable from the relation /12/

$$\frac{\partial \ln(1/c \cdot r)}{\partial(1/T)} = \frac{\Delta_v H_{H_20}^0 - \Delta_v H_{H_20}^\infty}{RT}$$
(9)

where $\Delta_{v}H_{H_{2}0}^{0}$ stands for the vaporization enthalpy of pure water.²By means of (8) and (9) from our data a value of 18,3 kJ/mole had been calculated for $(\Delta_{v}H_{H_{2}0}^{0} - \Delta_{v}H_{H_{2}0}^{0})$. Ranging from pure water to the pure molten magnesium chloride the enthalpy of vaporization should increase by this amount. From the curve in Fig. 3, this increase is apparently too small. But taking into account the great range of concentration from $R_{H} = 4.6$ to $R_{H} = 0$, the right order of magnitude is indeed obtained. References

- K. S. PITZER, Ber. Bunsenges. Phys. Chem. 85 (1981), /1/ 952 J. A. GOFF, "Humidity and Moisture", ed. by A. WEXLER Vol. 3, Reinhold Publishing Corp. N. York 1965, p.289 121 K. SATOH, Nippon Kaisui Gakkai Shi 28 (1974) 153, 182 131 M. R. WUKALOWITSCH, Thermodynamische Eigenschaften des Wassers und des Wasserdampfes; VEB Verlag Technik 141 1958, Berlin CH.-T. LIU, W.T. LINDSAY, OSW Report, Washington 1971, 151 Contract No. 14-01-0001-2126 C. DÄHNE, R. HUSCHENBETT, Freib. Forsch.-H. A 384 161 (1966), 31 171 R. H. STOKES, R. A. ROBINSON, J. Am. Chem. Soc. 70 (1948), 1870 H. BRAUNSTEIN, J. BRAUNSTEIN, J. Chem. Thermodyn. 3 /8/ (1971), 419 /9/ J. A. RARD, D. G. MILLER, J. Chem. Eng. Data 26 (1981) 33 /10/ M. CH. ABRAHAM, M. ABRAHAM, J. SANGSTER; J. Chem. Eng. Data 25 (1980), 331 /11/ J. SANGSTER, M.-CH. ABRAHAM, M. ABRAHAM, J. Chem. Thermodyn. 11 (1979), 619 /12/ M.-CH. ABRAHAM, M. ABRAHAM; J. SANGSTER; Chan,
- J. Chem. <u>58</u> (1980), 1480 /13/ H. F. HOLMES, C. F. BAES, R. E. MESMER, J. Chem. Thermodyn. <u>10</u> (1978), 983



Fig. 1: Experimental device for vapour pressure measurements



Fig. 2: Vapour pressure data for the system $MgCl_2-H_2O$ in the coordinates ln p - 1/T


Fig. 4: The temperature dependence of the activity of water in the coordinates ln a - \U03c4T (o rising and • falling temperature regime)



Fig. 3: The partial molar enthalpy of vaporization in dependence on the molar water/salt ratio $R_{\rm H}$ \bullet our values, $_{\rm X}$ DAHNE, HUSCHENBETT



Fig. 5: The partial molar excess entropy of water in dependence on the molar water/salt ratio R_H • our values.o HOLMES, BAES, MESMER







Fig. 5: The partial molar excess entropy of water in dependence on the molar water/salt ratio R_H ● our values, ○ HOLMES, BAES, MESMER



Fig. 6: The partial molar excess enthalpy of water against the partial molar excess entropy of water at 480 K



Fig. 7: The activities of water against the left-handside expression of equation 7 for different temperatures



Fig. 8: The parameter r of the B.E.T. equation as a function of temperature

THE BEHAVIOR OF WATER IN MOLTEN SALTS

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ABSTRACT

The differing behavior of water equilibrated with three separate molten salt solvents is discussed with respect to the chemistry of the solutions and the electroreductive mechanisms at gold electrodes.

INTRODUCTION

Generally water in molten salts is an undesirable impurity (1,2), but in some applications it is introduced into the molten solvent deliberately as a solute (as in the new gasification and fuel cell technologies). In this paper, the differing chemical and electrochemical behavior of water will be discussed on the basis of new data obtained for three different solvent systems in which water either (1) dissolves as a simple solute and obeys Henry's law as is the case for sodium nitrate-potassium nitrate mixtures (3-5), or (2) causes hydrolysis of the molten solvent as is the case for alkali metal carbonates and sulfates. The chemistry and electrochemistry of water has generated considerable discussion of late, and these new results should help to resolve some of the apparent anomalies implied in the earlier studies (1-5).

EXPERIMENTAL

The preparation of the melts, the experimental cells, electrode design, and procedures were similar to those described previously (5-8), except that in the molten carbonate work the gas reference electrode:

 $Au/p_{CO_2}(0.667)$, $p_{O_2}(0.333)//ternary$ carbonate eutectic

was employed. Gold working electrodes were used in all the measurements. The studies were conducted in the temperature range 250 to 560°C. The water partial pressure was maintained within the range 5 to 50 torr.

RESULTS AND DISCUSSION

Water in the Equimolar Sodium Nitrate-Potassium Nitrate Mixture. The behavior of water in this mixture has been studied at temperatures between 250 and 525°C equilibrated with water partial pressures between 5 and 50 torr. Under these conditions water can be reversibly taken up or removed from the melts. No electrochemical evidence for hydrolytic reactions was found (loc.cit.). Typical cyclic voltammograms for the reduction of water are illustrated in Figure 1. Only a single peak was observed on the first cathodic scan (for scan rates between 0.02 to 3.0 V/sec). On the reverse scan, the oxidation peak which can be related to the reoxidation process is absent in the potential region normally expected for a simple reversible electrochemical reaction. However, as the reverse scan continues, an anodic peak (Z) is observed at more anodic potentials, and on the subsequent cathodic cycle, a corresponding peak (Y). The features of the voltammograms at the more anodic region (around -0.5V) show dependence on the scan rate. At high scan rates, the peaks (labeled Y and Z in Figure 1) split into two components.

The cathodic peak current function, $i_Dv^{-\frac{1}{2}}$ (peak X), is dependent on the scan rate. It is larger at low scan rates and decreased to a constant value at high scan rates. This dependence is most marked at a temperature around 300°C. At temperatures greater than 350°C, and around 250°C, the peak current function is rather independent of the scan rate. The cathodic peak current (at constant scan rate, at which the peak current function is independent of scan rate) is proportional to the water partial pressure (5). The potential of the cathodic peak (X) E_p , shifts cathodically as the scan rate is increased. There is also a cathodic shift in the peak with increase in the water vapor pressure. The difference between half peak and peak potential shows a weak dependence on the experimental parameters such as scan rate and partial pressures of water. Generally, the values are less than 2.2RT/F but larger than 2.2RT/2F.

The above results, particularly the absence of a reverse anodic peak related to the primary cathodic peak (X) and the appearance of the redox system (Y/Z) in the much more anodic potential regions, imply that chemical reactions may be coupled to the electrochemical process involved. The enhancement of the current function (more than 20%) is bigger than expected even for a second order following reaction (chi changes from 0.446 to 0.527)(9,10). These facts indicate the involvement of an ECE mechanism. The enhanced current function and the wide separation of peaks (X) and (Z) are consistent with the presence of a chemical reaction, the product from which is more easily reduced than the water $E_2 > E_1$. It should be emphasized that the strong cathodic shift of the peak potential $E_p(X)$ with increasing partial pressure of water (3RT/FlnpH₂O) indicates that a second order catalytic reaction C

$$2RED + Z \neq OX + Product$$
(1)

interferes in the overall process. Furthermore, it is concluded from these experimental data that both schemes, E_1CE_2 and E_1C_c , act simultaneously (11,12). The experimental conditions such as scan rate, water concentration and temperature will determine which of the reaction pathways predominate in the overall process.

The results at 230 °C of the massive electrolysis of water containing melts (12 torr) at platinum cathodes showed that the ratio of hydroxide/nitrate was 2.381, and some gaseous product, thought to be hydrogen, was observed at the cathode (4). On the other hand, at 350° C with melts equilibrated at "very low water contents" (4), this ratio was reported to be 2.000 (4.13) but 2.20 at 227°C (14), and no hydrogen was detected in the supernatant argon by mass spectrometry. Zambonin <u>et al.</u> (4) interpreted their results in terms of two parallel reactions occurring simultaneously and corresponding to the two overall reactions:

$$H_{2}O + NO_{3}^{-} + 2e \neq NO_{2}^{-} + 2OH^{-}$$
 (2)

$$H_{2}O + e \downarrow H_{2} + OH^{-}$$
 (3)

The results of Geckle and Jordan (13,14) at 350°C are consistent with reaction (2). Since the publication of these results, some controversial discussions of the water reduction mechanisms has occurred (see Ref. 15). These observations can be accommodated by the "ECE" mechanism presented here.

с

 E_2

$$E_1 \qquad H_2O + e \neq H + OH^- \qquad (4)$$

$$NO_3^- + H \rightarrow NO_2^- + OH$$
 Path II (5)

$$2H(H_2) + NO_3^- \neq NO_2^- + H_2O$$
 (6)

$$OH + e \neq OH^-$$
 (7)

Although it had been implied that reaction (6) only occurs at higher temperatures (16), it was also suggested that such a reaction is catalyzed by precious metals and nitrite ions (17,18). In the present work, the strong influence of water concentration is undeniable and it is concluded that this reaction is significant, certainly at the electrode surface, even at lower temperatures. In addition, the melts used in these studies were carefully purified (NO₂ treatment) but because of the equilibrium

 $NO_3^- \neq NO_2^- + \frac{1}{2}O_2$ (8)

always contained some nitrite ions. The nitrite ion content was at the level predicted from the results of Nissen (19) even under inert argon gas, but three orders of magnitude greater (see Table 1) than that reported by Zambonin for his melts (15). The apparent inconsistencies between the results obtained for the electrolysis experiments discussed above can be explained simply in terms of the proposed new mechanism, and the influence of the water to nitrite ratios which would have been significantly different in the two sets of experimental conditions employed. For example, in Zambonin's experiments (230°C), the ratio H_2O/NO_2^- was around 50,000 compared to that estimated for Geckle's

experiments (350°C) where the H_2O/NO_2^- ratio is unity. The influence of the reaction pathways can clearly be seen to depend on the experimental conditions and the proposal that different overall reactions are necessary is superfluous in the light of the newly proposed mechanism.

Water in the Ternary Alkali Metal Carbonate Eutectic Mixture. The interaction of water with molten ternary alkali metal carbonate eutectic mixture at 460°C was studied over the range of water partial pressure from 5 to 50 torr. Figure 2 illustrates the cyclic voltammograms acquired when the carbonate melt was equilibrated with a water-argon atmosphere. Only one cathodic peak (X) appears but two anodic peaks (Y,Z) are seen. The anodic peak (Y) grows at the expense of peak (Z) as the scan rate is increased. Peak (Z) is most prominent at the lowest scan rates, shifting anodic with increasing scan rate. The cathodic peak current function $i_D v^{-\frac{1}{2}}$ shows a marked enhancement as the scan rate is lowered below 1.0 V/sec (Figure 3). The peak (X) moves in the cathodic direction with increasing scan rate, becoming independent of this latter parameter at its higher values. At a given scan rate, the peak potential $E_{p}(X)$ shifts anodically with increasing partial pressure of water and reaches a limiting value of $p_{\rm H_{2O}}$ around 32-39 torr, Figure 4. The cathodic half peak width Ep/2-Ep is constant (independent of scan rate and water partial pressure) and equal to 107 ± 7 mV. The peak separation $E_p(Y) - E_p(X)$, which is equal to 139 ± 8 mV, is independent of the partial pressure of water and scan rate. The ratio ia/ig depends on the scan rate and the partial pressure of water, tending to unity as these variables are increased.

From these results, it is concluded that the charge transfer process is followed by an irreversible dimerization reaction. At scan rates lower than 0.5 V/sec, the effect of a preceding reaction is sensed, since the magnitude of the change in the peak current function is considerably greater than that expected for a following irreversible limerization reaction.

These observations require some consideration of the solution chemistry involving water. The following experiments were carried out to aid in the resolution of this problem. Potassium hydroxide was added to the pure melt equilibrated with dry argon. No electrochemical response within the electrochemical window for the melt was observed. In addition, no change in the cyclic voltammograms obtained under wet argon was detected when potassium hydroxide was added to the wet melt. From these results, it is concluded that the hydroxide ions are electroinactive on gold and/or the solubility of this compound is limited at this temperature. Indirect evidence for the formation of hydroxide ions in the water containing melts was obtained in the following manner. The melt was equilibrated with wet argon until the stable "water response" was confirmed. At this time, dry argon replaced the original equilibrating gas and the cell was purged for about 12 hours until the initial melt background was obtained. When carbon dioxide was then substituted for the dry argon, the "water response"

redeveloped, the peak current passing through a maximum before the profile decayed to the initial background. No peak in these final cyclic voltammograms could be seen, showing that the carbon dioxide reduction was insignificant at this condition.

These results can be explained with the following model for the solution chemistry and electrochemistry. Water, when equilibrated with the melt, undergoes a reaction with carbonate ions to form bicarbonate and hydroxide ions in accord with the reaction:

$$H_2O + CO_3^{-2} \ddagger HCO_3^{-} + OH^{-}$$
 (9)

precipitating the hydroxide ions from solution. (The cathodic peak current at scan rates greater than 1 V/sec is proportional to the water partial pressure, thus supporting this stoichiometry under these conditions.) In the presence of dry argon, the bicarbonate ions decompose essentially by the process:

$$2HCO_3^- \neq CO_2 + H_2O + CO_3^{2-}$$
 (10)

On passing carbon dioxide, the reformation of bicarbonate ions then occurs by the reaction:

$$OH^- + CO_2 \stackrel{?}{\neq} HCO_3^- \tag{11}$$

 HCO_3 - ultimately decomposes via reaction (10). Further support for reactions (9) and (11) was obtained by introducing carbon dioxide into the wet argon stream. At any partial pressure of water, this caused an increase in the "water response" peak (X). In the cases where the atmosphere was rich in carbon dioxide (>75%) and at a fixed p_{CO_2} , the peak current of peak (X) was proportional to the square root of water partial pressure (20). The electroreduction thus involves bicarbonate ions, followed by the chemical dimerization of the hydrogen atoms to form molecular hydrogen:

$$HCO_3 + e \neq H + CO_3^2 \qquad (12)$$

$$2H \rightarrow H_2$$
 (13)

The anodic peak (Z) in the region -0.8 to -1.0V arises from the oxidation of this molecular hydrogen. Independent measurements of the oxidation of hydrogen (1 atm) in this melt showed a similar peak in this potential region whose characteristics with regard to the scan rate (anodic shift of 112 mV per decade of the scan rate (log_{10})) were remarkably close to the shifts observed for peak (Z).

<u>Water in the Ternary Alkali Metal Sulfate Eutectic Mixture</u>. The results for the alkali metal nitrate and carbonate solvents contrast the interaction of the water with the molten salt, the latter melt emphasizing the possibility of hydrolytic reactions. Since the

interaction of the proton with sulfate ions can occur to form stable bisulfate ions, it was anticipated for the water-sulfate system that reactions akin to that of (9) and (10) may take place under wet atmospheres. The identification of hydroxide and oxide ions is important in resolving such reaction schemes. Figure 5 shows partial cyclic voltammograms for the oxidation of hydroxide ions introduced into the melt by adding lithium hydroxide at two different concentrations. The half-peak potential indicates that the position of the peak is in the region 0.0 versus the silver reference and shifts cathodic with increasing concentration. This oxidation is considerably more anodic than that for oxide ion as can be seen in Figure 6. When water is introduced in the argon stream, the voltammograms in Figure 7 were obtained with the scan direction first anodic (7a) and then cathodic (7b). The measurements show that hydroxide ions are formed under the experimental conditions, the major anodic peak being shifted because of the concentration effect pointed out above, and the cathodic response is again due to the reduction of complexed hydrogen ions. The details of these processes are currently being investigated, but it suffices to say here that the chemistry is considerably more involved than in the previous melts because of the numerous sulfur derivatives that are possible in these systems.

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REFERENCES

- S. H. White, in <u>Ionic Liquids</u>, D. Inman and D. G. Lovering, eds. (London: Plenum, 1981), p. 185.
- 2. D. G. Lovering and R. M. Oblath, ibid., p. 165.
- 3. J. Braunstein, Inorg. Chim. Acta (Reviews), 2, 19 (1969).
- P. G. Zambonin, V. L. Cardetta and G. Signorile, J. Electroanal. Chem., 28, 237 (1970).
- S. H. White and U. M. Twardoch, in <u>Proceedings of the 3rd Intern</u>. <u>Symp. on Molten Salts</u> (New Jersey: The Electrochemical Society, Inc., 1981), p. 284.
- 6. S. H. White and M. M. Bower, ibid., p. 334.
- 7. S. H. White and U. M. Twardoch, Electrochim. Acta, 27, 1599 (1982).
- D. Inman, Dj. Jovanovic and S. H. White, J. Electroanal. Chem., 43, 37 (1973).

- 9. M. L. Olmstead, R. G. Hamilton and R. S. Nicholson, Anal. Chem., <u>41</u>, 260 (1969).
- 10. J. M. Saveant and E. Vianello, Electrochim. Acta, 12, 1545 (1967).
- 11. M. Mastragostino, L. Nadjo and J. M. Saveant, Electrochim. Acta, <u>13</u>, 721 (1968).
- 12. M. L. Olmstead and R. S. Nicholson, Anal. Chem., 41, 862 (1969).
- 13. T. A. Geckle, U.S. Atomic Energy Comm., TID-21511 (1965).
- 14. J. Jordan, J. Electroanal. Chem., 29, 127 (1971).
- P. G. Zambonin, in Extended Abstracts of the San Francisco ECS Meeting, May 1983, Abstract No. 772.
- E. Desimoni, F. Paniccia and P. G. Zambonin, J. Chem. Soc. Faraday Trans., <u>1</u>, 69, 2014 (1973).
- E. Desimoni, F. Palmisano and P. G. Zambonin, J. Electroanal. Chem., 84, 323 (1977).
- E. Desimoni, F. Paniccia, L. Sabbatini and P. G. Zambonin, J. Appl. Electrochem., 6, 445 (1976).
- D. A. Nissen, "The Chemistry of the Binary NaNO3-KNO3 System," Sandia Laboratories' Report SAND81-8007, 1981.
- S. H. White and U. M. Twardoch, submitted to Electrochim. Acta, 1983.

ΤA	BLE	1
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NITRITE CONTENT IN BINARY KNO3-NANO3 MIXTURE FOLLOWING DIFFERENT PURIFICATION TREATMENTS

		Nitrite Co	oncentration	n (mol/kg)
Method of	Temperature		Lite	rature
Preparation	<u>0°</u>	This Work	[19]	[15]
NO ₂ treatment, ACS material, Recrystallized	230 260 300	2.02·10 ⁻⁴ 3.39·10 ⁻⁴ 5.36·10 ⁻⁴	0.32·10 ⁻⁴ 1.25·10 ⁻⁴ 5.73·10 ⁻⁴	0.0021.10-4
Vacuum treatment Ultrapure/ Puratronic material	300	25.90.10-4	5.73.10-4	



Fig. 1. Cyclic voltammograms for the reduction of water on a gold electrode in molten KNO₃-NaNO₃ (50 mol%) at 295°C; p_{H_2O} = 10.2 mm Hg. Scan rate: a = 0.05V/sec; b = 1V/sec.







Fig. 4. Plot of the half peak potential $(E_{\rm P/2}^{\rm C})$ vs. logarithm of scan rate for the cathodic reduction process in molten ternary carbonate eutectic under H₂O-Ar atmosphere at gold electrode at 465°C. E_{P/2} vs. reference electrode CO₂/O₂ (25%/75%).



Fig. 5. Cyclic voltammograms acquired on a gold electrode (0.34 cm²) for the oxidation of hydroxide ions (concentrations: a = $2.8 \cdot 10^{-2}$ mol kg⁻¹, b = $8.8 \cdot 10^{-3}$ mol kg⁻¹) in the ternary alkali metal sulfate eutectic at 560°C. Scan rate = 1V/sec.



Fig. 6. Cyclic voltammograms acquired at a gold electrode (0.34 cm^2) in the ternary alkali metal sulfate eutectic at 560°C. Scan rate = 1V/sec under the following conditions: a) wet argon, p_{H_2O} = 21.85 mm Hg; b) dry argon and addition of lithium hydroxide, C_{OH} = $8.8 \cdot 10^{-3} \text{ mol/kg}$; c) dry argon and addition of lithium oxide, C_O^{2-} = $1.768 \cdot 10^{-2} \text{ mol/kg}$.



Fig. 7. Cyclic voltammograms acquired on a gold electrode (0.34 cm^2) for the ternary alkali metal sulfate eutectic equilibrated with the water $(p_H \ o = 21.85 \text{ mm Hg})$ argon atmosphere at 560°C; scan rate = 1V/sec. Initial scan direction: a = anodic; b = cathodic.

VAPOR PRESSURES OF HYDRATE MELTS CONTAINING LITHIUM NITRATE AND ALKALI NITRITES

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ABSTRACT

Measurements of the physical properties of hydrate melts have been made on only a very limited number of systems, mainly because few systems exist in the liquid state at temperatures below 200°C. Such data are needed to test generalized models proposed for electrolyte-water solutions. This paper reports the results of a vapor pressure study on hydrate melts containing a mixture of lithium nitrate and alkali nitrites over the concentration range 0.05-1.7 mol H_2O/mol cation at five temperatures between 110^o and 150^oC. The system is attractive because it exists in the liquid state over the whole range of composition from molten salt to pure water at temperatures above 110⁰C and is suitable for extending the vapor pressure measurements into the transition region where the electrolyte and water mole fractions are approximately equal. The vapor pressure obeys Henry's Law over the range 0-1 mol H₂O/mol cation; the same behavior was observed for hydrate melts containing LiNO₂-KNO₃. The results are discussed in light of the trends observed for the other hydrate melt systems already studied.

Introduction

Progress towards a general understanding of solutions containing electrolytes and water has been inhibited by a lack of information on hydrate melt systems, i.e., those solutions of electrolytes and water with insufficient water to complete the hydration sheaths of the ions. A major factor contributing to this state of affairs is the apparent existence of only a few hydrate melt systems at temperatures below 200°C, which severely limits the number of melt compositions accessible to experimental study. To date, only the systems LiNO3-KNO3-H₂O (1, 2, 3) and $AgNO_3$ -T1NO_3-H₂O (4, 5) have been studied over the entire range of composition from molten salt to dilute solutions of electrolytes in water. Recently, hydrate melts containing alkali nitrates and nitrites were identified (6) which exist in the liquid state at temperatures as low as 90°C over the whole range of electrolyte-water composition. This paper reports the results of a transpiration vapor pressure study on hydrate melts containing a specific composition of LiN03-KN02-NaN02 which is intended as the first in a series of investigations on this newly identified class of hydrate melts.

Experimental

The lithium nitrate, potassium nitrite and sodium nitrite were purchased from Alpha Products Co. and were used without further purification. The LiNO_3 was dried for 24 hours at 150°C and the alkali nitrites were dried a minimum of 48 hours at 85°C . The salt mixture consisted of 0.5199 mol LiNO₃/mol cation, 0.1684 mol KNO₂/mol cation and 0.3117 mol NaNO₂/mol cation, corresponding to approximately 50% LiNO₃, 20% KNO₂, and 30% NaNO₂ by weight. Mixtures for study were prepared by direct weighing of the compounds into a beaker, mixing, and then transferring the mixture to the transpiration cell. Water was added by difference weighing using a gas tight syringe fitted with a metal stopcork and a long, large bore needle.

The water vapor pressures were measured by a differential transpiration method, which has been previously described (1, 3), at five temperatures between 110° and 150° C and over the concentration range 0.05 to 1.7 mol H₂O/mol cation. The estimated uncertainty in the vapor pressures due to the measurement of pressure, temperature and water masses was ±1 torr. The observed reproducibility of the vapor pressures obtained from this and earlier studies was ±1 torr.

Results and Discussion

Table I summarizes the vapor pressures of hydrate melts containing .52 LiNO_3 -.17 KNO_2 -.31 NaNO_2 at 110.00°, 118.76°, 129.51°, 139.61° and 149.51°C. These results were calculated from the directly measured pressures and drying tube mass gains by the procedure previously described (1, 3) which includes corrections for the deviations of the water and carrier gas mixtures from ideality, solubility of the carrier gas (nitrogen) in the melt and the Poynting effect. Each value of the vapor pressure listed is the average of two runs at the specified water concentration and temperature.

The water fugacities listed in Table I were calculated from the equation

$f = p \exp(Bp/RT)$

where p is the vapor pressure, and B is the second virial coefficient of water. The water activities were calculated from $a_w = f/f_o$ where f_o is the fugacity of pure water.

Figure 1 summarizes the results in terms of vapor pressure as a function of water mole ratio, $R_{\rm H}$ (mol H₂O/mol cation). The LiNO₃-(K,Na)NO₂ system exhibits the same linear dependence of vapor pressure on water mole ratio found for the (Li,K)NO₃ system (1). This Henry's law behavior was also observed for (Li,K)NO₃ hydrate melts containing D₂O (2).

The vapor pressures of the $LiNO_3$ -(K,Na)NO₂ system at $110^{\circ}C$ deviate from linear dependence on R_H at water concentrations greater than about 1.2 mol H₂O/mol cation. This behavior is consistent with the infinite upper limit of the water mole ratio and the trend of the combined water activities for the (Li,K)NO₃ system obtained from a vapor pressure study (1) and an isopiestic study (7). The region of the nonlinear dependence of vapor pressure begins at a point where the system is in transition from one where water is the solute to one where water is the solvent. One of the attractive features of the LiNO₃-(K,Na)NO₂ system is that the magnitude of the vapor pressure allows for measurement by the differential transpiration method, through this water solute to solvent transition region.

The Henry's law constants, $K_{\rm H}$ = lim (f/R_H) listed in Table II $R_{\rm H}
ightarrow 0$

were obtained by least squares fitting of an equation of the form $f=K\cdot R_{\rm H}$ to the fugacity data at each temperature. At $110^{\rm O}$ C, only the data below 1.2 mol H₂0/mol cation were used to evaluate a Henry's Law

Table II

Henry's Law Constants for the System 0.52 LiNO₃-0.17 KNO₂-0.31 NaNO₂-H₂O

Temperature °C	Henry Law Constant
110.00	212.8
118.76	292.5
129.51	408.9
139.61	578.2
149.51	761.3

constant. The temperature dependence of the Henry's Law constant yields an average enthalpy of vaporization of water from the melt of 10.4 Kcal/mol over the temperature range $110^{\circ}-150^{\circ}C$. The enthalpy of vaporization of water from (Li,K)NO₃ melts over the same temperature range is also 10.4 Kcal/mol (1). The enthalpy of vaporization of pure water at $135^{\circ}C$ is 9.3 Kcal/mol (8).

Figure 2 summarizes water activities for several hydrate melt systems as a function of water mole fraction. The solid line represents the behavior of systems which obey Raoult's Law. Figure 3 summarizes vapor pressures for several hydrate melt systems, including preliminary data on the system $LiNO_3$ -KNO₂-H₂O at 129.51°C, as a function of water mole ratio.

Two related significant trends are apparent from the summaries. The $(Ag,Tl)NO_3$ system exhibits positive deviations from Raoult's Law and does not have a linear dependence of the vapor pressure on the water mole ratio. By contrast, the other hydrate melt systems show

negative deviations from Raoult's Law and a linear dependence of the vapor pressure on the water mole ratio at concentrations less than $R_{\rm H}$ = 1. A difference between the (Ag,Tl)NO₃ system and the systems showing negative deviations from Raoult's Law is the absence of a strongly hydrated cation in (Ag,Tl)NO₃ hydrate melts (4). It appears that the presence of a strongly hydrated cation like Li⁺ causes a hydrate melt system to have negative deviations from Raoult's Law and a region of linear dependence of the vapor pressure on the water mole ratio. Further evidence for the influence of the presence of a strongly hydrated cation on the vapor pressure and water activity behavior of hydrate melts is revealed by the (Ag,Tl,Ca)NO₃ system (5) which contains the strongly hydrated calcium ion and shows negative deviations from Raoult's Law and a linear dependence of the vapor pressure on the water strong hydrated calcium ion and shows negative deviations from Raoult's Law and a linear dependence of the vapor pressure on the water mole ratio.

Acknowledgment

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REFERENCES

- 1. Tripp, T. B., and Braunstein, J., J. Phys. Chem., 73, 1984(1969).
- 2. Tripp, T. B., J. Chem. Thermodynamics, 7, 263(1975).
- Tripp, T. B., "Molten Salts", The Electrochemical Society, 1976, p. 560.
- Trudell, M., Abraham, M., and Sangster, J., <u>Can. J. Chem.</u>, <u>55</u>, 1713(1977).
- Sangster, J., Abraham, M. C., and Abraham, M., J. Chem. Thermodynamics, 14, 619(1979).
- 6. Erickson, D. C., Energy Concepts Co., Annapolis, MD., private communication.
- Braunstein, H. and Braunstein, J., J. Chem. Thermodynamics, 3, 419(1971).
- "National Engineering Laboratory Steam Tables," Her Majesty's Stationary Office, Edinburgh, 1964.

TABLE I

Vapor Pressures, fugacities and activities for the system .52LiN0₃ -.17KN0₂ -.31NaN0₂

110.00⁰C

	Vapor		
P	Torr	Fugacity	Activity
ΨH	1011	rugacity	ACCIVICY
0.5451	115.3	115.1	.1091
0.5466	113.8	113.6	.1077
0.5678	121.7	121.5	.1151
0.6105	130.2	129.9	.1231
0.6437	138.0	137.7	.1305
0.6601	142.2	141.8	.1344
0.7308	157.5	157.1	.1488
0.7536	161.0	160.6	.1521
0.7786	166.6	166.2	.1575
0.8367	178.9	177.9	.1691
0.8515	182.9	181.3	.1718
0.9270	197.2	196.5	.1862
0.9334	198.0	197.3	.1870
1.0046	212.6	211.8	.2007
1.0236	221.1	220.2	.2087
1.0443	221.8	221.0	.2094
1.0533	226.4	225.5	.2137
1.1287	240.9	239.9	.2274
1.1713	248.8	247.8	.2348
1.2405	263.2	262.0	.2482
1.2855	269.9	268.7	.2546
1.2986	273.0	271.7	.2574
1.3525	282.0	280.6	.2659
1.3875	287.7	286.3	.2713
1.3939	290.8	289.4	.2742
1.5127	312.2	310.5	.2942
1.6140	327.2	325.4	.3084
1.7163	343.0	341.1	.3232
	118	3.76 ⁰ C	
0.2598	74.3	74.2	.05296
0.3139	91.9	90.8	.06582
0.3551	102.2	102.0	.07284
0.4052	117.7	117.5	.08485
0.4711	138.1	137.8	.09838
0.4967	144.7	144.4	.1031
0.5660	167.1	166.7	.1190

TABLE I Continued

	Vapor		
	Pressure		
R _H	Torr	Fugacity	Activity
0 5900	171 8	171 4	, 1223
0.5500	192 8	192.3	.1373
0.6924	203.9	203 3	1451
0.7511	222.2	221.5	.1581
0.7511	222.0	221.0	12002
	129	.51 ⁰ C	
0.0947	38.2	38.2	.01964
0.1724	70.1	70.0	.03604
0.1727	69.8	69.7	.03589
0.2631	108.7	108.5	.05585
0.2745	111.7	111.5	.05738
0.3477	144.7	144.4	.07433
0.3723	151.5	151.2	.07780
0.4526	186.8	186.3	.09590
0.4739	193.7	193.2	.09944
0.5727	234.3	233.6	.1202
	120	6190	
	135	9.61°C	
0.0679	41.9	41.9	.01615
0.1089	64.1	64.1	.02469
0.1622	93.4	93.3	.03594
0.2007	115.1	115.0	.04431
0.2579	147.7	147.4	.05681
0.2865	164.6	164.3	.06332
0.3580	210.3	209.8	.08084
0.3778	218.1	217.5	.08383
0.4759	276.8	275.9	.1064
	149	9.51 ⁰ C	
0 0626	16.2	16.2	01365
0.0620	40.2	40.2	.01480
0.1202	00.0	30.0	02898
0 1/30	100 1	109.0	.02090
0.1953	1/9.1	147 9	.03223
0.1933	161 3	161 0	04764
0.2696	207 9	207 5	.06136
0.2895	207.9	220.0	.06509
0.3494	266 0	265.2	.07847
0.3598	275 2	274 3	.08116
	213.2	21 4.5	



Figure 2. Water activity vs. water mole fraction for several hydrate melt systems.



Figure 3. Vapor pressure vs. water mole ratio for several hydrate melt systems.

VAPOUR PRESSURES AND THERMODYNAMICS OF MOLTEN HALIDE

MIXTURES

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ABSTRACT

Vapour pressure measurements by the Knudsen effusion method in combination with high-temperature mass spectrometry were used to obtain thermodynamic activity data of molten mixtures alkaline earth halide-alkali halide. The gas phase over these mixtures contains molecules of the pure halides as well as heterocomplexes. Using the experimental results of vapour pressure measurements, thermo-E dynamic parameters were calculated. The dependence of G^E on the kind of cations or anions supports our assumption about the structure of molten salt mixtures, derived by other physico-chemical properties.

In the last 15 years binary charge-unsymmetrical molten mixtures of the type alkali halide-alkaline earth halides were systematically studied in our laboratory. Such physico-chemical properties as phase diagrams, molar volumes, transference numbers, and molar electrical conductivities were measured. The last of these methods, measurement of electrical conductivities, was tested in the Molten Salts Standard Program organized by the Molten Salts Data Center.

In connection with the other methods vapour pressure measurements by the Knudsen effusion method in combination with high-temperature mass spectrometry were carried out to determine thermodynamic and transport properties of molten salt mixtures. In this way it should be possible to obtain information on the structure of melts.

Data on vapour pressures of bromide and iodide mixtures could not be found in literature. The systems calcium chloride-alkali chloride were studied by TOPOR et al (1) at higher temperatures using the quasi-static Rodebush-Dixon method. Vapour pressure data for the systems strontium chloride-sodium chloride, strontium chloride-potassium chloride (2) and barium chloride-cesium chloride (3) are published by KUSHKIN et al and SMIRNOV and co-workers, respectively. By the classical Knudsen effusion method vapour pressures of binary chloride and bromide mixtures of calcium, strontium, and barium with sodium, potassium, rubidium, and cesium were measured (4, 5). A direct comparison between literature values and our own vapour pressures of chloride mixtures shows a good agreement.

Experimental

Vapour pressure p can be calculated by the Knudsen equation 1

$$p = \frac{m}{A W t} (2 \pi R T/M)^{\overline{2}}$$

from the mass loss m accompanying the effusion process in the time t.

The	symbols	are	T-the	absolute temperature,
			R-the	gas constant,
			M-the	molar weight of vapour,
			A-the	effusion orifice area, and
			W-the	Clausing factor.

Effective orifice areas of Knudsen cells were determined microscopically considering the tabulated Clausing factors for geometry correction. The molecular effusion formula is applicable only to a small vapour pressure range. CARLSON (6) stated by effusion experiments with mercury that molecular flow exists to a pressure ≤ 10 Pa. In this region the molecules of the gas passing through the small effusion orifice move nearly independently of one another. At higher pressures the mean free path (Λ) of molecules is small enough in relation to the orifice dimensions (D) so that dependent motion prevails (hydrodynamical flow). In the Knudsen equation the factor 2π must be changed to e.

Different limits of transition from molecular flow to hydrodynamical flow expressed by the ratio Λ /D are given in literature. In this paper the equation for a hydrody-namical flow was used to calculate vapour pressures in the region Λ /D < 0.05.

Results

The vapour pressure of alkali halides is much higher than the vapour pressure of alkaline earth halides. So it could be assumed that the vapour over mixtures consists only of alkali halides to a good approximation. In the mass spectra of pure alkali halides ions from monomeric, dimeric, trimeric, and in some cases tetrameric molecules were observed. An extensive study of dimerization process

$$2 \text{ MX} \rightleftharpoons M_2 X_2$$

of alkali halides in gaseous phase was carried out.

From temperature dependence of mass spectra equilibrium constants of dimerization reactions and enthalpies of dimerization were calculated (Table I).

Table I. Temperature dependence of equilibrium constants of dimerization ln $K_D^{I} = A/T - B$ and enthalpies of dimerization $-\Delta H_D^0$ of alkali halides

salt	Α	В	-∆H _D (kJ/mole)	temperature range (K)
NaC1	20377	30.1646	169.4	873 - 1163
KC I	20470	32.3253	170.2	818 - 1118
RbC1	19635	33.1073	163.3	788 - 1113
CsCl	15083	29.8339	125.4	708 - 1043
NaBr	19151	31.1980	159.2	793 - 1103
KBr	18096	30.5968	150.5	783 - 1 10 3
RbBr	14 3 95	27.7597	119.7	758 - 1088
CsBr	17465	33.0468	145.2	678 - 993
NaI	15261	28.8781	126.9	723 - 1048
KI	15635	29.8592	129.7	748 - 1073
Rb T	15590	30.2483	129.2	733 - 978
CsI	14243	29.7522	118.4	683 - 958

In the vapour phase over bromide and chloride mixtures species other than monomers and dimers can be neglected in pressure calculation. In iodide mixtures - as an example in Fig. 1 the mass spectrum of the potassium iodide-calcium iodide system is shown - a higher content of calcium iodide molecules and heterocomplexes was observed.

Gaseous heterocomplexes of composition 1:1 were found over all mixtures. The contents of 2:1- and 1:2-heterocomplexes are essentially lower (Table II).

mixture	temperature (K)	MM'X3	^M 2 ^{M'X} 4
RbC1 - CaC1 ₂	1273	3.0	0.5
$RbBr - CaBr_2$	1073	1.1	0.5
RbBr - SrBr ₂	1073	0.4	0.1
RbBr - BaBr ₂	1073	0.2	
RbI - Cal	1073	3.1	1.0
$CsBr - CaBr_2$	1073	1.2	0.5
$CsBr - SrBr_2$	1073	0.3	0.1
CsBr - BaBr ₂	1073	0.1	0.01

Table II. Gaseous heterocomplexes over mixtures alkali halide-alkaline earth halide (%)

The absolute content depends on differences of ionic potentials, as is seen in the case of bromides, decreasing in the order calcium-strontium-barium. This dependence of properties of molten salt mixtures on ionic parameters, such as ionic potentials or charge densities of cations or polarizabilities of anions is characteristic of mixtures studied in this paper. Deviations of properties from ideality as a measure of interactions in molten ionic mixtures versus differences of charge densities of cations are presented in Fig. 2 and 3.

In Fig. 2 we plot the negative deviation of vapour pressure $-\Delta p$ from the "ideal pressure" at molar fraction x_{M} 'Cl₂ = 0.5 of molten chloride mixtures. Generally the alkaline earth cation has the higher charge density. But in the lithium chloride-barium chloride system the role of cations has changed. The difference of charge densities would have to be -1.68!

The excess free energy of mixing, G^{E} calculated on the basis of vapour pressure data may be another example (Fig. 3). Three dependences are shown: dependence of G^{E} on ion sizes of alkaline earth cations, of alkali cations, and of anions. In molten mixtures with great differences of charge densities of cations stronger interactions, expressed by the negative deviation of excess free energy from ideality, exist. An analogous behaviour was observed with increasing polarizabilities of anions.

On the basis of all our physico-chemical studies we could divide the investigated alkali halide-alkaline earth halide mixtures into three groups, using the quotient of charge densities of cations (Table III).

Table III. Dependence of interactions in mixtures on differences of charge densities of cations

group	$z/r_{M}^{2}2_{+}: z/r_{M}^{2}_{+}$	mixtures
A	> 1.5	(Na, K, Rb, Cs)X - CaX ₂ (K, Rb, Cs)X - SrX ₂ (K, Rb, Cs)X - BaX ₂
в	1.5 •••• 1.0	NaX - (Sr, Ba)X ₂
С	< 1.0	tiX - (Ca, Sr, Ba)X ₂

If the ratio is greater than 1.5 (group A), strong interactions exist in the mixtures. The anions are coordinated around the alkaline earth cation M^{2+} . In mixtures containing lithium halides the Li⁺ ion has the higher charge density. Thus it is a competition between cations of alkaline earth and lithium (group C). Mixtures with nearly ideal behaviour were arranged in the medium group Β.

References

- 1 Topor, L., Moldoveanu, I., Rev. Roum. Chim. 21, 495 (1976); <u>23</u>, 1353 (1978). 2 Kushkin, B. N., Rodyakin, V. V., Kuznetsov, S. I.,
- Zh. Neorg. Khim. <u>12</u>, 791 (1967). 3 Smirnov, M. V., Khalturina, L. K., Kudyakov, V. Y.,
- Khudolozhkin, V. N., Deposit. Doc. VINITI No. 7764-73. Emons, H.-H., Bräutigam, G., Thomas, R., Chem. Zvesti
- 30, 773 (1976).
- 5 Emons, H.-H., Kießling, D., Horlbeck, W., Wittenbecher, K., Chem. Zvesti, in print.
- 6 Carlson, K. D., Gilles, P. W., Thorn, R. J., J. Chem. Phys. 38, 2725 (1963).



Fig. 1 Mass spectrum of mixture potassium iodide-calcium iodide; $x_{CaI} = 0.4$; T = 1073 K.



Fig. 2 Deviation of vapour pressure from ideality
 versus difference of charge densities of cations.
 Chloride mixtures; T = 1243 K; O literature data, • own values.



- Fig. 3 Excess free enthalpy G^E of molten mixtures. a) dependence on alkali cations; T = 1243 K, 1) NaCl-BaCl₂, 2) KCl-BaCl₂, 3) RbCl-BaCl₂, 4) CsCl-BaCl₂; b) dependence of alkaline earth cations; T = 1073 K 1) KBr-CaBr₂, 2) KBr-SrBr₂, 3) KBr-BaBr₂; c) dependence on anions; T = 1073 K, 1) NaCl-SrCl₂, 2) NaBr-SrBr₂, 3) NaI-SrI₂.

PERFORMANCE OF ALUMINUM DEPOSITION FROM CHLORIDE MELTS

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ABSTRACT

Aluminum deposition from $KC1/AlCl_3$, $NaC1/AlCl_3$, and $LiC1/AlCl_3$ melts at variable temperatures (but at 700°C in most experiments) involves several factors which are detrimental for obtaining high current yields:

(i) Chlorine is dissolved in the melts and decreases current efficiencies for Al deposition by reoxidation of dispersed aluminum and by direct chlorine reduction at the cathode. Increasing chlorine solubilities and hence decreased current efficiencies are observed with increasing AlCl₃ concentration in the melt and --at least in melts of low AlCl₃ content-- with increasing temperature (1).

(ii) Dispersion (and subsequent reoxidation of dispersed aluminum) is favored at cathodes which are poorly wetted by Al, especially at vertical cathode faces in front of which the electrolyte is stirred vigorously by evolved chlorine gas. Carbon, due to the formation of thin Al carbide coatings, is not the most suitable cathode material because it is poorly wetted by liquid Al.

(iii) Higher oxygen content (Al_2O_3) in melts results in CO at the carbon anode which gives rise to rapid anode deterioration and - since CO readily dissolves as COCl₂ in the melts - in enhanced reoxidation of aluminum (yielding additional contamination of the electrolyte by finely dispersed carbon particles). For these reasons it seems desirable to change the technique for Al deposition from chloride melts by introducing well-wetted cathodes and dimensionally stable (i.e. non-corroding) anodes. The introduction of suitable diaphragms may also be of some advantage.

INTRODUCTION

Since the publication of ALCOA's patents (2), interest in the technique of aluminum electrowinning from chloride melts has increased steadily.

It is well-known that the ALCOA method still has to cope with some difficulties among which is a lower current yield than for Al deposition in the Hall-Heroult electrolysis.

Only very little is known about the details of the ALCOA process. Therefore, some experiments on Al deposition from NaCl-AlCl₃ melts were performed in a cell which allowed the visual observation of the electrolysis in order to obtain additional information on fluid dynamics and general physical behavior of electrolyte, gases and deposited metal within the electrolysis cell.

EXPERIMENTAL PROCEDURE

Fig. 1 depicts schematically the apparatus used which was constructed with the aim to allow visual inspection of the process, expecially the dispersion of electrodeposited metal (forming either brown fog or small but distinguishable droplets), the fluid dynamic behavior of the melt in front of the anode and the cathode, and formation of carbon particles and other insoluble materials in the melt.

The electrolysis vessel consisted of a quartz tube (quartz is relatively stable in chloride melts and is etched only very slowly by release of some SiCl₄ or SiO₂, respectively, into the melt). The vessel was heated by a gas burner and was insulated thermally by an asbestos screen equipped with an asbestos window which could be removed intermittently for visual inspection of the electrolysis process.

The electrodes (as indicated in Fig. 1) could be arranged vertically and horizontally at any desired distance between 5 mm and 50 mm. The aluminum electrode, immersed in the same electrolyte as used for electrolysis, was taken as reference electrode (R. Al el.). The reference electrode was connected to the measuring electrode by the usual (quartz) Luggin capillary. In some cases a diaphragm made of hard sintered Al_2O_3 (Staatliche Porzellanmanufaktur Berlin) was put between the vertically arranged electrodes. The electrolyte was prepared from thoroughly dried alkali chlorides. $AlCl_3$ was purified initially by double sublimation and later by distillation at pressures under 2 bars. Fig. 2 shows the vapor pressure of aluminum chloride vs temperature in order to demonstrate that $AlCl_3$ can be refluxed easily in the laboratory by applying conventional means and apparatus.

RESULTS

a) Voltammetry of Al deposition was performed on solid and liquid aluminum surfaces and at carbon electrodes. The voltammetric curves for Al deposition from LiAlCl₄, NaAlCl₄ and KAlCl₄ melts were very similar. Fig. 3a shows the voltammogram measured for deposition and dissolution of aluminum at liquid aluminum surface from a melt containing 60 mole % KCl and 40 mole % AlCl₃. The currentvoltage curve shows some hysteresis (10 to 15 mV) but in general it exhibits (up to a current density of 100 mA/cm²) nearly ohmic behavior with a formal impedance of 0.8 Ω cm² which must be due to an uncorrected IR-drop in the electrolyte (because of experimental reasons the tip of the Luggin capillary could only be kept at a minimal distance of 1 cm from the surface ; κ (KAlCl₄) -1Ω -cm⁻¹). Thus Al deposition and dissolution seem to proceed completely reversibly (as expected).

Fig. 3b shows the voltammogram measured at a carbon electrode (Sigri BK 02). The voltage range extends from -200 mV up to +2.5 V vs rev. Al el. so that the process of Al deposition as well as of Cl_2 evolution is observed.

Whereas chlorine evolution does not exhibit any peculiarities, the prewave of cathodic Al deposition is remarkably different from Al deposition on Al surfaces and very typical for Al deposition at carbon cathodes. The completely irreversible anodic peak with a current maximum at 1 V is due to reversal of the cathodic process observed by appearance of the prewave. The half-peak potential (+ 300 mV) of the cathodic prewave which is not mass transfer controlled and instead is attributed to a process which consumes current ($\int i dt$) proportional to the area of the electrode, leads to the assumption that the cathodic prewave is due to aluminum carbide formation (ΔG° (Al_4C_3)_{1000 K} = - 385.870 kJ/mol corresponding to a calculated formation potential of + 0.33 V vs rev. Al el.).

Since aluminum carbide is an insulator, it covers and blocks the carbon surface very effectively so that on further cathodic polarization and further increase of cathodic current, aluminum deposition and formation of liquid aluminum droplets may be observed only at singular points of the carbon surface. The mean surface density of active sites where aluminum is actively deposited as droplets does not exceed several ten to twenty per cm². b) Preparative Al deposition from NaCl/AlCl₃ (45/55 mole %) Melts. The aim of these experiments was to investigate the influence of electrode geometry (horizontal/vertical) and electrode wettability (by liquid aluminum) on current yields of cathodic Al deposition.

For these experiments the following electrode arrangements were used:

- a) Two rectangular vertical electrodes (2 x 4 cm²) with an electrode gap of 5 mm (upper electrode pair in Fig. 1)
- b) Two circular electrodes horizontally arranged with an electrode gap of 5 mm (lower electrode pair in Fig.
 l). The upper circular electrode was a perforated plate with approx. 50 % transparency and 2 mm Ø of the holes and served as chlorine evolving anode.

All experiments were performed with anodes made of graphitized carbon (Sigri BK 02) but different cathode materials were chosen. Total current-voltage curves were measured over the current density range 0.01 to 1.5 A/cm² and by extrapolation to zero current density "experimental decomposition potentials" were obtained.

Fig. 4 shows in its lower part the temperature dependence of the theoretical decomposition potential of NaCl-AlCl₃ melts (45 mole % AlCl₃, 55 mole % NaCl) in comparison to the "experimental decomposition potentials" of these melts and the measured cell voltages at standard current densities of 0.5 A/cm². Experimental decomposition potentials as well as experimentally determined cell voltages are influenced only slightly by the choice of the respective cathode materials (less than 50 mV at the highest current density of 1.5 A/cm²). This observation clearly shows that under stationary conditions Al deposition proceeds always at fresh Al surfaces. The upper part of Fig. 4 shows schematically what occurs at the carbon anode and cathode, respectively, at current densities of 0.5 A/cm² in the temperature range from 200° to 750°C.

<u>Cathode behavior</u>. At the cathode finely dispersed dendritic deposits are observed as long as the working temperature lies below the Al melting point of 660°C. In no case was it possible to melt down this metal powder to liquid metal because, due to traces of moisture or oxygen present in the melt, the small aluminum crystals are covered by a layer of alumina which prevents coagulation of the metal powder on melting. Below 660°C current
efficiencies for cathodic Al deposition are therefore always assumed to be virtually zero (Table 1). The situation is quite different for Al deposition above 660 °C. Then on carbon electrodes many small aluminum droplets are formed which on horizontally arranged cathodes eventually coalesce to form larger droplets or even a closed aluminum surface or pool which covers the cathode surface completely. On vertical carbon electrodes, however, the Al droplets which do not wet the surface show only very little Instead it is observed very often tendency to coalesce. that smaller aluminum droplets literally "explode" into the melt where a brown and glittering cloud of finely dispersed and minute aluminum droplets is formed which slowly settles to the bottom of the electrolyzer vessel. Usually the melt in an undivided cell is strongly agitated by anodically generated chlorine so that parts of this metal mist are moved to the anode where they undergo, at least partially, reoxidation to aluminum chloride. Furthermore, homogeneously dissolved chlorine (1) consumes some dispersed aluminum metal so that due to this pronounced and undesired metal dispersion at carbon electrodes, current yields for cathodic aluminum and anodic chlorine production do not exceed 50 % (second row, Table 1). At a horizontal carbon cathode lying below a perforated anode, current yields improve dramatically (to near 90 %) provided the carbon cathode is covered completely by a 'pool" of molten aluminum, so that the aluminum deposits on a completely closed surface of molten aluminum (row 4, Table 1). As long as small single droplets can be distinguished at the cathode, the "explosion" phenomena continue to occur and give rise to dispersion even at horizontal carbon cathodes; current efficiency does not exceed 60 %. It should be stressed that the use of a perforated horizontal anode above the horizontal cathode reduces greatly the convective motion of the electrolyte because the chlorine gas is allowed to escape through the electrode holes.

If instead of carbon cathodes, iron, steel or other cathode materials (TiB₂) are used which are "wetted" by liquid aluminum (i.e. at which the wetting angle of liquid aluminum approaches zero), then even at vertically arranged cathodes liquid aluminum is deposited with current efficiencies very close to 100 %. There is a distinct influence of the nature of the electrolyte on current efficiencies of Al deposition on carbon anodes. Cathodic current efficiencies obtained at vertical carbon cathodes decrease from ~45 % to below 20 % if KC1/AlCl₃ (60/40) is used instead of NaC1/AlCl₃ (60/40). This seems to be due to the enhanced chlorine solubility in KAlCl₄ melts compared to NaAlCl₄ melts (compare in (1) the difference between LiAlCl₄ and CsAlCl₄ melts).

Anode behavior

The pronounced chemical instability of the anode at lower temperature is most important, which is very likely due to the formation of chlorine-aluminum chloridegraphite intercalation compounds (4). These intercalation compounds are formed preferentially at the graphite grain boundaries so that the matrix of the graphitized carbon is destroyed rapidly. Because the Cl₂ decomposition pressure of the intercalation compound increases with increasing temperature, graphite anodes become more stable at higher temperatures. They are stable for no longer than -10 minutes at 250°C. Around 500°C their stability is somewhat better but only above 620°C they may be assumed to be reasonably stable. Nevertheless there is some doubt that graphite may be really a perfectly dimensionally stable anode because it may be corroded at high temperature by formation of carbon tetrachloride. According to JANAFtables the equilibrium constant for CCl4 formation at 700°C amounts to

$$K_{\rm p}$$
 (CC14) 1000 K = 7.10⁻³ bar⁻¹ (1)

2

so that in the presence of 1 bar of chlorine an equilibrium partial pressure for CCl_4 of nearly 10^{-2} bars has to be taken into account. The equilibrium constant for CCl_4 formation decreases with increasing temperature, so that carbon anodes become more stable at higher temperatures.

c) Cathodic Al deposition in the presence of Al₂O₃ Some electrolysis experiments were performed upon the addition of 2.5 to 3.5 mole % Al₂O₃. The presence of oxo-anions in the melts at such high concentrations is very disadvantageous for the performance of cathodic Al deposition at any cathode material, whereas at carbon anodes the oxo-anions are preferentially discharged to form CO or COCl₂ which is dissolved in the melt. At the cathode in the presence of Al₂O₃ one observes that

(i) Droplets of liquid aluminum which do not stay in contact with the cathode react relatively rapidly with dissolved phosgene to form Al oxychloride and carbon. 4 A1 + 3 COCl₂ \rightarrow 3 AlOCl + 3 C + AlCl₃

Single aluminum droplets are soon covered with a thin carbon layer and redissolve (depending on their size) in 10 to 20 minutes.

(2)

(ii) Because aluminum oxochloro complexes are discharged at the electrode preferentially (5), the oxo-ion concentration at the cathode increases to an extent which exceeds the solubility product of Al₂O₃. Aluminum oxide is coprecipitated with aluminum (and carbon) so that no longer a smooth cover of Al (on well wetted cathodes) or a multitude of single Al droplets (on non-wetted carbon electrodes) is deposited but a firmly adhering sludge of Al/Al₂O₃/C from which aluminum cannot be recovered and which, after some time, blocks the cathode or fills the electrode gap giving rise to anode/cathode short circuits. In KA1C14 melts these reactions decrease current efficiency to a larger extent than in NaAlCl_L melts because CO, $COCl_2$ and Al_2O_3 solubilities seem to be higher in K-melts than in Na- (or Li-) melts.

Cathodic Al deposition at vertical electrodes of different cathode materials

Since poor Al wettability of carbon cathodes gives rise to dispersion and reoxidation of aluminum, different metals were investigated as cathode materials in order to evaluate their suitability. All of these metals are wetted well by liquid Al.

Table 2 compares the results for Al deposition obtained in short-term experiments (3 to 8 hrs) with current densities of 0.5 A/cm^2 in KCl/AlCl₃ (60/40) in KCl/AlCl₃ (60/40) melts for carbon and the wettable metals stainless steel, titanium, zirconium, tungsten, and the refractory material TiB₂ (from Elektroschmelzwerk Kempten GmbH). At all wettable metal cathodes comparable current efficiencies were obtained. As expected, stainless steel is strongly attacked by dissolution into the liquid aluminum (which is nearly saturated with iron). Titanium and zirconium cannot be used either since they are rapidly alloyed and further deteriorate by dissolution of the base metal into liquid aluminum (which was not expected from the published phase diagrams). Tungsten is stable for a short time, but a thorough inspection reveals that after only 8 hours of operation, there is some deterioration due to the

beginning of alloying with aluminum. Only titanium diboride does not show any deterioration.

Thus it is quite clear that refractory metal compounds like carbides and borides with free enthalpy of formation which exceeds the free enthalpy of Al alloying may be used as wettable cathodes. Ti, Zr and W (and particularly steel) may be used only as support materials for those refractory metals if a perfectly dense layer of the refractory material can be formed on the metal support.

CONCLUSION

The aim to develop further aluminum electrowinning from chloride melts by decreasing cell voltages below 3.5 V (for instance by reducing still further the electrode distance) and by raising simultaneously current efficiencies might call for a new cell concept which uses separator divided cells with vertical electrodes. For this purpose, but with some benefit from ALCOA's technology, solutions for the following material problems should be found in:

- Development of low-cost cathodes which are wetted by aluminum but have a low solubility in it (refractory metals or materials coated by refractory metals).
- Development of non-carbonaceous anodes with high intrinsic electrical conductivity, anodic corrosion resistance and low Cl₂ overvoltage.
- 3) Development of corrosion resistant and electrically insulating materials for cell bodies, tubes, and heat exchangers, which would allow to handle the anodically generated chlorine at temperatures up to 1000 K.

ACKNOWLEDGEMENT

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REFERENCES

- R.A. Carpio, L.A. King, A.P. Ratvik, T. Ostvold, and H.A. Øye, Light Metals, 325 (1981)
- [2] Aluminum Company of America DBP 2213226, 2244036, 2244040, 2251262 (1972)

- [3] JANAF, Thermochemical Tables 2nd ed., NSRDS <u>37</u>, (1971)
- [4] A. Baiker, E. Habegger, V.K. Sharma, and W. Richarz, Carbon, 19, 327 (1981)

 \sim

 [5] A. Bjørgum, Å. Sterten, J. Thonstad, and R. Tunold, "Passivation of the cathode by alumina deposition from aluminum chloride-sodium chloride melts". Euchem Conference on Molten Salts, La Gaillarde, May 1982, Extended Abstract B 5. <u>T a b l e l</u> Deposition Yields for Cathodic Al Deposition

Electrode	Temperature	Al current yield
graphite horizontal and vertical	200 - 650°C	virtually 0
graphite vertical	600°C	small droplets 40 - 50 %
graphite horizontal	660°C	larger droplets 45 - 60 %
Al-regulus horizontal	660°C	95 %
iron or other wetting cathodes (vertical)	660°C	95%

<u>Table 2</u>

* Mean value of several	experiments	performed from 3 to
TIB ₂ **	85	Material unchanged
Tungsten	60	Slightly changed by alloy formation
Zirconium	78	Deteriorated by alloy formation and dissolution
Titanium	68	Deteriorated by alloy formation and dissolution
Stainless steel	63	Surface corrosion by dissolution
Carbon (EK 78, Sigri)	15	Stays intact
Cell, Cathode Material Current	Carbon Anode Yield [%]*	Material Performance
Performance of Di For Al Deposition (T = 1000 K, i=0.5 A/cm ² ,	fferent Cath From KC1/A1C Vertical E1	ode Materials 1 ₃ :60/40 Melts) ectrodes, Undivided

8 hours each.
** Delivered from Elektroschmelzwerk Kempten.



Fig. 1



Fig. 2



Fig. 3a

Fig. 3b



Fig. 4

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OXYGEN EVOLUTION AT PLATINUM AND CERAMIC OXIDE ANODES IN CRYOLITE-ALUMINA MELTS

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ABSTRACT

Polarization measurements were carried out with Pt, SnO_2 , Fe_2O_3 , and Fe_3O_4 anodes in a cryolite bath containing a nominal 7w/o CaF, saturated with Al₂O₃ and Al metal at 970°C. Water present in the Bath appears to play a catalytic role in the O₂ evolution mechanism. Platinum and SnO_2 were observed to act as reversible O₂ electrodes in low cryolite ratio (1.10) baths. The usefulness of electrochemical parameters for predicting anode corrosion rates is limited by the unknown rate of chemical corrosion by bath constituents during cell testing.

Introduction

Overpotential during anodic polarization and corrosion resistance are two key parameters for consideration in the development of non-consumable anode (NCA) electrodes for the electrowinning of metals in high temperature molten salts. Fabrication of an NCA for the Hall process with acceptable corrosion rate is made difficult by the aggressive nature of the cryolite electrolyte toward most metals, refractory hard metals, and ceramic oxide compositions during anodic polarization. The reversible Hall cell potential is increased by ~1.0 volt at 970°C when carbon is replaced with an NCA because of the resulting loss in depolarization of the anode reaction by carbon(1).

> Reversible Potential(V) at 970°C

^{A1} 2 ⁰ 3	+	$3/2C \rightarrow 2A1 + 3/2CO_2$	1.186	(Eqn.	1)
Al ₂ 03	→	2A1 + 3/20 ₂	2.213	(Eqn.	2)

Most of this increase will be made up through the expected reduction in operating voltage because of lower NCA₂ overpotential, 0.2 vs. 0.5V for carbon at 800 mA/cm²(2), and lower bath resistance for reduced anode-cathode spacing(3). The purpose of this work was to evaluate

various ceramic oxide compositions for use as anodes in the Hall process.

Experimental

The electrochemical test cell was contained in a twopiece gas-tight Inconel jacket (Figure 1). The bottom section was lined with a graphite crucible which contained the cryolite bath. A ceramic plug provided with holes for the electrode configuration was placed above the crucible to prevent excessive heat loss from the bath. Conax packing glands mounted in the water-cooled top section of the Inconel jacket provided gas-tight entry ports for electrodes, thermocouple and bath purging. Each electrode sample was suspended by a Pt current lead and lowered slowly to minimize the effects of thermal shock. The active surface area was limited to the bottom face of the sample by an alumina sheath which also provided electrode support. The Al reference potential was provided by a pool of Al in contact with the bath. A small increase in potential occurred with time as a result of alloy formation between the molten Al and Mo contact wire. Periodic removal of this alloy from the wire and maintenance of the pool resulted in a stable Al reference.

The bath was made from commercial grade components as shown in Table I. Synthetic cryolite containing a nominal 7w/o CaF₂ was saturated with both alumina and Al metal.

Table I

Bath Components

Component*	Source	Ingredients	Percent
Synthetic Cryolite	Alcoa	Cryolite (AlF ₃ ·3NaF) Free Al_2O_3 SiO ₂ Moisture	$\begin{array}{rrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrrr$
		L. O. I.	2.0 - 6.0
Aluminum Fluoride	Kaiser	Alf	92.0
Calcium Fluoride	MCB	Caf	min. 98.0
Alumina	Alcoa	$A1_20_3$ Na ₂ 03	99.5 0.5
Aluminum	Belmont	Al ²	99.9

*A bath made from components listed above would include small quanities of the following elements: Li, Be, Mg, Ti, V, Cr, Mn, Fe, Cu, Ga, Mo, and Ag. Bath Charge = 1,800 grams. The bath cryolite ratio (expressed here as the weight ratio of NaF to AlF₃) was adjusted by additions of AlF₃. One unknown factor is the amount of moisture present in the initial bath composition. Large quantities of water (150-200 g) were expelled during the slow bath heat-up. The initial bath cryolite ratio was always larger than expected for the initial composition: reaction of water with AlF₃ to give additional Al₂O₃ and volatile HF during bath heat-up would explain this. Carbon particles were removed by purging the bath with O₂. Polarization measurements for Pt and ceramic oxide anodes were made in baths saturated with dissolved O₂. The bath was maintained at temperature (970°C) for periods of 2 to 3 weeks without any major problems. Values for the cryolite ratio, CaF₂ content, and Al₂O₃ during periods of cell operation. Excess Al₂O₃ and CaF₂ solids form a bottom layer in the bath.

Steady state IR corrected polarization curves were obtained for Pt and a number of sintered high density ceramic oxide anodes. Measurements were made with a PAR Model 173D potentiostat with log current convertor plug-in module and the Model 175 programmer. Polarization data was plotted continuously on an Omnigraphic 2000 series X-Y recorder while sweeping the anode potential at a scan rate of 0.2 mV/sec. IR corrections were obtained by the current interrupt method. Open circuit cell potentials were observed with the digital display on the Model 173D potentiostat after electronically switching the cell current from 1.0A to zero amperes. The Pt anode (0.25" dia. x 0.5" rod) was heli-arc welded to a 40 mil Pt wire current collector. Metal oxide anodes were prepared by standard ceramic processing methods: ball-milling of powder mixtures, calcining, isostatic molding of screened powders, and high temperature sintering under conditions of controlled atmosphere and temperature profile. Anode densities were better than 98% theoretical.

Results and Discussion

A typical polarization plot for the O₂ evolution reaction on Pt and the corresponding IR corrected curve are shown in Figure 2. The anode was pre-polarized at a current density of \sim 3100 mA/cm² for a period of two hours prior to scanning toward lower potentials. In this curve the cathodic branch due to O₂ reduction was observed for potentials below 2.13V. Anode potentials are plotted relative to the potential of the Al-pool reference. The open circuit potential observed on Pt for the decomposition of alumina was 2.18V. This value was observed for a period of 30-35 sec. only after O₂ was evolved anodically at a high current density for a period of 1-2 minutes. The thermoelectric potential at the Mo/Al interface (Al-negative lead) was measured from room temperature to 640°C. The estimated 16mV addition (extrapolated value at 970°C) gives a corrected decomposition potential of 2.20V, close to the theoretical value of 2.213V (Eqn. 2). The IR corrected curve for this polarization plot has two Tafel regions: a low slope region (70 mV) which extends from \sim 30 mA/cm² to 1 A/cm² and a high slope region (148 mV) for larger current densities. In general the anodic and cathodic branches of a polarization plot were not reproducible below \sim 30 mA/cm². The Tafel region for current densities less than 30 mA/cm² is discussed later for one polarization plot where the Pt anode behaved as a reversible O₂ electrode.

Kinetic parameters for the O, evolution reaction on Pt and the bath cryolite ratio are listed in Table II for several polarization experiments. The average value for

Table II

KINETIC PARAMETERS & BATH RATIO FOR THE O2 EVOLUTION REACTION ON Pt*

Cryolite Ratio	Tafel Low	Slope	e (MV) <u>High</u>	Reversible ^O Potential(V)
1.42	73		161	1.93
1.45	70		148	2.12
1.37^{x}	75		133	2.11
1.39.	67		111	1.96
1.0 ×		67		2.01
1.08		57		2.12
1.09		63		2.19
1.10	63		150	2.15

*Electrode prepolarized anodically for 2 hours at ${\sim}3000~\text{mA/cm}^2\text{.}$

XEstimated Value: Method not calibrated for cryolite ratios between 1.25 and 1.39 and below 1.08.

^OPotential at intersection of anodic and cathodic branches.

the small Tafel slope is 67 ± 4 mV. There is no apparent trend toward lower Tafel slope values as the cryolite ratio of the bath is decreased. With one exception the large 2 slope observed for current densities greater than 1 A/cm² disappears in low cryolite ratio baths. Variation in the

alumina concentration may account for this result. The alumina concentration can vary throughout the cell espe-cially after prolonged periods of anodic polarization (4). During polarization measurements the over-potential will be sensitive to changes in the bulk concentration of alumina near the anode/electrolyte interface at high current densities. Overpotential will increase if the bulk concen-tration near the anode is less than the normal saturated value due to a variation in experimental parameters such as the O, purge rate or the temperature profile in the bath. Bath Stirring would help to alleviate this problem also. This sensitivity resulted in a greater average deviation of the large Tafel slope (138+16 mV) in high cryolite ratio baths (>1.37). Larger slope values were observed by Thonstad in a previous study carried out at 1000°C in a bath of hand-picked Greenland cryolite saturated with alumina (5). Values for the small slope varied from 82 to 90 mV while values for the large slope varied from 245 to 255 mV. The mechanism in Table III provided good agreement with his Tafel slope values. These results suggested that the presence of small mounts of water in the bath has no major influence on the mechanism for 0, evolution.

Table III

MECHANISM FOR THE OXYGEN EVOLUTION REACTION IN THE ABSENCE OF WATER AS A MAJOR BATH IMPURITY

Tafel Slope of RDS* At 970°C (mV)

1.			0 ²⁻	\rightarrow	o _{ad} -	ł	2e	247
2.	0 ad	+	0 ^{2–}	\rightarrow	02ad -	ł	2e ⁻	82
3.			0 2ad	\rightarrow	0 ₂ (g)			62

*Rate determining step

The mechanism in Table III is not compatible with the smaller Tafel slope values of Table II obtained from steady state polarization measurements. Water is present in our bath most likely in the form of hydroxide ions. The present results suggest that water plays a catalytic role in O_2 evolution. A more likely mechanism involves the discharge of a OH⁻to form an adsorbed OH species, OH_a. The steps listed in Table IV are generally accepted for such a mechanism in alkaline solutions where OH⁻ is the dominant anion. The Tafel slopes for step 2 (165 mV) and step 3 (62 mV) are in better agreement with the results presented in Table II. At low current densities where the

Table IV

MECHANISM FOR THE OXYGEN EVOLUTION REACTION IN THE PRESENCE OF WATER AS A BATH IMPURITY

					Tafel Slope (RDS* at 970°C (mv)	Of
1.		он → он	a +	e ⁻	492	
2.	OH ad	$+ \text{OH} \rightarrow \text{O}_{ad}$	+	^н 20	+ e 165	
3.	0 ad	$+ \circ_{ad} \rightarrow \circ_2^{-}$	g)	-	62	

*Rate determining step

coverage by O_{ad} is small, the recombination rate is slow. Since the O_{ad} species are not necessarily adjacent surface migration plays a role in limiting the rate of recombination. In this case step 3 is rate determining with a Tafel slope of 62 mV. At higher current densities where coverage by O_{ad} is larger recombination is no longer limited by surface migration. Here the second charge transfer step at a given surface site appears to be rate determining with a Tafel slope of 165 mV.

The disappearance of the high Tafel slope region in baths with low cryolite ratio may be influenced by changes in surface coverage by the Al-F complexes present in the bath due to changes in bath composition. Addition of AlF₃ to lower the bath cryolite ratio will cause an increase in the concentration of the AlF₄ anion. A moderate increase in surface coverage by adsorption of additional AlF₄ anions could hinder surface migration without seriously limiting the number of surface sites available for OH adsorption. In this case O_{ad} recombination (step 3) would remain rate determining at higher current densities.

A typical polarization plot for the O₂ evolution reaction on SnO₂ and the corresponding IR corrected curve are shown in Figure 3. The anode was pre-polarized at a current density of $1A/cm^2$ for a period of 30 minutes prior to scanning to lower potentials. The cathodic branch (O₂ reduction) starts at 2.13V. The IR corrected curve has two Tafel regions; a low slope region (53 mV) which extends from ~ 9 to 55 mA.cm² and a high slope region (126 mV) for larger current densities. The anodic and cathodic branches of a polarization plot were not reproducible below 9 mA/cm². Kinetic parameters for O_2 evolution on SnO_2 and the bath cryolite ratio are listed in Table V. Stirring had no

Table V

KINETIC PARMETERS & BATH RATIO FOR THE O. EVOLUTION REACTION ON Cu/Sb-DOPED snO_2^{*2}

Cryolite	Tafel Sl	ope (mV)	Reversible ^O
Ratio	Low	High	Potential (V)
1.07 ^x	57	130	2.17
1.07.	57	142	2.14
1.09 [×]	53	126	2.13
1.09	60	120	2.15

*Electrode prepolarized anodically for 30 minutes at ~ 1000 mA/cm².

Stirred bath

Potential at intersection of anodic and cathodic branches.

obvious effect on the polarization curves. The average value for the small and large Tafel slopes is 57 mV and 130 mV, respectively in a low cryolite ratio bath. These values although somewhat lower than the corresponding values for Pt in a high cryolite ratio bath suggest that the mechanism on Pt and SnO₂ are similar. For SnO₂ this requires that the O_d recombination step not remain rate determining at large current densities in low cryolite ratio baths.

The polarization curve of an NCA with large corrosion rate is different in shape from the polarization curve for Pt, one metal that shows no signs of corrosion during O₂ evolution in cryolite baths for current densities less than $3A/cn^2$. Four polarization parameters; the reversible potential (RP), the crossover current density (CCD), overpotential (n) at the CCD, and n at 800 mA/cm² were measured in an attempt to provide an initial indication of the expected anode corrosion rate. Steady state IR corrected polarization curves for Pt, SnO₂, Fe₂O₃ and Fe₃O₄ are shown in Figure IV. An initial examination of these curves shows that the preferred Cu/Sb-doped SnO₂ anode with low corrosion rate has a polarization curve similar in shape to that of Pt while the curves for both Fe₂O₃ and Fe₃O₄ anodes with large corrosion rates behave differently at potentials below the decomposition potential of alumina.

Platinum behaves as a reversible O2 electrode in low cryolite ratio baths. The RP for Pt obtained in a bath with cryolite ratio of 1.09 at 970° C was 2.19V. The corrected value of 2.206V includes the thermoelectric potential of the Mo/Al interface and is close to the theoretical value of 2.213V for the decomposition potential of alumina at 970°C. The reversible behavior of Pt may result from the presence of a Pt-O alloy formed during a 2 hour anodic polarization at high current density prior to the start of polarization measurements. This alloy behaves more like a reversible O_2 electrode than Pt in acid solutions of H_2SO_4 and HF (6). The Tafel slope in the current density region below 30 mA/cm² is 34 mV for the Pt curve in Figure 4. This suggests that the reaction mechanism at low current densities involves a Pt (VI) surface complex. The Tafel slope for dissociation of this complex as the RDS is 41 mV. The mechanism in Table VI is comprised of one series of steps which gives the desired result. Formation of a bulk Pt-O alloy, Pt, O, which is

Table VI

MECHANISM FOR THE OXYGEN EVOLUTION REACTION ON A Pt-O ALLOY

Tafel S	hope Of
RDS	At
970°0	(mV)

1.	Pt	+	20H \rightarrow PtO _{ad} + H ₂ O + 2e	247
2.	nPt	+	$PtO_{ad} \rightarrow Pt_{n}O + Pt,$ $n \leq 4$ bulk Pt	124
3.	Pt0 ad	+	$20H \rightarrow Pt(0_{ad})_2 + H_20 + 2e^-$	82
4.	$Pt(0_{ad})_2$	+	$20H \rightarrow PtO_3 + H_2O + 2e$	49
5.	Pt03		\rightarrow PtO _{ad} + O ₂ (g)	41

*Rate determining step

stable at high temperature (7) completes the process and restores catalytic activity to the surface. Surface etching and expansion of the Pt lattice (7) during prepolarization may be more favorable for formation of Pt-O alloy at small current densities. Pt is less reversible as an O_2 electrode, i.e. the RP is lower, in a bath where the cryolite ratio is higher (>1.3, Table II).

Polarization parameters and the corresponding corrosion rate of SnO_2 , Fe_2O_3 and Fe_3O_4 are listed in Table VII for comparison with Pt. The curve for SnO_2 is similar to that of Pt and indicates that SnO_2 is nearly reversible as an O_2 electrode in a low cryolite ratio bath. Reversible behavior was not observed in a bath with higher cryolite ratio (1.54); the RP was only 1.8V. The corrosion rate of 1 in./yr. listed in Table VII for SnO_2 in a bath with cryolite ratio of 1.20 increased to 1.5 in./yr. when the bath ratio was increased to 1.5. These results with Pt and SnO_2 suggest that less corrosion can be expected under bath conditions where the anode behaves more nearly as a reversible O_2 electrode, i.e. in a low cryolite ratio bath. As discussed below this behavior is dependent on the anode experiencing a low rate of chemical corrosion.

Anode compositions Fe_2O_3 and Fe_3O_4 do not act as reversible O_2 electrodes in Cryolite since the RP is only 1.82 and 1.93, respectively; far less than the nearly reversible value of 2.19V observed for Pt. In each case the CCD is 3 times larger than for SnO₂. Values for these two parameters alone suggest that $Fe_2O_3^2$ and Fe_3O_4 should corrode much faster than SnO₂ (as observed) but at similar rates. However larger values of n at the CCD and at 800 mA/cm² suggest that Fe_2O_4 should corrode at a somewhat faster rate than Fe_2O_3 (which was not observed). Since polarization measurements include only the electrochemical component of corrosion the large increase observed in the corrosion rate of Fe_3O_4 (1000 in./yr.) must be due primarily to chemical corrosion processes, i.e. extensive anode attack by the bath components during anodic polarization. This limits the usefulness of polarization measurements for predicting anode corrosion rates.

Conclusions

Water present in the cryolite bath appears to play a catalytic role in the mechanism for O₂ evolution on Pt. Both Pt and SnO₂ were observed to act as reversible O₂ electrodes during steady state polarization measurements in baths with low cryolite ratio. Formation of a stable Pt-O alloy during prepolarization at a high current density may account for the reversibility of Pt observed at low current densities. Chemical corrosion of NCA electrodes by bath components during cell testing limits the usefulness of electrochemical parameters obtained from polarization measurements for predicting accurate corrosion rates of potential NCA electrode compositions. Table VII

COMPARISON OF PARAMETERS FROM IR CORRECTED POLARIZATION CURVES IN FIGURE 4 WITH CORROSION RATES

Anode Composition	$\frac{RP^{A}(V)}{KP^{A}(V)}$	CCD ^B (mA/cm ²)	n (V) ^C At CCD	n (V) ^C At 800 mA/cm	Corrosion Rate (In./Yr.)
Pt	2.19	0	ł	0.16	0
Cu/Sb-doped Sn0-	2.17	^д 6	0.032	0.24	Г
2.6 w/o TiO ₂ - doped Fe ₂ O ₃	1.82 ^E	28	0.015	0.18 0.21 ^F	36
5.0 w/o TiO2- doped Fe ₃ 04	1.93 ^E	06	0.035	0.34	1000

- Potential at intersection of anodic and cathodic branches. Current density above which 02 evolution becomes dominant anodic process. A B
- Based on 2.18V decomposition potential observed for Pt by open circuit potential method. υ
 - From polarization curve in Figure 3.
 - Reversible potential is a mixed potential for anode വല
 - corrosion/0, reduction. Гч
- Value for extended Tafel region (---).

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REFERENCES

- 1. JANAF Thermochemical Tables, Second Edition, Dow Chemical Company, Midland, Michigan, June 1971.
- Inert Anodes for Aluminum Smelting, Final Technical Report for the Period 1980 October 01 - 1981 September 30, Aluminum Company of America, Alcoa Laboratories, Alcoa Center, PA 15069.
- Kari Billehauf and H. A. Oye, Inert Anodes for Aluminum Electrolysis in Hall-Heroult Cells, Aluminum 57 (2), 146 (1981), Aluminum 57 (3), 228 (1981).
- Bratland D., Brun M., Grjotheim K., and Thonstad J., Light Metals Vol. 1 (1979) pp. 397.
- 5. Thonstad J., Electrochimica Acta 13, (1968), pp. 449.
- 6. Hoare J. P., Electrochimica Acta, 27 (1982), pp. 1751.
- 7. Hoare, J. P., Electrochimica Acta 26, (1981), pp. 225.



Figure 2 - Polarization Plot & IR Corrected Curve for O_2 Evolution on Pt

Figure 1 - Electrochemical Test Cell



Figure 4 - Polarization Plots & IR Corrected Curves for O_2 Evolution on Pt, SnO_2 , Fe_2O_3 and Fe_3O_4

THE ELECTROCHEMICAL BEHAVIOR OF SULFIDE IONS IN MOLTEN CRYOLITE

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ABSTRACT

The electrochemical behavior of sulfide ions in molten cryolite (Na3AlF6) has been studied by cyclic voltammetry using graphite electrodes at 1323 K. The oxidation of sulfide ions is found to proceed via a quasi-reversible mechanism, i.e., one in which the current is controlled by both diffusion and charge transfer kinetics,

$$s^{2-}$$
 $\xrightarrow{k_{s},\beta}$ $s+2e^{-}$

The transfer coefficient β and the standard rate constant k_s are estimated to be 0.5 and 0.0042 cm/sec, respectively. The apparent diffusion coefficient for sulfide ions in cryolite at 1323 K is about 3.93×10^{-5} cm²/sec.

INTRODUCTION

Since the work of Delarue (1,2) on the anodic oxidation of sulfide ions in molten salts, many investigations have been published on the subject. However, as indicated by the reviews (3-5) written on the electrochemical behavior of sulfide ions in molten salts, the mechanism of the reaction is still controversial and cannot be interpreted in an unambiguous manner.

The electrochemical behavior of sulfide ions in molten salts is of considerable interest from both fundamental and applied viewpoints. The oxidation of sulfide ions offers challenging fundamental research since the chemistry and electrochemistry of sulfur-sulfide in molten systems are quite complex. From the applied viewpoint, knowledge of the electrochemical reaction of sulfide is important for (i) battery technology such as high-temperature secondary batteries (6) and (ii) metallurgical molten-salt processes such as metal electrowinning from sulfides (5).

Most of the previous such studies reported in the literature were carried out on sulfides in chloride melts at a temperature range of 700-850 K. Recently, in connection with research on the production of aluminum via the electrolysis of Al₂S₃, the present authors investigated the anodic oxidation of sulfide in MgCl₂-NaCl-KCl eutectic (7), AlCl₃-MgCl₂-NaCl-KCl melts (8), and LiF-NaF eutectic (9) at a higher temperature (1023 K). The electrochemical behavior of sulfide in molten cryolite (Na₃AlF₆) at 1323 K was also studied using the technique of cyclic voltammetry. The results obtained from that study are presented in this paper.

EXPERIMENTAL

The cell in the present work consisted of three electrodes inserted into a pyrolytic boron nitride crucible (5.2 cm dia., 7.2 cm high, Union Carbide) containing a blended mixture of molten cryolite and Al₂S₃. The boron nitride crucible was dipped into alumina granules held in a stainless steel crucible. The steel crucible was placed inside a furnace tube. The flanged top of the furnace tube was sealed to another flange consisting of inlet ports that provided access to the melt. The furnace tube was heated by a three-zone Mellen furnace (Model C-2-121) with a Mellen temperature controller (Model 919).

A three-electrode system was used for all measurements. The working electrode was a graphite rod (0.63 cm dia., Union Carbide, grade ECV) insulated with hot-pressed boron nitride (Carborundum) so that only a defined surface area was exposed to the molten salt. Another graphite rod served as the counter electrode. A Pt wire was used as a quasi-reference electrode.

The molten salt was prepared from an accurately weighed and blended mixture of cryolite and Al₂S₃ reagent (Cerac Pure, 99.9% pure) inside a helium atmosphere glovebox. The mixture was charged into the boron nitride crucible and brought out of the glovebox, and the cell was quickly assembled under argon. An argon atmosphere was maintained above the cell in all experiments. For cyclic voltammetric measurements, standard voltammetric instrumentation was employed.

RESULTS AND DISCUSSION

For background information, voltammetry of pure cryolite without sulfide added was carried out. A typical voltammogram of the melt at 1323 K is shown in Fig. 1. The voltammetric curves for cryolite resemble those reported in the literature for Na₃AlF₆ (10, 11) and NaF (12). The steeply rising cathodic current observed at about $-0.5 V \underline{vs}$. Pt reference electrode (all potentials given vs. Pt reference electrode) is attributed to aluminum deposition. An anodic peak was observed at approximately +2.5V. This anodic peak represents the so-called critical current, i.e., the maximum current that is attained before the normal anode reaction is superseded by the anode effect, which is attributable to dewetting of the electrode by fluorocarbon compounds. As shown in Fig. 2, the background current of molten cryolite is quite small in the potential range +0.6 to -0.2V. Within this potential range, voltammograms of the cryolite melt containing Al_2S_3 show a pair of peaks: the anodic oxidation of sulfide ions and, on the reverse scan, the cathodic reduction of the oxidation products (Fig. 3).

The arodic oxidation of sulfide in cryolite was studied at two Al₂S₃ concentrations, 1.3×10^{-5} and 3.1×10^{-5} mol/cm³. Voltammograms for 1.3 x 10^{-5} mol/cm³ sulfide in cryolite melt at sweep rates of 10-500 mV/sec are shown in Fig. 3. The properties of the voltammetric curves obtained at both sulfide concentrations can be summarized as follows:

(i) Peak potential for the oxidation of sulfide, E_p^a , shifts anodically with increasing sweep rate, v.

(ii) Plots of the peak current, i_p , <u>vs</u>. the square root of sweep rate, $v^{1/2}$, are straight lines (Fig. 4). The slope of these lines is proportional to the concentration of Al₂S₃.

(iii) The separation between the anodic peak potential and the cathodic peak potential, $\left| E_p^a - E_p^c \right|$, increases as v increases (Table I).

Table I

Potential Separation Data* for the Oxidation of Sulfide in Cryolite at 1323 K

-t	1.3 x 10 ⁻⁵ mol/cm ³ Al ₂ S ₃	$\frac{3.1 \times 10^{-5} \text{ mol/cm}^3 \text{ Al}_2\text{S}_3}{2}$
v(mV/sec)	$\left E_{p}^{a} - E_{p}^{c} \right $ (mV)	$\begin{vmatrix} E_p^a - E_p^c \end{vmatrix} (mV)$
10	125	125
20	120	125
50	185	180
100	285	290
200	360	345
500	500	490
*Corrected	for ohmic drop.	

The above properties are in agreement with the criteria for a quasi-reversible charge-transfer mechanism (13), i.e., one in which the current is controlled by both diffusion and charge transfer kinetics. For this type of reaction mechanism, if the sweep rate is slow enough, the reaction approaches reversible behavior. At slow sweep rates, at 1323 K, the anodic-to-cathodic peak separation and the peak-to-half-peak separation of a quasi-reversible reaction approach 253/n and

126.5/n mV, respectively, where n is the number of electrons involved in the electrochemical reaction. The voltammograms indicate that, at sweep rates of 10 and 20 mV/sec, the reactions obtained for sulfide ions are reversible, and the experimental values for the potential separations suggest two as the number of electrons involved for the anodic oxidation of sulfide ions. Using the Randles-Sevcik equation for reversible reactions (13) and the experimental values for i_p at 10 and 20 mV/sec, an average value of 3.93×10^{-5} cm²/sec was obtained for the diffusion coefficient of sulfide in molten cryolite at 1323 K.

Thus, it is hypothesized that the oxidation of sulfide ions in cryolite involves the following reaction:

$$s^{2-} \xrightarrow{k_{g},\beta} s + 2e^{-}$$
 (1)

where $k_{\rm g}$ is the standard heterogeneous rate constant and β is the transfer coefficient.

The shape of the voltammogram for a quasi-reversible oxidation reaction depends on β and k_g . For large values of β , the anodic peak is much sharper and the peak current is larger than those of the corresponding cathodic peak. The opposite is true for small values of β . For $\beta = 0.5$, the anodic-to-cathodic peak current ratio is equal to unity. The experimental values for the ratio of anodic-to-cathodic peak currents obtained at different sweep rates and the two different sulfide concentrations in this study are approximately one, thus suggesting that $\beta = 0.5$.

The standard heterogeneous rate constant k_s can be derived from a working curve, developed by Nicholson (14), showing variation of the peak separation $\left| E_p^a - E_p^c \right|$ with the kinetic parameter Ψ , which is defined as

 $\Psi = \frac{k_{s}}{\left(\pi \frac{nFv}{RT} D\right)} \frac{1}{2}$ (2)

where F is the Faraday, D is the diffusion coefficient, R is the universal gas constant, and T is the temperature. It was found that only the values of peak separation at 100 and 200 mV/sec in Table I could be used to estimate $k_{\rm S}$. From these peak separation values and Nicholson's working curve, $k_{\rm S}$ was calculated to be about 4.2 x $10^{-3}~{\rm cm/sec}.$

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REFERENCES

- 1. G. Delarue, Bull. Soc. Chim. Fr., 906 (1960).
- 2. G. Delarue, Bull. Soc. Chim. Fr., 1654 (1960).
- R. P. Tischer and F. A. Ludwig, in "Advances in Electrochemistry and Electrochemical Engineering," Vol. X, H. Gerischer and C. W. Tobias, Editors, p. 391, John Wiley and Sons, New York (1977).
- V. Plichon, A. deGuibert, and M. N. Moscard-Levelut, in "Ionic Liquids," D. Inman and D. G. Lovering, Editors, p. 387, Plenum Press, New York (1981).
- Nguyen Quang Minh and N. P. Yao, "The Extraction of Metals by Molten-Salt Electrolysis of Sulfides". To be published in "Advances in Molten-Salt Chemistry," Vol. 5, G. Mamantov, Editor, Elsevier Scientific Publishing Co. (New York).
- E. J. Cairns, in "Comprehensive Treatise of Electrochemistry. Volume III: Electrochemical Energy Conversion and Storage," J. O'M. Bockris, B. E. Conway, E. Yeager, and R. E. White, Editors, p. 341, Plenum Press, New York (1981).
- Nguyen Quang Minh, R. O. Loutfy and N. P. Yao, J. Electroanal. Chem. Interfacial Electrochem., 131, 229 (1982).
- Nguyen Quang Minh, R. O. Loutfy, and N. P. Yao, "Preliminary Study of the Electrolysis of Aluminum Sulfide in Molten Salts," Argonne National Laboratory Report, ANL/OEPM-83-3 (1983).
- Nguyen Quang Minh and N. P. Yao, J. Electrochem. Soc., <u>130</u>, 1025 (1983).
- A. Kerouanton and V. Plichon, C. R. Acad. Sci., Ser. C, <u>280</u>, 497 (1975).
- A. J. Calandra, C. E. Castellano, and C. M. Ferro, Electrochim. Acta, 24, 425 (1979).
- A. J. Calandra, C. M. Ferro, and C. E. Castellano, Electrochim. Acta, 25, 201 (1980).

13. E. R. Brown and R. F. Large, in "Techniques of Chemistry. Volume I, Physical Methods of Chemistry. Part II A, Electrochemical Methods," A. Weissberger and B. W. Rossiter, Editors, p. 452, Wiley-Interscience, New York (1971).

14. R. S. Nicholson, Anal. Chem., <u>37</u>, 1351 (1965).



Fig. 2 Background Current of Molten Cryolite in the Potential Range +0.6 to -0.2V. T = 1323 K, Electrode Area = 0.32 cm², v = 100 mV/sec



Fig. 3 Voltammograms of the Oxidation of Sulfide Ions in Molten Cryolite at Different Sweep Rates. T = 1323 K, Electrode Area = 0.32 cm^2 , Concentration = $1.3 \times 10^{-5} \text{ mol/cm}^3$



Fig. 4 Plots of i_p vs. v^{1/2} for the Anodic Oxidation of Sulfide Ions In Cryolite. T = 1323 K, Electrode Area = 0.32 cm² ▲: 1.3 x 10⁻⁵ mo1/cm³, O: 3.1 x 10⁻⁵ mo1/cm³

CORROSION OF METALS AND ALLOYS BY MOLTEN SALTS CONTAINING ALUMINUM IONS

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Abstract

The hot corrosion of metals and alloys has normally been investigated in the laboratory using simplified sulfate melts. These have not contained aluminum, employing rather added lithium cations to lower the melting point to plant operational temperatures. Lithium is not found in superheater deposits and a consideration of deposit analyses indicated that the next most abundant cation, after sodium and potassium, was aluminum: only 15 mol% is needed to lower the melting point to 550°C. Corrosion tests with this melt have shown little difference in the rate of hot corrosion determined using the lithium-containing melts, but a very different mechanism. The generation of oxide ions in the melt upon oxidation of nickel (the metal studied in most detail) caused an aluminum-rich layer, 0.2 mm thick, to build up within the melt, adjacent to the scale, and the later precipitation of an insoluble residue within the bulk melt. This residue contained no nickel and, surprisingly, could not be identified by X-ray analysis as one of the 14 known modifications of alumina. The rate determining step for the dissolution of scale into the melt was found to be that of the passage of nickel-sulfato complexes through the aluminum-rich layer. Suggestions are made for the incorporation of the implications of this finding into future hot corrosion research.

1. Introduction

Corrosion by molten salts contributes significantly to the cost of electricity generation from fossil fuels. In coal-fired boilers, the molten salts are principally alkali metal sulfates, while in oilfired furnaces, vanadates are additionally found. Hot corrosion also occurs in gas turbines, particularly on the first stage nozzle guide vanes and rotor blades. The aggressive liquid deposits derive from impurities in the fuel and the combustion air and form on metal surfaces at temperatures of 550°C and above. Since it is not economically practicable to use impurity-free fuels hot corrosion must be investigated, and minimized to the best of our ability.

In such investigations it is obviously important to employ a molten sulfate mixture which is representative of that occurring in practice. Analyses of deposits for the cations present do not reflect the relative proportions found in the fossil fuel used. Some cations are concentrated in the molten deposit by one or more orders of magnitude: the concentration of the vanadium present in fuel oil is one well known example. In this study we focus on deposits, containing aluminum cations, expected on superheater and reheater tubes in coal fired power plants. However, the presence of very similar deposits are expected at those sites in gas turbines where hot corrosion occurs. Thus our findings can apply equally in this area.

2. Composition of the Deposit

Hot corrosion deposits are generally described, rather than fully identified, as alkali metal sulfates. The deposits are formed from the impurities in coal, and in this context the impurities may be defined as any inorganic constituent and any element other than carbon, hydrogen and oxygen.

Inorganic constituents of coal are primarily ash-forming, and can be sub-divided into inherent or extraneous mineral matter. Inherent mineral matter, generally less than 2% by weight, comprises those inorganic compounds once part of the original plant substance. The main elements are Fe, Ca, Mg, P, K, Na, Si, Al and Mn.

The remainder of the ash-forming substances are extraneous mineral matter, having been mixed with the plant material during coal-formation, or introduced later by contamination with mineral-laden water. They may also be derived from the roof of the seam during mining.

The mineral matter in coal may be classified into six main groups (1,2), and these are shown in Table 1. (A large number of associated minerals are also present in coal, but in negligible amounts in this context.) Of the minerals listed, kaolinite, pyrites and calcite comprise around 95%.

Group		Examples
Shale	muscovite hydromuscovite illite bravaisite montmorillonite biotite	(K,Na,H ₃ 0 ₃ ,Ca) ₂ (A1,Mg,Fe,Ti) ₄ - (A1,Si) ₈ 0 ₂₀ (OH,F) ₄
Kaolin	kaolinite livesite metahalloysite	A1 ₂ 0 ₃ .2Si0 ₂ .xH ₂ 0
Sulphide	pyrite, marcasite, F	eS ₂
Carbonate	ankerite, Ca(Fe,Mg,M calcite, CaCO ₃ siderite, FeCO ₃	n)(CO ₃) ₂
Chloride	sylvite, KCl halite, NaCl	
Oxide	quartz, SiO ₂ haematite, Fe ₂ O ₃ magnetite, Fe ₃ O ₄	

Table 1 <u>Classification of Mineral Matter Occurring in Coal</u>(a)

(a) See Refs. 1 and 2.

Sulfur and chlorine are the two most important impurities which are not ash-forming. The normal weight percent range for sulfur is 1-4%, but up to 10% has been found. Chlorine levels in coal are normally 0.2-0.4%, but there is currently a trend towards the use of higher chlorine coals (up to 0.8 weight%), and this has focussed interest on the possibility of chloride ions being present in superheater deposits and thus participating in the corrosion process.

Chlorine occurs in the mineral form mainly as NaCl, with very little KCl, and this form probably accounts for around one half of the chlorine content. The form of the remainder is not clear. In the combustion zone NaCl is volatilized, and an exchange mechanism has been proposed (3) whereby potassium is replaced by sodium in the alumino silicates, allowing the formation of KCl vapor. The temperatures in the combustion zone are also sufficient to volatilize silica from shales and kaolins, and decompose carbonates to give CaO and MgO.

Table 2 gives reported chemical analyses for the fused inner white layer of superheater and reheater deposits. The year associated with the various reports is given because we believe the latest ones reflect improved analysis techniques and procedures. However, a considerable scatter of the data is readily seen. This arises in part from the difficulties inherent in obtaining representative samples, but also from variations between power station fuel supplies, and operating temperatures and conditions.

The earlier analyses refer to the now older, and less efficient, 220 megawatt boilers, and show sodium and potassium cations generally predominating over the alkaline earth cations. The iron in these deposits originates from both the coal and the superheater and reheater tubes and its concentration is thus expected to be time-dependent. Since (Na,K)S04 eutectic melts above 800°C, and the operating temperatures of these tubes is around 600°C, another cation has to be added to produce a lower melting eutectic. That cation has in the past been lithium, but the (Li, Na, K)S04 eutectic, while melting around 550°C, contains 78 mole% lithium, not a major component of superheater deposits. Laboratory tests using this eutectic have provided insight into hot corrosion, but we wished to use a more typical melt.

The later analyses, reflecting the coming on-line of the larger 660 megawatt generating plant, show generally some increase in the sodium and potassium levels in the deposits, but larger increases in aluminum levels. The calcium and magnesium levels are possibly now somewhat lower.

These conclusions are not clear cut from the data in Table 2, which contains only a selection of analyses of inner fused deposits. (It is traditional to give the constituents as their oxides: it does not imply they are present in that form.) A total analysis means that Chemical Analyses of Fused Inner Layer of Superheater and Reheater Deposits

Table 2

(expressed as percentages, by weight of air-dried sample)

Analysis	si0 ₂	A12 ⁰³	Fe0	Fe ₂ 03	Ca0	MgO	k ₂ 0	Na ₂ 0	so3	Ref	Year
Total	9.7	3.2	5.9	15.0	5.8	1.4	7.4	3.3	38.9	7	1960
Water Soluble	0	2.9	0	1.8	4.0	1.0	5.0	5.7	35.1	۲ س	10201
Water Insoluble	15.6	5.9	1.1	8.5	3.0	0	0.1	1.3	5.4	`	0061
Total	52.4	7.2	H	8.6	2.4	2.7	2.5	0.6	15.6	ø	1960
Water Soluble	0.1	6.2	0.9	3.8	1.7	0.6	10.5	2.0	37.2	6	1963
Water Soluble	0.8	3.2	2.77	2.26	1.6	0.3	5.9	6.4	29.7	10	1962
Total	14.8	13.6	Ŧ	9.5	÷	H.		2 . 0*	39.4	11	1952
Total	15.8	0.6	Ŧ	11.8	3.9	0.8	0 •0	5.9	43.3	12	1955
Total	11.5	8.0	ı	10.0	3.9	1.1	6.8	8.6	45.5	13	1968
Water Soluble	0.08	33.89	÷	4.36	0	*16	10.50	1.63	34.1	14	1968
4 not	given				*	express	sed as c	ombined	percent	tage	

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the figures represent the combined water-soluble and -insoluble contents. Analyses for chloride are infrequently reported, and are thus not included. Table 3 contains similar analyses of the outer, mainly fly-ash, layers of deposits. A comparison of Tables 2 and 3 shows, as expected, more silica in the outer layer, and an enrichment of the inner layer in the alkali metals with respect to the fly-ash composition. However, there seems to be no common Na to K ratio within the fused layer, and we therefore based our search for an appropriate, simplified, yet representative melt using a ratio of unity, i.e. upon the (Na, K)SO4 eutectic.

We thus investigated the effect of added aluminum upon the melting point of (Na, K)SO4 eutectic (4). Only relatively small additions of aluminum were needed to produce dramatic reductions in the observed melting point. The composition chosen for this work contained 15 mole % aluminum, and equal portions of sodium and potassium. This mixture melted around 550°C, and was stable under a synthetic flue gas atmosphere. The important component of the gas was the small concentration of SO3, which prevented decomposition of the melt, (and the appearance of Al₂O₃), seen when the mixture was held molten in air.

An infrared investigation of the differences in structure and cation interactions within (Na, K, Al)SO4 and (Li, Na, K)SO4 (solified) melts has been published (4), and we here now examine the interaction of the aluminum-containing melt with metals and alloys, considering initially in detail melts containing nickel coupons.

3. Experimental

A coupon, approximately 8 mm x 8 mm x 1 mm, of metal or alloy is placed in an optical silica cell (Fig. 1) containing molten sulfate. The cell is located in a specially designed furnace (5), heated largely from above to create a known, representative thermal gradient down the melt, and a synthetic flue gas mixture is passed over the upper surface of the melt. The furnace is sited in the large cell compartment of an Applied Physics Cary 14 H spectrophotometer, the optics of which are essentially reversed to prevent any light emitted by the hot sample affecting the pen position on the recorder. The conventional record of light absorbed by only the sample as a function of wavelength is thus obtained. The optical path of the instrument is modified with masks so that only a horizontal slot of light (1-2 mm high) passes through the molten salt. Consequently the spectra, and hence the concentration, of dissolved species are recorded as a function of time and distance from the coupon in the melt experiencing the thermal gradient. In addition, periodic visual inspections of the corrosion process can be made.

At the end of various exposure times to both lithium- and aluminum-containing sulfate melts, including some standard crucible tests, the melt was quenched and the metal coupon, with adhering melt,

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Chemical Analyses of Outer Friable Layer of Superheater and Reheater Deposits . • • ¢ . --

	so3
sample)	Na ₂ 0
-dried	К ₂ 0
от алг	MgO
verght,	Ca0
es, by v	Fe ₂ 03
ercentage	Fe0
ed as p	A1 _{2⁰3}
(express	sio ₂
	Analysis

Analysis	si0 ₂	A12 ⁰ 3	Fe0	Fe_2O_3	Ca0	Mg0	К ₂ 0	Na ₂ 0	so3	Ref	Year
Water Soluble	0.06	3.02	щ	1.69	1.(02*	5.0	1.57	16.7	14	1968
Total	45.9	18.7	Ŧ	23.1	2.5	1.9	2.2	1.1	0.8	ω	1962
Total	41.4	16.8	Ħ	24.3	7.4	0.5	2.6	3.4	3.0	12	1955
Total	38.8	17.2	0.0	16.9	6.5	1.3	3.4	2.2	11.5	7	1960

∔ not given

* expressed as combined percentage
was separated from the remaining solidified melt. The coupons were prepared by conventional metallurgical procedures for subsequent electron micrograph (EM) and electron probe microanalysis (EMPA) studies. The quenched melt was subjected to elemental analysis and X-ray powder investigations.

4. Results and Discussion

The main finding concerning the crucible tests was that the aluminum-containing sulfate melt was somewhat more aggressive than the lithium-containing melt. The extent of corrosion appeared to be increased by a factor of around two, from weight loss measurements.

The main difference in the mode of behavior showed up as the slow appearance of an insoluble white material after several hours in aluminum-containing melts in the presence of, particularly, nickel coupons. Initially this solid was considered as alumina, from the interaction of the aluminum cations in the melt with the oxide ions generated in the corrosion process. No oxide of lithium is expected to be insoluble under these conditions.

The white solid was observed as a fine uniform dispersion throughout the melt at the end of experimental runs. We have not been able to identify it as exclusively Al₂O₃, or even majorly as having an alumina structure from X-ray diffraction measurements.

4.1. Examination of Quenched Melts

Of the various metal specimens investigated, the white solid appeared in greatest quantity and in the shortest time in the presence of nickel coupons, and thus we have concentrated on this system.

After removing the corroded coupon the solidified melt was tested for water-solubility. In each case, a white insoluble residue was obtained, approximately 5% (by weight) of the initial sample. To ensure no soluble material remained with or within the solid, extensive heating and leaching, using large volumes of distilled water and an ultrasonic bath, were performed. Upon X-ray diffraction, the residues produced extremely complex patterns, and no clear identification was possible.

The results are summarised in Table 4 for the X-ray powder analysis for the residues obtained after corrosion runs at various nickel coupon temperatures, and contained in silica cells (Fig. 1). The thermal gradient in all cases had been close to 130° C, and synthetic flue gas (16% CO₂, 4% O₂, 0.4% SO₂, balance N₂) had passed continuously over the melt surface. The apparent presence of water-insoluble mixed-sulfates is thus surprising. We stress that nickel compounds were entirely absent from the precipitate.

Metal Temperature (°C)	Major Constituents	α-A1203 Component ^a
587	Possibly NaAl(SO4)2 ^b + some unidentified	Minor
606	Possibly KNaSO4 ^C	Minor
616	Unidentified pattern	Minor
632	Similar to 606°C	Minor

Table 4 X-Ray Powder Diffraction Analysis of Water-Insoluble Residues from Melts After Corrosion Runs

^a JCPDS 10-173; ^b JCPDS 27-631; ^c JCPDS 20-927

The infrared spectra of solidified melts were therefore recorded, using the KBr-disc technique. The spectra of four solidified melts, from the corrosion runs at the four coupon temperatures (Table 4), were measured and compared with the spectrum of a "pure" sample. This was one that had been held in the molten state for several hours, but with no nickel coupon (and thus no corrosion products) present, and in which no precipitate was observed to form. No significant differences were seen between the four coupon-containing melts: some differences were noted between these and the pure melt spectrum, but none helped definitively to identify the precipitate. However, information upon the melt structure, and the effect thereon of corrosion product dissolution, was obtained, and the results published (4).

The appearance of the precipitate in the (Na, K, Al)SO₄ melt only in the presence of metals, particularly nickel, is interesting. The addition of oxide ions (as Na20) to the pure melt causes the immediate formation of α -alumina, but a corroding metal brings about a different reaction. X-ray diffraction analysis here failed to identify the solid as primarily alumina. Fourteen different Al203 structures are contained in the NCPD file, and of these only α -Al203 was observed as a minor constituent. Possibly Al203 can adopt an unlisted structure when formed under these conditions, or have a complex combination of modifications which make identification impossible. The presence of diffraction patterns attributable to mixed sulfates implies inclusion or incorporation of such species during precipitate formation in the melt. In our view, however, this is unlikely, because of the extensive leaching treatment. The alternative we favor is that the precipitate either contains, or may be (related to), an insoluble aluminumsulfate mineral, several of which are known to exist.

4.2. Metallographic Examination of Corroded Specimens

EM (electron microscopy) and EMPA (electron microprobe analysis) were used to examine the corroded coupons. In general there were no significant variations between coupons exposed at different temperatures. The micrographs of a nickel coupon corroded at 616°C are typical (Fig. 2). The specimen was ground to 600 grit silicon-carbide paper along one edge to expose the bare metal, and is thus viewed with adherent solidified melt on both faces.

The feature which we believe is unique to aluminum-containing melts is the presence of a pronounced layered structure in the melt at the scale-melt interface. This inner layer, approximately $\overline{0.2}$ mm thick, is rich in aluminum and nickel, but deficient in potassium, relative to the outer layer, which is assumed to be representative of the bulk melt. EMPA studies of iron and chromium samples (6) revealed a thin aluminum-rich layer with iron, but not with chromium. However, the extent of scale formation with chromium was too small to be detected, and the mechanism for producing an aluminum- and chromiumrich layer within the melt may have been absent. At the time of writing, similar analyses on various nickel-based alloys and stainless steels are incomplete, but will be presented at the meeting.

4.3. Nature of the Inner Layer

In the hot corrosion of metals by molten sulfates the oxide layer on the metal surface is continuously being dissolved into the molten salt. The stabilities of the dissolved corrosion products, (largely transition metal-sulfato complexes), decrease with increasing temperature, and these species migrate outwards across the temperature gradient resulting from the heat flux. At the higher temperatures at the melt-ash interface most of these species, notably the iron and chromium complexes, decompose, being removed from solution as the insoluble oxides.

The rate-controlling step for hot corrosion has generally been considered as the rate of transport of the various sulfato complexes across the molten salt layer. Using our new technique (5) for the continuous monitoring of hot corrosion, termed EASE (Electronic Absorption Spectroscopy Experiments), we have recently shown (6) that the rate of migration across the thermal gradient is relatively rapid, and cannot therefore always be the rate controlling step, especially in the case of nickel. We now here propose and examine the idea that, where the inner layer is seen, the rate controlling step is the transport of transition metal-sulfato species across this layer.

That this layer is involved is almost inescapable, since the rate of scale buildup on nickel is rapid, and often faster than the rate of concentration increase of nickel within the melt (6).

4.4 Initial Reactions

All our metal specimens were pre-oxidized, generally in air for 24 h at 550°C, before being exposed to the melt. This was done to make the experiments representative of boiler conditions, in which oxidation of tube surfaces occurs before molten deposits form. Thus the first reaction is the interaction between oxide and the melt and, in the case of nickel, rapid penetration of the oxide scale by the melt.

Anodic oxidation of nickel,

$$Ni \longrightarrow Ni^{2+} + 2e,$$
 (1)

then occurs, and a corresponding reduction of sulfate ions,

$$SO_4^{2^-} + 8e^- \longrightarrow S^{2^-} + 40^{2^-}$$
 (2)

Sulfur trioxide will also be present in the melt, having been formed in the synthetic flue gas <u>via</u> the platinized Kaowool catalyst (Fig. 1), (in generating plant by the catalytic action of Fe₂O₃ in fly-ash). It will be transported through the sulfate melt as a consequence of the sulfate-pyrosulfate equilibrium, viz.

$$s_{0_4}^{2^-} + s_{0_3} \stackrel{2^-}{\leftarrow} s_{2_4}^{0_7} s_{2_4}^{2^-}$$
 (3)

Sulfur trioxide may also be reduced to give sulfide and oxide ions,

$$SO_3 + 8e^- \longrightarrow S^{2-} + 30^{2-}$$
 (4)

Oxide ions can also arise from the acid-base equilibrium that exists in molten sulfates,

$$s0_4^{2-} \neq s0_3 + 0^{2-}$$
 (5)

and from partial reduction of sulfate to yield sulfur dioxide, which is essentially insoluble in molten sulfates,

$$SO_4^{2-} + 2e^- \longrightarrow SO_2 + 20^{2-}$$
 (6)

The dissolved oxide ions from the scale, and generated oxide ions at the solid-liquid interface, react with the aluminum cations in the melt to form Al_2O_3 , and thus displace these reactions to the right, thereby enhancing the oxidation (corrosion) of the metal, and producing SO₂ gas at the solid-melt interface.

4.5. Transport Characteristics

With aluminum-containing melts there is thus a ready mechanism

for providing a precipitate at the solid-melt interface, within the melt, which might be expected to hamper the diffusion of nickel sulfato complexes into the bulk melt. Under conditions of rapid corrosion, oxide ions would later be able to diffuse into the bulk melt and in due course alumina or, as we now know, an insoluble aluminum-containing compound will appear in the melt. We have not yet been able to determine if the solid appears further and further from the solidmelt interface with increasing time, or if it appears uniformly within the melt after certain criteria are attained. The former is difficult to observe, and the latter could seem like the former, under the combined effects of appropriate particle size and gravity. Our periodic inspections indicated a uniform distribution of the insoluble material throughout the melt after several hours, but more experiments are required, and under isothermal conditions.

However, the aluminum-rich inner layer in the melt may be of different composition or structure to that of the bulk precipitate, and further work regarding this layer is planned. At present we can note that the bulk precipitate contains no nickel, or any originally present was leached out. Thus, assuming the same composition for bulk precipitate and inner layer, the transport of nickel through this material can be expected. The criteria for a different composition for the inner layer would have to include an open structure or pore size which would permit transport through the material, and in addition the capacity to contain, and possibly also retain, large concentrations of nickel, and other transition metal-sulfato complexes. We note that alumina has been used successfully in the chromatographic separation of transition metal complex ions in molten salts (15).

This inner layer must also allow through it sulfate and pyrosulfate ions, and sulfur dioxide (and possibly trioxide) gas. This is to enable the scale formation process, in the case of nickel, to continue. However, the evolution of gas, seen apparently at the solidmelt interface, any arise at the scale-melt interface, or within the melt, at the inner layer-bulk melt junction. In the former case, some disruption of the inner layer would be expected, and possibly erratic metal dissolution rates as a function time, but this was not found (6), and currently we favor the latter site.

4.6. Dissolution Rates

The rate of transport of corrosion products (transition metalsulfato complexes), the rate controlling step, across the inner layer is obtained by determining the total concentration of these species in the bulk melt as a function of time (6). The concentration, at any time, of these corrosion products in the inner layer may be determined using the Tyrell equation (16) for the flux of corrosion products in a medium. This requires chemical diffusion and Soret coefficients, but these are not known for our conditions, but suitable alternatives are available (17,18). For nickel, dissolution rates obtaining after 2.5 h at 632° C and 5 h at 587° C coupon temperatures were determined (6) as approximately 3.72 and 0.51 mg cm⁻²h⁻¹ respectively, (equivalent to 4200 and 570 nm h⁻¹, 9350 and 1250 mil year⁻¹, respectively). Fitting these rates into the Tyrell equation for a 0.2 mm layer gives a concentration difference equivalent to 16% (by weight) of nickel at 632° C and 2% (by weight) at 587° C. These would relate to values which an open net-work aluminum-containing material might reasonably be expected to hold.

5. Conclusions and Implications

(1) It is reasonable, and appropriate, that laboratory tests of the hot corrosion of metals and alloys by molten sulfates should, in the future, particularly for superheater corrosion studies, employ melts containing aluminum ions.

(2) The generation of oxide ions by the corroding metal causes an aluminum-containing layer within the melt and adjacent to the metal scale. Transport of corrosion products into the bulk melt is limited by this layer. Its composition is uncertain, and it is not, as might be expected, a common form of alumina.

(3) We propose that this finding may lead to economic benefits. We suggest that instead of seeking for better corrosion-resistant metals or coatings to withstand hot corrosion, the interaction between the metal surface and the corrodent could be tailored to produce within the melt an inner layer which has a very slow rate of transport of corrosion products across it into the melt, and retards scale formation. This could be achieved by either the use of an appropriate surface metal treatment or coating, or by addition of an appropriate chemical to the fuel, particularly during start-up.

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References

- (1) J.B. Nelson, B.C.U.R.A. Monthly Bulletin, 17, 41 (1953).
- (2) W. Spackman and R.G. Moses, Mineral Industries Experimental Station, Penn. State Univ., Bulletin Number 75 (September, 1961).
- (3) P.J. Jackson and J.M. Ward, J. Inst. Fuel, 29, 154 (1956).
- (4) T.R. Griffiths and K. King, J.C.S. Faraday Trans. I, <u>77</u>, 2763 (1981).
- (5) T.R. Griffiths, K. King and D. Mortimer, High Temp. Technology, <u>1</u>, 43 (1982).
- (6) T.R. Griffiths, K. King and D. Mortimer, Power Industry Research, <u>2</u> (1983), in press.
- (7) P. Sedor, E.K. Diehl and D.H. Barnhart, Trans. Amer. Soc. Mech. Eng., Series A, <u>82</u>, 181 (1960).
- (8) W. Nelson and C. Cain, Trans. Amer. Soc. Mech. Eng., Series A, <u>82</u>, 194 (1960).
- (9) A.M. Adams and E. Raask, in "The Mechanism of Corrosion by Fuel Impurities", Eds. H.R. Johnson and D.J. Littler, Butterworths, London (1963).
- (10) A.M. Edwards, G.J. Evans and L.S. Howes, J. Inst. Fuel, <u>35</u>, 121 (1962).
- (11) J.H. Carlile, J. Inst. Fuel, 25, 256 (1952).
- (12) C.H. Anderson and E.K. Diehl, Amer. Soc. Mech. Eng. Paper Number 55-A-200 (1955).
- (13) C.H. Anderson and C.W. Goddard, J. Inst. Fuel, <u>41</u>, 357 (1968).
- (14) J.C.P. Garrett and D. Penfold, CEGB, N.W. Region Report 17/68 (1968).
- (15) D.M. Gruen, Nature, <u>178</u>, 1181 (1956).
- (16) H.J.V. Tyrell, "Diffusion and Heat Flow in Liquids", Butterworths, London (1961).
- (17) D. Inman, D. Jovanovic and S.H. White, Electroanal. Chem. Interfacial Electrochem., <u>43</u>, 37 (1973).

(18) V. Backlund, J. Dupuy, S. Gustafsson and A. Luden, Z. Naturforsch, <u>A22</u>, 471 (1967).







Figure 2 Electron microprobe analysis of a corroded nickel coupon and adhering melt, showing nickel-rich and aluminum-rich regions in the melt. Clockwise, (A) nickel; (B) potassium; (C) aluminum; (D) electron image. Arrow indicates upper coupon surface. Coupon temperature 616°C, magnification X25.

CORROSION STUDIES OF IRON, NICKEL AND INCOLOY 800 IN SODIUM-POTASSIUM NITRATE MELTS AT 250-550°C

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ABSTRACT

The corrosion behavior of iron, nickel and Incoloy 800 alloy (I800) electrodes in molten $(Na,K)NO_3$ has been investigated over a temperature range of 250-550°C. Anodic polarization curves as well as open circuit potential measurements for Fe, Ni and I800 show evidence of spontaneous passivation when these metals are in contact with the melt at any temperature studied. Intergranular corrosion and pitting have been found in I800 at potentials more anodic than the steady state potential, this phenomenon being more important at the lowest temperature investigated (250°C), than at the highest (550°C). Results of metallographic examination of the samples are presented.

INTRODUCTION

Studies of the corrosion behavior of possible container materials are quite important as part of the development of molten (Na,K)NO₃'s as heat transfer fluids in solar collectors at temperatures in the range 250-550°C (1). Although corrosion of iron, nickel, some steels and to a lesser extent chromium has been studied in molten nitrates, most of these studies involve temperatures well under 550°C and results are not directly applicable to high temperature, molten salt receiver systems (2-7). Literature data indicates that iron and nickel passivate spontaneously in contact with the $(Na,K)NO_3$ melt giving no detectable amount of ionic species of the metals in the fused salt. Passivating films are mainly magnetite (Fe_3O_4) and NiO. Although the long term corrosion behavior of Incoloy 800 (I800) in molten nitrates in closed loops has been studied (8-10), no electrochemical studies appear to have been carried out on this material. I800 appears to be a suitable container over the temperature range proposed for operation of solar receivers using the molten nitrates as heat transfer fluids.

RESULTS AND DISCUSSION

Open circuit potentials and polarization curves for Fe, Ni and 1800 were measured at various temperatures. A gold pseudo-reference electrode was employed in these studies. In the case of iron, nitrite oxidation can be seen and an apparent limiting current is achieved. As iron is polarized further anodically, an initial passive region is formed (Figure 1). The E-log i curves appear to show Tafel behavior for about one decade. Massive evolution of a brown gas, presumably NO_2 , starts to appear in this range. Beyond the Tafel region, the electrode depolarizes sharply, indicating a breakdown of passivity. For experiments at 548°C, the E-log i curves are complex and not terribly reproducible. Initial cathodization of the electrode eliminates the initial passive region.

The behavior of nickel is complex; breakdown of the passive film is rather sharp depending on the anodic potential to which the polarization is carried. For instance, polarization of Ni to +0.73 V vs the Au reference gives a retrace, on scan reversal, of the initial anodic polarization curve. The surface is covered by a thin blue/black film. Scan reversal on anodic polarization at +0.78 V, however, yields continuing increasing currents (Figure 2). The electrode develops pits which spread on its surface, and a thin black film.

With I800, polarization curves somewhat similar to those for Fe are obtained; the limiting current for the oxidation of nitrite is not as well defined at the I800. However, the most striking observation is the fact that a sharp breakdown potential is observed at lower potentials than for iron, and that these breakdown potential decrease - are less anodic - at lower temperatures. Such a polarization curve is shown in Figure 3 for 250°C. If the potential scan is reversed after the breakdown potential, one obtains a closed current loop, the size depending on the reversal potential. After such experiments the melt shows an orange color, and dichromate ion was determined to be in the melt. As the temperature is increased, the closed current loop, even after entering an apparently unpassivated region, is much smaller than those obtained at lower temperatures, indicating the initially passive film is quickly reformed. Figure 4 shows such a polarization curve at 547°C.

Metallographic examination of the I800 shows marked dependence on the temperature and polarization conditions. At 250°C, no significant change in the surface can be observed at the open circuit potential. Polarization to potentials where nitrite is oxidized forms a transparent, light-blue film on the surface. At potentials slightly more anodic than the breakdown potential, the electrode surface shows very defined grain boundaries as well as pits spread out over the surface. Figures 5 and 6 show unetched and etched views of the same field of an 1800 sample taken into the breakdown region and cycled at 250°C. Fissures seen in Figure 5 are shown to be intergranular cracks in Figure 6 caused by dissolution of chromium depleted regions in grain boundaries. An SEM photograph in Figure 7 shows evidence of pitting and intragranular cracking as well. This would not be as deleterious to mechanical properties as the intergranular attack. The more anodic the potential, once the breakdown potential is attained, the stronger the surface attack. Above 350°C, a thin transparent brown/blue film is observed, which becomes more intense as the temperature increases. The higher the temperature, the thicker the film formed. At potentials more anodic than the nitrite oxidation wave, pits as well as a brown/ black film are observed. At 547°C, the highest temperature studied, no pits were found under any conditions; a very thick brown film is obtained after anodic polarization experiments to +1.54V vs the Au reference. Figure 8 shows an electrode polarized at 547°C. A thick brown oxide film is formed, but no pitting is evident. Table I shows open circuit potentials and breakdown potentials, obtained as that potential where the anodic current undergoes a sharp increase.

Table I

Open circuit potentials, vs Au reference, and breakdown potentials for Fe, Ni and I800 at various temperatures.

T,°C	E _{OC} (V) Iron	e _b (V)
258 345 398 548	-0.277 -0.200 -0.040 -0.015	+1.23 +1.31 +1.49 - (not observed)
	Nickel	
345 398 548	-0.105 -0.030 +0.002	+0.78
	1800	
250 350 452 500 547	-0.300 -0.100 -0.030 -0.017 -0.005	+0.85 +0.98 - - (not observed) -

1800 samples etched in oxalic acid at high current densities showed similar etch-pit formation to those found in the molten nitrate at 250°C. Grain boundaries were observed to have been heavily attacked and within the grains etch pits (geometric-sided depressions) were formed in areas of high dislocation densities and erosion has occurred around the TiC/N phases of the I800. These observed microstructures, though not showing as severe surface deterioration as those produced in the molten nitrate bath at 250°C, have similar features. A protective passivating oxide film has been unable to develop or be maintained, and the chromium depleted grain boundary regions which would have provided a pathway for slow chromium diffusion to the surface under film forming conditions have dissolved. As Bradshaw has indicated (10), I800 under static, long term conditions in the molten nitrate at 530°C had an outer iron oxide layer, probably Fe_3O_4 , and a continuous layer beneath it which appeared to be a mixed spinel oxide, Fe(Fe, $Cr)_2O_4$. Sub-surface discontinuous phases consisted of a Cr-rich oxide phase, and apparently a pure Ni phase. It thus appears that I800 is protected by a much more protective oxide film at higher temperature than at lower, at least over the 250-550°C range. Very recent work by Bradshaw on corrosion of I800 in a thermal convection loop molten nitrate has indicated the formation of pits on a coupon immersed for approximately 5000 hours at 333°C (11). He reports that the pits appear to have sharply defined boundaries, indicating attack on individual grains. Thus, the electrochemical experiments appear to be in general accord with these most recent long-term corrosion studies.

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REFERENCES

- 1. L. N. Tallerico, SAND 79-8015, Technical Report, Sandia
- Laboratories, Livermore, California, August, 1979. A. J. Arvia, J. J. Podesta and R. C. Piatti, Electrochim. Acta, 2. <u>17</u>, 33 (1972).
- 3. T. Notoya and R. Midorakawa, Denki Kagaka, <u>41</u>, 865 (1973).
- A. Conte and S. Casadio, Rec. Sci., <u>36</u>, 343 (1966). 4.
- 5. H. S. Swofford and H. A. Laitinen, J. Electrochem. Soc., 110, 814 (1963).
- 6. A. A. El Hosary, A. Baraka and A. I. Abdul-Rahman, Brit. Corres. J., 11, 228 (1971).
- B. J. Brough and D. H. Kerridge, Inorg. Chem., 4, 1353 (1965). 7.
- R. W. Bradshaw, Abstract No. 210, The Electrochemical Society, 8. Fall Meeting, Denver, Colorado, October, 1981.
- 9. R. W. Carling, L. M. Kramer, R. W. Bradshaw, D. A. Nissen, S. H. Goods, R. W. War, J. W. Munford, M. M. Karnowsky, R. N. Biefeld and N. J. Norem, SAND 80-8052, Sandia National Laboratories, Livermore, California, March, 1981.
- R. W. Bradshaw, SAND-8210, Sandia National Laboratories, 10.
- February, 1982. R. W. Bradshaw, SAND82-8911, Sandia National Laboratories, January, 1983. 11.





Fig. 1. E-log i curves for IRON.(o) Fig. 2. E-log i curves for NICKEL; T = 250°C, ---, +1.17V (precatho- ---+0.73V. ----+0.78V. dized at -0.80V); (**D**) T = 398°C, T = 345°C. --- +1.48V.



Fig. 3. E-log i curves for I800; ---+0.85V, -·-·+0.88V, ···+0.95V. $T = 250^{\circ}C.$

Fig. 4. E-log i curve for I800; ----+0.46V, ···+0.84V, ---+1.20V. $T = 547^{\circ}C.$



Fig. 5. Electrode, sectioned cross section, 250° C, 4 hr. Unetched.



Fig. 6. Same as Fig. 5; same field of view. etched.



Fig. 7. Same as Fig. 5; SEM.



Fig. 8. Electrode, sectioned cross section of 547°C. Etched.

OXIDE ION CHEMISTRY AND CORROSION IN MOLTEN ALKALI NITRATES AND NITRITES

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ABSTRACT

It has generally been assumed that corrosion in molten alkali nitrates proceeds by the participation of oxide ions (0^{2-}) directly from the melt. Such an assumption is erroneous because oxide ions are completely converted to peroxide and superoxide ions in dry melts and to hydroxyl ions in melts exposed to water vapor. Oxide ions, however, could be stabilized by the addition of nitrite. To check whether corrosion in such melts depended on the concentration of oxide ions, experiments were carried out on zirconium and Zircaloy-2 in melts containing alkali metal nitrates, nitrite and hydroxide under different conditions. The oxide ion concentration in the melts is estimated to vary from 10^{-12} to $<10^{-20}$ m (mole kg^{-1}); too small to account for the observed kinetics and polarization data. An analysis of the corrosion data, reported in the literature, for iron and carbon steel, shows that the oxide ion concentrations existing in the nitrate melts have no relation to the observed kinetics of oxidation. The source of oxide ions has to be the reaction of nitrate, nitrite and hydroxyl ions with the anion vacancies emerging on the surface.

INTRODUCTION

Several inorganic eutectic mixtures containing alkali metal nitrates are promising candidates for thermal storage systems (1); therefore, corrosion studies in these molten salts have recently gained technological importance. In interpreting the mechanisms of corrosion in molten nitrates and nitrites it has generally been assumed that the oxide ion species, 0^2 -, participates directly from the melt (2-5). Such an assumption, however, is ill-founded when the stability and hence the concentration levels of 0^2 - in these melts are considered. For example, at 573 K, the concentration of oxide ions, produced by the self-dissociation of nitrate ions, is estimated to be $\approx 10^{-12}$ m (m = mole.kg⁻¹). However, the existence of oxide ions, even at such a low concentration, is highly questionable because of their reactivity towards NO₃⁻, dissolved oxygen and water vapor in the melt. Zambonin and Jordan found that the voltammograms obtained using rotated platinum disk electrodes were similar with additions of Na₂O and Na₂O₂ to the nitrate melt (6). Their investigations revealed that oxide ions in dry

melts and to hydroxyl ions in melts exposed to water vapor; under such conditions, the concentration of oxide ions could be $<\!\!<\!\!10^{-20}$ m (7).

The concentration of oxide ions at the self-dissociation level of 10^{-12} m could, however, be maintained by adding sufficient nitrite (one of the products of the reaction of 0^2 - with N03⁻) and having a blanket of inert gas or a vacuum over the melt. Corrosion measurements in molten alkali nitrates have been reported where no special precautions were taken to stabilize the oxide ions; yet the mechanisms proposed have assumed the participation of oxide ions directly from the melt (2,4,5). Moreover, even a concentration of 10^{-12} m is found to be too low to account for the observed kinetics of oxidation of iron and steel at 573 K in the nitrate melts. A reappraisal of the role of oxide ions in the mechanism of corrosion in molten alkali nitrates and nitrites is thus warranted. Oxidation and polarization measurements carried out on zirconium and Zircaloy-2 in melts containing alkali metal nitrates, nitrite and hydroxide are presented here; analysis of the results shows that the source of oxide ions has to be the reaction of nitrate, nitrite and hydroxyl ions with the anion vacancies emerging on the surface.

EXPERIMENTAL

Zirconium and Zircaloy-2 samples were cut from rolled and annealed sheets; elemental analysis data are shown in Table I. Samples were paddle-shaped and the large test sections had a surface area of \sim 10 cm². Following the mechanical polishing step, they were pickled in a bath of hydrofluoric and nitric acids. The sodium and potassium nitrates were 99.99% pure; the purity of the other salts varied from 97 to 99%. Experiments were carried out in NaNO₃[41]-KNO₃[59], NaNO₂[40]-NaNO₃[7]-KNO₃[53], NaNO₃[40.5]-KNO₃[58.8]-NaNO₂[0.7], NaNO₂[100], LiNO₃[100] and LiNO₃[95]-LiOH[5]; the numbers listed refer to percentages by weight. Dry argon was bubbled through the melt containing the hydroxide at all times. The other melts were generally kept open to air; however, for comparison purposes, in a number of experiments, the cell containing the melt was evacuated by connecting to a vacuum system capable of pumping down to a pressure of 1.3 mPa or argon was bubbled through the melt.

The apparatus and the procedure followed for oxidation and polarization measurements are described in detail elsewhere (8). Vycor and stainless steel vessels were used as containers for the nitrate and nitrite melts; for the hydroxide containing melt a vessel made of Zircaloy-2 was used. Polarization data obtained in the nitrate and nitrite melts are reported here. A large area platinum wire gauze formed the counter electrode. A platinum wire fused in glass was used as a general reference electrode; its potential was frequently checked against a Ag/Ag⁺ (0.07 m in KN0₃-NaN0₃) reference electrode. The potentials are quoted relative to the silver electrode. When a sample oxidized and polarized in one melt was polarized in another melt

sufficient time, usually half an hour, was allowed for the attainment of steady potential. Only weight gain measurements were made with some control samples. For comparison purposes polarization and voltammetric data were obtained using small area wire electrodes of platinum, iron, zirconium and Zircaloy-2. All oxidations and polarizations were carried out at 573 K.

RESULTS

Thin film (≤ 125 nm) growth: Two typical sets of curves showing the changes in potential with time and the kinetics of oxide growth in the initial stages are shown in Figures 1 and 2. The potentials on immersion were highly negative and they shifted in the positive direction with increasing oxidation; maximum changes occurred within the first 2 to 3 h after which they stayed nearly steady. Zirconium was always at a slightly more negative potential than Zircaloy-2. The steady potentials attained in nitrite and hydroxide containing melts (still negative) were slightly positive to those in the nitrate melts. Otherwise, in the cases of both zirconium and Zircaloy-2 the potentials attained and their variation with time was independent of the melt and the environment over the melt.

Oxide growth up to 24 h was followed by observing the changes in the interference colours developed on the sample; the colours were related to oxide thicknesses by comparison with a chart of oxide films grown anodically to various formation voltages (9). Generally two to three predominant colours, corresponding to a variation in oxide thickness of 10 to 20 nm, were revealed by the optical examination; average thickness was estimated by taking into account the extent of coverage of these colours. The thickness at the end of a 24 h oxidation was obtained from weight gain measurements. The oxidation followed a near parabolic rate law and the rate decreased from a weight gain of \sim 280 µg/dm²h in the first hour to \sim 35 µg/dm²h near the end of the 24 h period; a weight gain of 1 mg/dm²h is equivalent to an oxide thickness of 67.3 nm. A tendency towards slightly increased rates of oxidation was observed in the nitrite and hydroxide containing melts. The kinetics of oxide growth were essentially the same when the melts were exposed to air, or evacuated and covered in a blanket of argon.

<u>Thick film (up to 1 µm) growth:</u> The kinetics of oxidation covering a range of weight gain from 1.5 to 15 mg/dm² (oxide 100 nm to 1 µm thick) are shown in Figure 3. A slightly faster rate of oxidation is observed in the melts containing nitrite and hydroxide than in the nitrates. The rate law followed changes from a near parabolic to a cubic one with the transition occurring at a gain of 4.5 mg/dm² in the case of zirconium and at \sim 6.5 mg/dm² in the case of Zircaloy-2; the rate of oxidation decreases from \sim 40 to \sim 3.5 µg/dm²h during these periods of oxide growth. Bubbling argon through the melts or evacuating the cell affected the kinetics little.

successively in the binary nitrates, ternary nitrates-nitrite and sodium nitrite; the reverse cathodic and the forward anodic portions are shown. Oxidation current was evaluated by extrapolation of the linear anodic part and finding the intersection of the corrected cathodic curve and the extrapolated anodic curve (8). There was a good agreement between the oxidation currents obtained from polarization measurements and the oxidation rates calculated from the weight gain data (8). It is important to note here that polarization of an oxidized zirconium sample in different melts gives essentially the same oxidation current; as evidenced by the kinetics of oxidation in these melts (Figure 3(b)), this is to be expected. A set of polarization curves for Zircaloy-2 in the binary nitrates is shown in Figure 5; these were traced following oxidation of the sample in the same melt to various times. The linear portions of the anodic curves scan a shorter range of potentials than in the case of zirconium; the oxidation currents obtained from the polarization curves matched the kinetically derived oxidation rates well (8).

<u>Wire electrodes:</u> A typical voltammogram, traced at 20 mV/s, for platinum in the binary nitrate eutectic containing 10^{-1} m NaNO₂, is shown in Figure 6(a). The various peaks and their significance are interpreted as follows (10): cathodic peaks located at -1.68 and -1.9 V are due to the formation of insoluble sodium and potassium oxides on the electrode surface and their oxidation to the peroxides are associated with the corresponding anodic peaks at -1.29 and -1.56 V, respectively. Oxidation of the nitrite ion and its associated limiting current are observed at +0.3 to +0.9 V and at +1.2 V the sharp rise in current is due to the oxidation of the nitrate ion. A voltammogram obtained in the binary nitrates had similar features except that the saturation current due to nitrite ion oxidation was considerably less; in sodium nitrite the peaks due to insoluble oxide formation and its oxidation were not distinct and the rise in anodic current, due to the oxidation of the nitrite ion, occurred at 0 V. Polarization curves traced at the usually employed scan rate of 0.5 mV/s are shown in Figure 6(b); time of immersion in the melt had no effect on these curves.

Changes in the polarization curves, with time of immersion in molten binary nitrates containing 10^{-1} m NaNO₂, for iron, zirconium and Zircaloy-2 wire electrodes are shown in Figures 7, 8 and 9. In the case of the iron electrode, a sharp rise and fall in anodic current during the initial polarization, similar to that reported by Arvia et al. (2), was not observed. The behaviour of the wire electrodes was found to be quite similar to that of the large area samples. With increasing oxidation, the rest potentials moved in the positive direction, the oxidation currents decreased and the linear portions on the anodic curves scanned a decreasing range of potentials; thus the rest potentials and the shape of the polarization curves showed a tendency to

approach those of the platinum electrode. This tendency was most obvious in the case of iron and decreased as Fe > Zr-2 > Zr, in the same order as their rest potentials varied with iron staying positive to Zircaloy-2 and zirconium.

DISCUSSION

<u>Oxide ion chemistry:</u> Investigations concerning the electrochemical nature of the oxygen electrode in molten KNO_3 -NaNO₃ have suggested the existence of the following equilibria in the melt

$$NO_3^{-} \neq NO_2^{+} + O^{2-}$$
 ...1

$$0^{2^{-}} + N0_{3}^{-^{+}} + N0_{2}^{-^{+}} + 0_{2}^{2^{-}} \dots 2^{2^{-}}$$

$$0_2^{2^-} + 2N0_3^- \neq 2N0_2^- + 20_2^- \qquad \dots 3$$

 $0_2^{2^-} + 0_2 \stackrel{?}{\neq} 20_2^- \qquad \dots 4$

$$0^{2^{-}} + H_{2}0 \stackrel{2}{\approx} 20H^{-}$$
 ...5

At 500 K, the equilibrium constants for the equations 2 to 5 are 3, 6.7×10^{-11} , 3.5×10^5 and 10^{18} , respectively. Oxide ions (0^{2-}) are thus rapidly converted to peroxide, superoxide and hydroxyl ions. Therefore, an oxygen electrode in the nitrate melts is treated as one involving a one electron transfer according to the equation

$$0_2 \stackrel{-}{\downarrow} 0_2 + e \qquad \dots 6$$

However, data supporting a two electron transfer equilibrium

$$0^{2-} \neq \frac{1}{2} 0_2 + 2e \qquad \dots 7$$

have also been reported. It is recognized now that these studies were

carried out in glass containers and that the 0^{2-} ion might have been stabilized by the reaction (11)

$$0^{2^{-}} + x \operatorname{Si0}_{2} \neq (\operatorname{Si0}_{2})_{x} 0^{2^{-}} \dots 8$$

The other obvious means of stabilizing 0^{2-} ions is to add sufficient nitrite to the melt and to avoid exposure to oxygen and water vapor. At 573 K for example, a maximum oxide ion concentration of 10^{-12} m can be expected in dry KNO₃-NaNO₃-NaNO₂ melts kept under vacuum or a blanket of inert gas. But in melts of KNO₃-NaNO₃ under all conditions and KNO₃-NaNO₂-RaNO₂ exposed to atmospheric conditions, the oxide ion concentration could be as low as 10^{-20} m, or less (7).

<u>Mechanism of corrosion</u>: For interpreting the corrosion of iron and steel in molten nitrates $p0^{2-}$ (= $-log[0^{2-}]$) vs. potential diagrams, which reveal the thermodynamic stability of the various regions involved, have been constructed and used (3). The main equilibria involved are shown in Figure 10. Oxide growth is supposed to proceed by the following anodic reactions (2,4,5)

$$Fe+0^{2-} = Fe0+2e$$
 ...9

$$3Fe0+0^{2} = Fe_{3}0_{4}+2e$$
 ...10

$$2Fe_{3}0_{4}+0^{2} = 3Fe_{2}0_{3}+2e$$
 ...11

But the discrepancy between the mechanism and the corrosion kinetics (parabolic rate law) becomes obvious when the flux of oxide ions and the rate of oxidation are compared. Assuming a diffusion coefficient of 5×10^{-6} cm²/s for oxide ions in the melt (the same as that for the diffusion of hydroxyl, peroxide and superoxide ions in nitrate melts) and the smallest possible barrier layer thickness of 0.2 nm (the size of a mean hole radius in molten salts) at an electrode surface the flux of oxide ions arriving at 573 K can be calculated as 2.8 µg/dm²h for an oxide ion concentration of 10^{-12} m. For samples oxidizing in nitrate melts (5) and melts exposed to atmospheric conditions (2.4), the flux of oxide ions reaching the surface would be $\leq 2.8 \times 10^{-8}$ µg/dm²h. From the weight gain/loss data reported (4.5) the average rate of oxidation decreases from 500-800 µg/dm²h in the initial 10 h period to 200 µg/dm²h in the subsequent 100 h; the rates are $\sim 10^{10}$ times the estimated flux of oxide ions.

The main regions established by the $p0^{2-}$ vs. potential diagram are correct; but at the experimental conditions the stability of the oxide phases is determined by the rest potential and the concentration of oxide ions in the melt. For example in reference (2), specific mention is not made of the reference electrode used but a Ag/Ag⁺ electrode is implied by referring to a previous publication. Then assuming an oxide ion concentration of 10^{-12} m in the melt, as suggested by the authors, the passivation potential on immersion of -0.25 V and the Ag/Ag⁺ reference zero would be located at -2.1 and -1.85 V on the diagram; these are marked as 'a' in Figure 10. Then the rest potentials reported in reference (4) and measured in the present study would be those marked as 'b' and 'c' in the figure. It can readily be seen that at these potentials, even assuming an oxide ion concentration of 10^{-12} m in the melt, the iron and steel are to remain immune to oxidation; a conclusion contrary to the results obtained. A more realistic approach is that the oxide ion concentration in these melts is somewhere within the range of 10^{-20} to 10^{-12} m. Then the observed immersion potential of -0.8 V and a final rest potential of -0.4 V (attained following hours of oxidation) would fix the Ag/Ag⁺ reference zero at ~ -0.8 V, as shown by the dotted line, in the $p0^{2-}$ vs. E diagram.

In the present study, the rate of oxidation of zirconium and Zircaloy-2 decreased gradually from 300 to 30 μ g/dm²h during the thin film growth and then to 3 μ g/dm²h during the thick film growth period. The kinetics followed a near parabolic rate law initially and then a cubic rate law; therefore surface reactions, e.g., arrival of oxide ion species to the surface from the melt, are not controlling the rate of oxidation. The oxidation rates and the kinetic behaviour were independent not only of the composition of the melts but also of the environment over them. The oxide ion concentration would have varied from 10^{-12} m in the specific cases of nitrate-nitrite melts kept under vacuum or argon to $< 10^{-20}$ m in all the melts generally kept exposed to atmospheric air; too low to account for the observed oxidation rates. In melts exposed to air the concentration of dissolved oxygen is estimated to be 10^{-5} m and of peroxide and superoxide ions to be $\sim 10^{-7}$ m (7); such levels are high enough for these species to participate in the oxidation process. However, the concentrations of these species in the melt under a vacuum or an argon atmosphere would still be extremely small. Therefore, a general mechanism operating under a variety of conditions in these melts could be the reaction of nitrate and/or nitrite ions with the anion vacancies emerging on the surface

$$\Box^{++} + NO_{3}^{-}/NO_{2}^{-} \rightarrow \Box + NO_{2}^{+}/NO^{+} \qquad \dots 12$$

Zirconium dissolving in the oxide at the metal-oxide interface creates the oxygen ion vacancies; oxide growth is controlled by the diffusion of oxygen ions which is shown to be occurring along oxide crystallite boundaries (12). The cathodic half of the reaction at localized conducting sites might then be

$$NO_2^+/NO^+ + e \rightarrow NO_2/NO$$
 ...13

and/or

$$0_2 + e \rightarrow 0_2$$
 ...14

to complete the oxidation process. In the case of iron and steel, corrosion proceeds by the diffusion of cations in the magnetite layer and oxygen ions in the hematite layer. At the hematite-salt interface, the reaction would be the same as equation 12 and at the magnetite-salt interface the reaction would be the oxidation of Fe^{2+} ions

$$3Fe^{2+} + 4NO_3^{-} \rightarrow Fe_3O_4 + 4NO_2^{+} + 2e$$
 ...15

Polarization measurements: The voltammograms and polarization curves obtained for platinum in the nitrate and nitrate-nitrite melts indicate that although reduction and oxidation of the nitrate and nitrite ions occurs at potentials highly cathodic and anodic to the rest potential, considerable current flows under steady state polarization conditions (cf. Figure 6(b)). The possible reactions contributing to the current flow are the anodic reaction 6 and the cathodic reactions 13 and 14. When zirconium or iron is corroding in these melts ionic and electronic transports are occurring through the growing oxide film; ion current is associated with the diffusing species in the oxide and the reactions 12 and 15 at the oxide-salt interface and the electron currrent is associated with reactions 13 and 14 at the oxide-salt interface. On immersion in the melts iron, zirconium and Zircaloy-2 attain highly negative potentials with respect to platinum indicating that the thin oxide films existing on their surfaces are resistive to electron transport. As a result the reactions 13 and 14 and the reaction 6 occur at potentials more cathodic and anodic, respectively, than on platinum. Anodic polarization curves thus reveal a linear portion of gradually increasing current, that is characteristic of ion transport occurring through the growing oxide film, prior to the sharp increases in current due to reaction 6. When the polarizations are carried out immediately after immersing an unoxidized metal/alloy in the melt, these linear anodic portions would However, contributions to the oxide growth by the applied field during polarizations decrease rapidly with increase in oxide thickness and then the linear anodic portions represent mainly the variation of the ion current with the applied potential.

In the case of iron the absence of an anodic peak in the prepassivation region, during the initial polarization, would imply that a passive film was already existing on the surface or was formed during the time elapsed between immersion and polarization. The linear anodic portion distinctly evident in the initial polarization curve represents the growth of the passive magnetite layer. With increasing oxidation the changes observed in the rest potential and polarization curves indicate that this magnetite film, resistive to electron flow, is converted into a duplex film of magnetite and hematite having a good electronic conductivity. The behaviour of the oxidized iron electrode thus becomes similar to that of platinum.

In the cases of zirconium and Zircaloy-2 electron conduction is localized at impurity (iron) and intermetallic sites which exist as second-phase precipitates in the metal and alloy (8). A thin film of zirconia existing on these precipitates leads to highly negative immersion potentials initially. Migration of iron through this thin zirconia layer and formation of iron oxides lead to increased electron transport at these sites and to changes in the rest potentials towards the positive direction. However, the electronic conductivity of these oxide films does not increase to the levels attained by the oxide films on iron and steel. Thus the potentials of oxidized zirconium and Zircaloy-2 stay negative to platinum and iron and the anodic polarization curves reveal linear portions even after hundreds of hours of oxidation. The observation that the oxidation currents derived from these linear anodic portions agree with the oxidation rates obtained from the kinetic data confirms that these anodic linear portions represent the variation of the ion current through the growing oxide with the applied potential.

CONCLUSIONS

The concentration of oxide ions (0^{2-}) in molten alkali nitrates and nitrites is too low to account for the observed rates of corrosion or iron, steel, zirconium and Zircaloy-2. Oxide ions for oxide growth are provided by the reaction of nitrate/nitrite ions with emerging anion vacancies or cations at the oxide-salt interface. Analysis of the polarization curves obtained on corroding samples yields oxidation currents which agree with the kinetically derived oxidation rates. The higher the resistance of the growing oxide to electron transport, the more negative are the rest potentials and the more distinct are the anodic linear portions representing ion transport through the growing oxide films.

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REFERENCES

- R.T. LeFrois and H.V. Venkatasetty, Proceedings of the International Symposium on Solar Energy, Eds. J.B. Berkowitz and I.A. Lesk, p.16, The Electrochemical Society, Princeton, 1976.
- (2) A.J. Arvia, J.J. Podesta and R.C.V. Piatti, Electrochimica Acta, <u>17</u>, 33 (1972).
- (3) S.L. Marchiano and A.J. Arvia, ibid., 17, 861 (1972).
- (4) A. Baraka, A.I. Abdel-Rohman and A.A. El Hosary, Br. Corros. J., <u>11</u>, 44 (1976).
- (5) C.M. Chen and G.J. Theus, Electrochemical Corrosion Testing, ASTM STP 727, Eds. F. Mansfeld and U. Bertocci, p.303, 1981.
- (6) P.G. Zambonin and J. Jordan, J. Am. Chem. Soc., <u>89</u>, 6365 (1967); ibid., <u>91</u>, 2225 (1969).
- (7) P.G. Zambonin, J. Electroanal. Chem., 32, App.1, (1971).
- (8) N. Ramasubramanian, J. Electrochem. Soc., 127, 2566 (1980).
- (9) N.J.M. Wilkins, Corrosion Science, 4, 17 (1964); 5, 3 (1965).
- (10) M.H. Miles and A.N. Fletcher, J. Electrochem. Soc., <u>127</u>, 1761, (1980).
- (11) A.A. El Hosary, D.H. Kerridge and A.M. Shams El Din, Ionic Liquids, Eds. D. Inman and D.G. Lovering, p.339, Plenum Press, New York, 1981.
- (12) B. Cox, Advances in Corrosion Science and Technology, Vol.5, Eds. M.G. Fontana and R.W. Staehle, p.173, Plenum Press, New York, 1976.

TABLE I INGOT ANALYSIS

Material	Sn	Fe	Cr	Ni	Amount
Zirconium	< 10	80	20	< 10	ppm
Zircaloy-2	1.46	0.13	0.08	0.05	wt%



















Fig.8 Curves similar to those in Fig.7 obtained for a zirconium wire electrode, 0.3 cm² in area.



Fig.9 Curves similar to those in Figs.7 and 8 obtained for a Zircaloy-2 wire electrode, $0.47\ \mathrm{cm}^2$ in area.







Fig.11 Schematic diagram of polarization curves resulting from electron transfer reactions at the oxide-salt interfaces and ion transport through the growing oxide films.

SOLUBILITY OF THE NiO FUEL CELL CATHODE IN Li₂CO₃-K₂CO₃ MELTS AS DETERMINED BY CYCLIC VOLTAMMETRY

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ABSTRACT

Development of molten carbonate fuel cells is concerned with the stability of the NiO (lithiated) cathode. Observations of metallic nickel deposits within the electrolyte matrix have prompted investigation into modes of operation to enhance NiO stability as well as a search for alternative cathode materials. In this paper, cyclic voltammetry has been applied to examine $\rm Ni^{2+}$ concentration in $\rm Li_2CO_3-K_2CO_3$ melts with NiO present. A test cell with three gold electrodes, one being the reference with 1/3 $0_2 - 2/3$ CO_2 gas purge, employed voltage limits +0.2 to -1.0 V. Data and physical samples were collected at temperatures between 823 and 1023 K. The Li2C03-K2C03 melt compositions ranged from 65 to 38 mol % Li₂CO₃. Solubility of NiO as a function of of increasing temperature (823-1023 K) differed for the respective dry carbonate melt compositions, increasing in a range from 5 to 45 wt ppm Ni for 62 mol % Li₂CO₃, while decreasing in a range from 15 to 5 wt ppm Ni for 38 mol % Li₂CO₃. In 50 mol % Li₂CO₃, NiO solubility increased from 10 wt ppm Ni at 823 K to 30 wt ppm Ni at 1023 K. Humidified cathode gas significantly increased NiO solubility (up to 10 X). The increase was partially reversed by dry gas purge with a 2 to 4 fold increase of Ni concentration remaining even after days of dry gas purge. Humidified gas did not affect the coefficients of the respective NiO solubility functions with temperature.

I. Introduction

Observations of metallic nickel deposits in the electrolyte of molten carbonate fuel cells (MCFC) have prompted investigation of lithiated NiO cathode solubility. Under the current trend toward pressurized operation of the fuel cell cathode, NiO is not likely to survive the 40,000 h of operation desired for commercial cells (1,2). Therefore, a major effort in MCFC development is to improve cathode stability, including a search for alternative materials (3). Identification of operating conditions which enhance NiO stability would therefore be of interest. In previous studies (2,3), lithiated NiO solubility measurements have focused on the standard MCFC cathode conditions of 823-1023 K temperature in $62 \mod %$ Li₂CO₃-K₂CO₃ under l atm of dry 30% CO₂ - Air (3). Ingram and Janz (4) showed the influence of carbon dioxide partial pressure on NiO solubility. However, the effects on NiO solubility of the Li/K ratio of the carbonate melt and humidity in the MCFC cathode environment have not yet been examined.

In this study, cyclic voltammetry (CV) is used to quantify Ni^{2+} concentrations arising from NiO solubility by the reaction

$$NiO + CO_2 \neq Ni^{2+} + CO_3^{2-}$$
 [1]

for the temperature range 823 to 1023 K and for electrolyte compositions of 62, 50, and 38 mol % Li₂CO₃. Cyclic voltammetry was chosen for this study because it provides an interactive and responsive analytical tool. To reduce time to attain equilibrium, the carbonate test melts were well agitated and gas-contacted by a 1/3 O₂ - 2/3 CO₂ gas sparge. The CV current peak responses were calibrated for Ni concentration by analytical results of physical samples since the planar diffusion correlation (5) is not applicable.

II. Experimental

The three-electrode test cell for cyclic voltammetry (CV) in molten carbonate was constructed with gold and high-density alumina (Coors, AD-998) components (Fig. 1). Because Al₂O₃ forms a surface coating of LiAlO₂ in the presence of Li₂CO₃-K₂CO₃, the Al₂O₃ sample cup is pretreated with carbonate melt. The sample cup is suspended in a tube furnace with cell components mounted beneath a stainless steel end flange using baffles to reduce heat loss. Both working- and counterelectrodes are gold wires (0.965 mm dia) with approximately 0.5 cm^2 exposed area, which form a figure "8". They are supported by Al203 tubes (0.476 cm OD - 0.238 cm ID). The reference electrode is of the same construction and is purged with a 2/3 CO₂ - 1/3 O₂ gas mixture (Matheson) through the support tube. A thermocouple is centered between the electrodes in an Al₂O₃ sheath. The test melt ranges in volumes from 3 to 12 cm³ and provides an electrolyte depth of 0.2 to 1.0 cm. This melt is well mixed and gas-contacted by the gas sparge (0.25 1/min) of the reference electrode.

Tests are controlled in a voltage range of +0.2 V to -1.2 V vs. the reference electrode by a PARC Model 75 Universal Programmer driven by a Stonehart Associates Model BC1200 Potentiostat. Operating parameters for the cyclic voltammograms were established through trial. The potential of a clean nickel wire vs. the 2/3 CO₂ - 1/3 O₂ reference electrode was -0.6 V. Winnick and Ross (6) have likewise observed reduction of NiO to Ni at -0.6 V under similar conditions. The typical scan of 100 mV/sec initiated at 0.0 V in the cathodic direction gave distinguishable peaks of Ni²⁺ \rightarrow Ni^o at -0.8 V and anodic peak of Ni^o \rightarrow Ni²⁺ at -0.4 V.

Potential-bracket opening experiments (Fig. 2) to greater cathodic limits revealed no change in the cathodic current peak, but increasing anodic current peaks. Anodic current peaks begin to appear only when the cathodic limit exceeds -0.6 V. Faster scan rates (200 mV/sec) increased peak heights proportionally. This evidence supports a deposition/stripping mechanism for the CV current peaks. The anodic peak from a -1.0 V cathodic limit was selected for the NiO solubility comparison, because it provided the greatest discernment in the given range of temperature and electrolyte composition.

Temperature was changed at random to exclude time dependent effects. One hour was found to be sufficient to obtain equilibrium following temperature change. Under a given set of conditions, the cyclic voltammograms were reproducible for days at a time. Electrolyte composition changes were made at room temperature with a tube through the furnace end flange. Twelve hours were allowed for electrolyte composition change or for recovery from loss of $\rm CO_2$ purge. Purge gas was bubbled through water at room temperature for humidified gas experiments. The effect of humidity on NiO solubility used CVs taken after at least 1 h of dry gas purge and most often after days of dry gas purge.

About 40 physical samples (50-200 mg of the melt) were taken with an Al₂O₃ pipette subsequent to a CV run. These samples were analyzed for nickel by Inductively-Coupled Plasma/Atomic Emission Spectroscopy (ICP/AES) to provide a calibration of the peak currents of the CV. The calibrating factor was 30 \pm 3 wt ppm Ni per mA of the anodic peak (Fig. 3). Scatter of values from physical samples above the calibration curve was expected, because some physical samples contained traces of NiO particulate. Samples were also analyzed for Li⁺/K⁺ ratio and OH⁻/CO₃²⁻ ratio. The OH⁻ ion analysis by aqueous acid/base titration was difficult and had low reliability. Values did not clearly distinguish between dry and humid purge gas. Another analytical method will need to be found for these analyses.

The voltammograms were recorded on 50 mV/cm scale corresponding to 0.5 mA/cm. Current peak heights were measured vertically from the baseline for cyclic voltammograms using the -1.0 V cathodic limit with a 10% accuracy. With an approximate 10% error in nickel concentration for the physical sample analyses, an overall error of 20% for determinations by the CV analysis is likely.

III. Results

Initial work centered on examining the viability of cyclic voltammetry for analyzing low levels of $\rm Ni^{2+}$ ion in carbonate melts. Cyclic voltammograms on blank solutions (<5 wt ppm Ni by ICP/AES) produced no distinguishable current peaks (Fig. 4). However, after introduction of NiO to the carbonate melt, current peaks do arise at -0.8 V cathodic and -0.4 anodic. In anticipation of developing an in situ analytical method for MCFC, addition of LiAlO₂ powder (the

matrix material for electrolyte tiles) to the carbonate melt was shown to have no effect. The effect of temperature change upon current peak height is also seen in Fig. 5. Here, the Ni²⁺ voltammogram current peaks of 38 mol % Li₂CO₃ melt decrease with an increase in temperature, 823 to 1023 K. Also, at higher temperatures a greater baseline "tilt" occurs independently of melt composition, as influenced by the increased kinetics of the MCFC cathode reaction

$$1/2 \ 0_2 + CO_2 + 2e^- \neq 2CO_3^{2-}$$
 [2]

In tests with air purge or loss of $CO_2 - O_2$ purge gas flow, the CV peaks for nickel diminished as would be expected.

After the test cell was purged periodically with humidified $CO_2 - O_2$ gas, NiO solubility was irreversibly increased by 2-4 times (Fig. 6). The CV peak for nickel was nearly a factor of 10 greater during the humid purge than in the initially dry melt. These results agree well with the following reaction:

$$H_{2}O + CO_3^{2-} \neq CO_2 + 2OH^-$$
. [3]

The increased pCO_2 being chemically produced increases NiO solubility, but even after subsequent purge with dry $O_2 - CO_2$ gas the effect of OH⁻ persists. Figure 7 illustrates that 1 mol % OH⁻ addition to the carbonate melt likewise produced an irreversible increase in the nickel CV peaks. The significant increase of NiO solubility due to humidity would appear especially deleterious to MCFC life in that the cathode gas is expected to contain up to 20% H₂O.

The solubility of NiO as a function of temperature (823-1023 K) for three carbonate melt compositions is presented in Fig. 8. The gaseous environment of 1/3 O₂ - 2/3 CO₂ at atmospheric pressure is an underlying parameter, because

$$NiO + CO_2 \neq Ni^{2+} + CO_3^{2-}$$
. [4]

The Li₂CO₃-K₂CO₃ phase diagram indicates two eutectic compositions at 62 mol % and 42 mol % Li₂CO₃, respectively. Of particular interest is the switch in NiO solubility as a function of temperature between the two eutectic compositions from a positive coefficient at 62 mol % Li₂CO₃ to a negative coefficient at 38 mol % Li₂CO₃. The NiO solubility in 62 mol % Li₂CO₃ as determined by CV increases with temperature from \sim 5 wt ppm Ni²⁺ at 823 K to nearly 45 wt ppm at 1023 K. Whereas, with 38 mol % Li₂CO₃, the other practical extreme in composition, the solubility of NiO decreases from 15 wt ppm Ni at 823 K to 5 wt ppm Ni at 1023 K. The intermediate composition of 50 mol % Li₂CO₃ shows less temperature sensitivity of NiO solubility ranging from 10 wt ppm to 30 wt ppm Ni with increasing temperature. The cause of the change in the solubility temperature dependence is not yet understood. The oxo-acidity of the carbonate melt is a likely contributor to the NiO solubility mechanism in that

$$NiO \neq Ni^{2+} + O^{2-}$$
. [5]

A decrease in the Li⁺/K⁺ ratio would suggest an increase in 0^{2-} ion (7) and, therefore, reduced NiO solubility. An additional consideration is a change in the degree of NiO lithiation. Bronstein et al. (8) report a reduced degree of NiO lithiation in the presence of lower lithium-activity carbonate melts. Lithiation of NiO in carbonate melts of less than 62 mol % Li₂CO₃ has yet to be studied.

Figure 8 shows the approximate 4-fold irreversible increase in NiO solubility in the 38 mol % LipCO3 melt as a result of purging with humidified gas. Even after days of dry gas purge, the increased NiO solubility was maintained. Further, the negative coefficient in NiO solubility function with temperature is maintained. After a humidified gas purge, the intermediate equimolar electrolyte composition exhibits a "U"-shaped NiO solubility function with temperature--60 wt ppm concentration at 823 K and 1023 K and 30 wt ppm at 923 K. Figure 9 shows the incremental increase in NiO solubility in 62 mol % Li2CO3-K₂CO₃ as 1 mol % LiOH additions were made. After humidified gas purge, an added irreversible increase to the NiO solubility occurs. Bartlett and Johnson (9) observed a color change for NiO in carbonate melt exposed to humidified gas purge, which suggests a change in NiO composition. Further work in analyzing the degree of hydroxide incorporation into the NiO or change Ni oxidation state could provide an understanding of the increase of NiO solubility due to humidity. Equilibrium levels of OH⁻ in carbonate melt likewise need further examination for carbonates of various Li^+/K^+ ratios. The CO₂ - O₂ sparge is believed to allow only very low levels of OH⁻ in carbonate (Eq. 3). Therefore, the irreversible increase in NiO solubility due to humidity is somewhat unexpected.

IV. Summary and Conclusions

The correspondence between physical sample analysis and CV analysis for nickel in carbonate melts in the tested range of Li^+/K^+ ion ratio and for temperatures ranging from 823 K to 1023 K indicates that CV is a viable analytical method for providing responsive results for NiO solubility. We have shown that the Li^+/K^+ ion ratio of the carbonate melt changes the solubility of NiO as a function of temperature with a positive coefficient for 62 mol % Li₂CO₃ melt and a negative coefficient for 38 mol % Li₂CO₃ melt. It was also shown that humidified purge gas to the carbonate melt significantly increased NiO solubility. The increase was found to be irreversible and maintained the coefficient of the solubility function with temperature as determined in the dry melt. Additions of OH⁻ to the carbonate melt provided
similar results. At this time, the influence upon NiO solubility of the competing equilibrium states in the melt and the NiO itself is not understood.

An accurate assessment of NiO stability under alternative operating environments may lead to acceptable modes of MCFC operation with a NiO cathode. Coordination of operating temperature with carbonate composition and humidity should enhance NiO cathode stability. This work has indicated cathode gas humidity to be a controlling factor in determining NiO cathode stability for molten carbonate fuel cells.

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REFERENCES

- R. Dean Pierce, "Molten Carbonate Fuel Cells Technology Status," Proc. Fuel Cells Symposium, pp. 67-81, Institute of Gas Technology, November 16-18, 1981.
- C. E. Baumgartner, "Molten Carbonate Fuel Cell Cathode Studies," Extended Abstracts of Electrochemical Soc., Vol. 82-1, pp. 624-625 (1982).
- J. Sim, G. Kucera, J. L. Smith, A. Breindel, and R. D. Pierce, "Development of Cathode Materials for the Molten Carbonate Fuel Cell," Proc. 1982 National Fuel Cell Seminar, pp. 108-112 (1982).
- M. D. Ingram and G. J. Janz, "The Thermodynamics of Corrosion in Molten Carbonates: Application of E/pCO₂ Diagrams," Electrochimica Acta 10, 783 (1965).
- 5. T. Berzins and P. Delahay, J. Am. Chem. Soc. 75, 555 (1953).
- J. Winnick and P. N. Ross, Jr., "Kinetics of the 02/CO2 Reaction in Molten Carbonate: Reaction Orders for 02 and CO2 on Porous NiO," J. Electrochem. Soc. 128, 991 (1981).
- 7. B. Tremillon, "Diagrammes D'Equilibre Potentiel-Acidite' (E $p0^{2-}$) Dans Les Sels et Hydroxydes Alcalins Fondus," Pure and Appl. Chem. <u>37</u>, 395 (1974).
- H. R. Bronstein, S. Cantor, D. H. Smith, and J. Braunstein, "Study of Reaction Forming Lithium-doped Nickel Oxide," Extended Abstracts of the Electrochemical Soc., Vol. 80-2, pp. 385-387 (1980).
- H. E. Bartlett and K. E. Johnson, "Electrochemical Studies in Molten Li₂CO₃-Na₂CO₃," J. Electrochem. Soc. <u>114</u>, 457 (1967).



Fig. 1. Test cell consists of three gold electrodes (a) the reference is purged with 1/3 0₂ - 2/3 CO₂ gas and (b) and (d) serve as working and counter electrodes, (e) sample electrode (<u>e.g.</u>, Ni) for EMF measurements.







Fig. 2. Potential-bracket opening experiment 62 mol % Li₂C0₃-K₂CO₃. Anodic peak increases with cathode limits greater than -0.6 V <u>vs</u>. the reference electrode.



Fig. 4. Ni peaks appear after addition of NiO to melt. These peaks are symmetric about -0.6 V vs. the reference electrode.



Fig. 5. Cyclic voltammograms at 823, 923, and 1023 K for Ni²⁺ in humidified 38 mol % Li₂CO₃-K₂CO₃ indicate reduced solubility with increased temperature.



Fig. 6. Effect of humidity in 38 mol % Li₂CO₃-K₂CO₃ at 1023 K on NiO solubility. Dry purge gas does not totally reverse the increase in NiO solubility.



Fig. 7. Effect of OH addition on NiO solubility in 65 mol % Li₂CO₃-K₂CO₃ at 1023 K.



Fig. 8. Solubility of NiO cathode in three carbonate melts 62, 50, and 38 mol % Li₂CO₃-K₂CO₃ as a function of temperature in a 1/3 O₂ -2/3 CO₂ gas atm.



Fig. 9. NiO solubility increases arising from LiOH addition to initially dry 68 mol % Li₂CO₃-K₂CO₃ and further increases as a result of humid purge gas (1/3 O₂ -2/3 CO₂).

THE SOLUBILITIES OF FeS₂ AND FeS IN LiC1-KC1 EUTECTIC MELTS

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ABSTRACT

Solubilities of ${\rm FeS}_2$ in LiCl-KCl eutectic melts between 720 and 900 K are represented by the equation:

log (mole fraction, X_{FeS_2}) = - $\frac{5157.33}{T}$ + 0.666

They were measured by a new optical technique. This was necessitated by an excessive scatter in the solubility data determined by chemical analysis of the melts after establishing equilibria between the melts and FeS₂ by diffusion and counter diffusion.

The solubility of FeS in these melts determined chemically also had an excessive scatter. In addition, the optical technique was inadequate, as no satisfactory solid FeS sample could be procured. Therefore, the solubilities were calculated from the equilibrium constant of the reaction

 $FeS(s) + 2 (LiCl)_{e'lyte} = (FeCl_2)_{e'lyte} + (Li_2S)_{e'lyte}$

using relevant thermodynamic data.

INTRODUCTION

Rechargeable cells are being developed using Li-Al or Li-Si negative electrodes, iron sulfide or iron disulfide positive electrodes, and LiCl-KCl melts contained in boron nitride cloth separators as electrolytes (1,2,3). These cells have performed for over 10,000 h (2), but the specific energy starts declining after about 3000 h. Post-test examination of some of the recent compact cells which had Li-Al electrodes indicated very fine iron particles associated with lithium sulfide particles within the boron nitride separators (4). The degradation in performance of these cells may be caused by the loss of positive electrode active materials through their solubilities in the electrolyte. The iron sulfides in the positive electrodes themselves might have dissolved slightly in the electrolyte and reacted with dissolved lithium yielding iron and lithium sulfide particles. Boron nitride fibers could provide nucleating sites for their deposition. Therefore, it is necessary to have solubility data for the iron sulfides to evaluate this hypothesis. This investigation was a part of this effort and was conducted to measure the solubilities of FeS and FeS₂ in LiCl-KCl eutectic electrolyte at different temperatures.

As a first attempt, the solubilities were measured by equilibrating the LiCl-KCl melts with the respective solutes inside specially designed sealed silica capsules at different temperatures and determining the solute contents by chemical analysis. A large scatter was observed in these measurements. This scatter was caused by the difficulty in chemically determining the very low contents of the solutes in the equilibrated melts. Therefore, a new optical technique was developed. In general, this technique consists of sealing weighed amounts of solute and solvent inside a transparent silica capsule under vacuum. The capsule is slowly heated inside a furnace equipped with viewing ports. After the electrolyte has melted, the solid solute particle is observed occasionally with a microscope. At

a certain temperature, the solute dissolves completely in the melt, and the solubility is determined from the weighed amounts of solute and solvent and the observed temperature of dissolution. The technique was tested by determining the solubilities of Li_2S in LiCl-KCl eutectic melts. These solubility data were in agreement with data in the literature (5).

EXPERIMENTAL

Materials

Electrolytes obtained from two sources were used in these studies. First, LiCl of 99.6% purity and KCl of 99.9% purity were combined to form the eutectic mixture [58 m/o LiCl-42 m/o KCl; m.p. = 625 K (6)]. This mixture was purified by bubbling chlorine through the melt at 775 K for 4h, and subsequently removing the chlorine by bubbling with helium for lh. Second, a high-purity eutectic was obtained from Anderson Physics Laboratory and used for the majority of the tests.

A section of a large naturally occurring crystal of pyrite (FeS_2) was cleaved off and broken into sample size pieces. These pieces were analyzed under a microscope capable of 30X magnification, and only pieces having smooth and shiny surfaces [indicating no entrapped silica (SiO_2) impurities] were selected for testing. Chemical analyses of such specimens revealed an iron content of 46.3 weight percent (w/o) compared to the theoretical value of 46.55 w/o.

Inside a helium-atmosphere dry box, a quantity of high purity FeS (63.1 w/o Fe by chemical analysis against 63.53 w/o theoretical Fe) was placed in a graphite container with a tightly fitting cover which was cleaned by firing at about ~1300 K in a helium atmosphere. The container was placed in a flat-bottom silica tube which was closed with a rubber stopper having helium inlet and outlet ports. The silica tube was taken out of the dry box and positioned in a

high-frequency furnace heating coil. The graphite container was heated to ~1550 K, kept at this temperature for about 30 min and then cooled in flowing helium. The silica tube with the content was transferred into a dry box. The FeS lump was taken out of the graphite container and crushed into small pieces for use in the solubility measurements using the chemical technique.

Apparatus and Procedure

<u>Chemical Analysis Technique</u>. Sealed silica (Vycor) capsules of different designs, as shown in Fig. 1, were used to hold the melts. These different designs were tested in an attempt to minimize the convective transport of fine undissolved solute particles during equilibration (i.e., to attain equilibrium by diffusion and counter diffusion only) and to minimize compositional changes due to transport of the melt from the different compartments of the capsule during quenching. To further reduce the chances of convective transport of the solute particles, silica shot was placed on the inner small solute tube. Any errors due to segregation were avoided by using the whole amount of melt from the lower limb. The results from these different designs were similar, therefore, the capsule of the design shown in Fig. 1A was arbitrarily used.

Before use, the silica capsules were cleaned a few times with soap and water, then with alcohol, and dried at 475 K. They were fired in hydrogen at 1100 K for 1 h.

Inside a helium-atmosphere dry box, enough LiCl-KCl eutectic mixture was melted in the silica capsules (Fig. 1, A,B,C) to fill only the bottom extensions. After removing gas bubbles from the melt, the second smaller tube with the solute reactant pieces (FeS or FeS_2) was placed inside the silica capsule. An additional amount of LiCl-KCl mixture was slowly added, taking care to keep the mixture molten and to submerge the smaller tube completely. The melt was slowly solidified, avoiding gas bubble entrapment. The silica capsules were then

taken out of the dry box and sealed under a vacuum of $\sim 10^{-3}$ torr.

A layer of thermal insulation was placed in the bottom of a stainless steel container, 200 mm long and 57 mm ID. Eight stainless steel tubes, 150 mm long and 14 mm ID, were positioned in the container and the annular space was filled with sand. The sealed silica capsules were placed inside the smaller stainless steel tubes which were then covered by another layer of thermal insulation.

A vertical tubular furnace (450 mm long, 75 mm diameter) with a uniform temperature zone about 150 mm long was used to heat the melts. The other instruments used in conjunction with the furnace included a proportional band temperature controller, a potentiometer and calibrated Chromel-Alumel thermocouples.

The stainless steel container was placed in the predetermined uniform temperature zone of the vertical tubular furnace and the empty space in the furnace was packed with thermal insulation. The furnace was heated to a desired temperature and kept at this temperature for the equilibration period. From the results of experiments carried out for different lengths of time, the equilibration period was determined to be about 15 days. However, the test samples were generally allowed to equilibrate about 30 days, and in some cases even 55 days. At the end of the equilibration period, the samples were quenched in oil, the limb containing the equilibrated solidified melt was broken off, and the solubility was determined by chemical analysis of the total contents in the limb for iron.

In the case of silica capsule D, Fig. 1, the same preparatory procedure was followed except the smaller silica tube with the solute was positioned at the very beginning, the LiCl-KCl mixture was added in stages and melted until the level of the melt was above the capillary. During the equilibration period, the silica capsule was not placed in the smaller stainless tube, rather it was submerged into the

sand inside the bigger stainless steel container.

Optical Technique. The transparent test capsules were made by closing one end of a 10 cm long piece of 25 mm OD silica tube and adding a neck (20 cm long by 15 mm OD) to the open end. A ground glass joint was attached to the neck, while the base of the capsule was provided with a small protrusion (3 mm deep by 5 mm ID) for facilitating sample location. The capsules were washed with soap and water, acetone and finally distilled water using an ultrasonic cleaner. They were oven-dried at 375 K and cooled to room temperature. A preweighed solute sample was inserted into each capsule which was then transferred into a helium-atmosphere (typically less than 1 ppm 02, N2 or H20) dry box. Predetermined amounts of LiC1-KC1 eutectic were weighed inside the drybox and placed inside the respective capsules. Each capsule was closed inside the dry box using a ground glass joint and stopcock assembly. The loaded capsule was then removed from the drybox and sealed at the base of the neck under a vacuum of $\sim 10^{-3}$ torr using common glassblowing techniques. A liquid nitrogen cold trap was used between the mechanical pump and the capsule to prevent back diffusion of vapors from the pump into the sample zone.

A description of the apparatus used in this optical technique is shown in Fig. 2. Briefly, the sealed capsule, together with three calibrated thermocouples and two optical prisms, were mounted in a stainless steel test fixture to insure system rigidity. Two of the thermocouples were positioned near the bottom of the melt area, the other near the top. This fixture was inserted into a two-zone, vertical tubular clamshell heating element furnace (3.8 cm ID by 40 cm long). One of the lower thermocouples was used in conjunction with a proportional band temperature controller to control the temperature of the lower furnace zone. The other two thermocouples were used in conjunction with a digital temperature readout system and a data acquisition system to monitor the melt temperature. The top furnace

zone (above the sample zone) was heated only to maintain a constant temperature throughout the test zone. It was regulated manually by means of an autotransformer.

Initially, the furnace was equipped with two viewing ports, which with the aid of the prisms, allowed transmission of light from the source through the test capsule to the microscope. Later, a third port, opposite the lower port, was introduced for versatility in lighting and observing the sample. The ports were covered with transparent silica plates to eliminate air circulation, while the top and bottom of the furnace were closed with thermal insulation. A 300-watt Xenon lamp was used to illuminate the sample capsule, and a stereomicroscope capable of 70X magnification was used to view the sample.

After the electrolyte was melted, the solid solute particle was observed occasionally with the microscope. The temperature was slowly raised in steps. Near the dissolution temperature, it was increased in approximately 5° increments and kept at each temperature at least 6h. At a certain temperature, the solute would dissolve completely in the melt, and the solubility was determined from the weighed amounts of solute and solvent and the observed temperature of dissolution.

RESULTS AND DISCUSSION

FeS₂ Solubility

The solubilities of FeS_2 in LiCl-KCl eutectic melts at different temperatures determined by the chemical analysis technique are presented in Fig. 3. An excessive scatter in the data is observed. This scatter may be due to the difficulty in determining the very low solute content of the solidified melt by chemical analysis. However, the lower limits of the solubility are in agreement with those determined by a filtration technique (Fig. 3) reported by Hall (7).

The solubility of twelve FeS_2 samples in LiCl-KCl eutectic electrolyte at different temperatures determined using the optical technique are given in Table I. They are also represented graphically in Fig. 3 where the solid line represents a least squares fit to the data. The FeS₂ solubility data can be further represented by the equation

$$\log X_{\text{FeS}_2} = -\frac{5157.33}{T} + 0.666 \quad , \qquad [1]$$

where X_{FeS_2} = mole fraction of FeS₂ in eutectic salt, and T = temperature in degrees K. These results indicate FeS₂ is markedly less soluble in eutectic than determined by the above equilibrium techniques. At comparable temperatures, the solubility appears to be two to three orders of magnitude less than in the above studies.

The slope from Fig. 3 can be used to calculate the relative partial molar enthalpy of solution of FeS_2 in the LiCl-KCl melt. At equilibrium between the pure solid FeS_2 and the melt,

$$\mu_{(s)} = \mu_{(l)}$$
 [2]

where $\mu_{(s)}$ and $\mu_{(l)}$ are the chemical potentials of FeS₂ in the solid and liquid phases, respectively. If pure solid FeS₂ is defined as the standard state, then

$$\mu_{(s)} - \mu_{(s)}^{0} = \mu_{(l)} - \mu_{(s)}^{0} = \overline{\Delta H} - T \overline{\Delta S} = 0$$
 [3]

where $\overline{\Delta H}$ is the relative partial molar enthalpy of solution and $\overline{\Delta S}$ is the relative partial molar entropy of solution. In addition we assume Henry's law, χ^{\dagger}

$$\mu_{(l)} - \mu^0_{(s)} = RT \ln a_{FeS_2} = RT \ln \frac{FeS_2}{X_{FeS_2}}$$
[4]

where R is the gas constant, a_{FeS_2} is the activity of FeS₂ with respect to pure solid FeS₂, X'_{FeS_2} is any mole fraction of FeS₂ below

the solubility limit and $1/x_{\mbox{FeS}_2}$ is the activity coefficient of \mbox{FeS}_2 on the assumption that it remains constant below its solubility limit. And

$$\overline{\Delta S} = \overline{\Delta S}^{ex} + \overline{\Delta S}^{id} = \overline{\Delta S}^{ex} - R \ln X'_{FeS_2}$$
[5]

where $\overline{\Delta S}^{ex}$ is the excess partial molar entropy of solution and $\overline{\Delta S}^{id}$ is the ideal partial molar entropy of solution.

By substituting the value of $\mu_{(\ell)} - \mu^0_{(s)}$ from Eq. [4] and that of $\overline{\Delta S}$ from Eq. [5] into Eq. [3], and rearranging the terms, the following equation can be obtained;

$$\ln x_{\text{FeS}_2} = -\frac{\overline{\Delta H}}{RT} + \frac{1}{R} \quad \overline{\Delta S}^{\text{ex}}$$
[6]

Therefore, the slope of a plot between ln X_{FeS_2} and 1/T will be equal to $-\overline{AH}/R$ if our assumption of Henry's law behavior is valid.

Proceeding in this manner, the partial molar enthalpy of solution of FeS_2 was calculated from the data presented in Fig. 3. The partial molar enthalpy was calculated to be 23.5 kcal/mole which is about twice that of Li_2 S [13 kcal/mole (5)]. This higher enthalpy indicates a greater degree of difficulty for FeS₂ to be accommodated into the melt.

FeS Solubility

The solubilities of FeS determined by the chemical analysis technique (Fig. 4) had an excessive scatter similar to that observed in the case of FeS_2 solubilities. In addition, an attempt at measuring the solubility of FeS by the optical technique was unsuccessful. The FeS samples, prepared by equilibration with FeS_2 , did not dissolve uniformly. Therefore, the solubilities were calculated as follows.

CALCULATION OF THE SOLUBILITY OF FeS

The dissolution of FeS in LiCl-KCl melts may be represented by the reaction (see Reference (8),

$$FeS(s) + 2(LiCl)_{e'1vte} = (FeCl_2)_{e'1vte} + (Li_2S)_{e'1vte}$$
[7]

This reaction has been used by Saboungi, et al., (8) to calculate solubility products and to determine the solubility of FeS in the electrolyte by an electrochemical technique. The equilibrium constant, K, for the reaction in terms of activities (a_i) of the reactants and products is given by,

$$K = \frac{a_{\text{FeCl}_2}^* a_{\text{Li}_2} S}{a_{\text{LiCl}}^2 a_{\text{FeS}}}$$
[8]

where $a_{FeCl_2}^{\star}$ is the activity of FeCl₂ with respect to an infinitely dilute solution as the standard state, such that $a_{FeCl_2} / X_{FeCl_2} = 1$ when X, the mole fraction of FeCl₂ \rightarrow 0. The activities of the other compounds are with respect to pure solids as their standard states. Therefore $a_{FeS} = 1$ and

$$K = \frac{{}^{X}FeCl_{2}}{{}^{2}} {}^{X}Li_{2}S {}^{Y}Li_{2}S}{{}^{2}a_{LiCl}}$$
[9]

where $\gamma_{\text{Li}_{2}S}$ is equal to the reciprocal of the saturation mole fraction of $\text{Li}_{2}S$, $\chi_{\text{Li}_{2}S}^{\text{Sat}}$. This is true on the assumption that the activity coefficient of $\text{Li}_{2}S$ is constant below the saturation mole fraction. This assumption is reasonable when the values of the saturation mole fractions are very small (Table II). As per the dissolution reaction, $\chi_{\text{Li}_{2}S}$ is equal to $\chi_{\text{FeCl}_{2}}$, then,

$$K = \frac{x_{FeCl_2}^2 \gamma_{Li_2S}}{a_{LiCl}^2}$$
[10]

The standard free energy change $\left(\Delta G^0_R\right)$ of reaction [7] is given as

$$\Delta G_{R}^{0} = \Delta G_{Li_{2}S}^{0} + \Delta G_{FeCl_{2}}^{*} - \Delta G_{FeS}^{0} - 2\Delta G_{LiCl}^{0}$$
^[11]

The standard state for $\Delta G_{FeCl_2}^{\star}$ is again an infinitely dilute solution such that $a_{FeCl_2}/X_{FeCl_2} = 1$ when $X_{FeCl_2} \rightarrow 0$, while the standard states for the other compounds are pure solids. Using Eq. [11] and the data given in Table II, ΔG_R^0 is calculated to be 27909, 28232 and 28793 cal at 673, 723 and 800 K, respectively.

Since

$$\Delta G_R^0 = - RT \ln K , \qquad [12]$$

by substituting Eq. [10] into Eq. [12] we get

$$\Delta G_{\rm R}^{0} = - RT \ln \frac{\frac{X_{\rm FeCl_2}^{2} \gamma_{\rm Li_2}S}{a_{\rm LiCl}^{2}}}{a_{\rm LiCl}^{2}} .$$
 [13]

The a_{LiCl} in the LiCl-KCl eutectic melts at different temperatures has been reported elsewhere (9) and is given in Table II. It is assumed that the a_{LiCl} remains constant on the dissolution of FeS in the LiCl-KCl melt.

Taking the values of ΔG_R^0 calculated above and the data in Table II the mole fractions of FeCl₂ were calculated using Eq. [13]. They were found to be 6.5 x 10^{-7} , 1.5 x 10^{-6} and 4.16 x 10^{-6} at 673, 723 and 800 K, respectively (Fig. 4). As per reaction [7], these equilibrium concentrations of FeCl₂ are also the solubilities of FeS in LiCl-KCl eutectic melts at the respective temperatures.

The standard free energy change of reaction [7] can also be calculated by considering the following individual reactions,

FeS	+ 2[Li].	= $Li_{2}S + Fe$	[]	141
T C D	• 4144141		1.	74

 $2Li = 2[Li]_{A1}$ [15]

 $2LiCl = 2Li + Cl_2$ [16]

 $Fe + Cl_2 = FeCl_2$ [17]

which add up to

 $FeS + 2LiCl = Li_2S + FeCl_2$ [7]

Tomczuk, et al., (10) report the potential of reaction [14] to be 1.343, 1.338 and 1.333 V at 673, 723 and 773 K, respectively. Sharma and Seefurth (11) report the potentials for reaction [15]. Calculating the free energy changes of reactions [14] and [15] and combining them with the free energy changes of reaction [16] (12) and reaction [17] (Appendix), the free energy change, ΔG_R° , for reaction [7] was calculated to be 27760, 28284 and 28013 cal at 673, 723 and 773 K, respectively. Proceeding as before, the solubility of FeS in LiCl-KCl eutectic melts was calculated from the values of ΔG_R° for reaction [7]. The solubility was found to be 6.9 x 10⁻⁷, 1.6 x 10⁻⁶ and 3.2 x 10⁻⁶ at 673, 723 and 773 K. These values are in good agreement with the values calculated above and with those calculated by Saboungi, et.al., (8) (Fig. 4). They are also comparable with the solubilities of FeS₂ in the LiCl-KCl eutectic melt at the corresponding temperatures.

Proceeding as in the case of FeS_2 , the partial molar enthalpy of solution for FeS was calculated from the slope of Fig. 4. It was found to be 15.6 kcal/mole.

Calculation of the Solubility of FeS in Li_2S Saturated Electrolyte

Since the cell electrolyte is saturated with Li_2S during discharge, it is of significant importance to determine the solubility of FeS in the saturated melt. This can be determined from relation [13] where $a_{\text{Li}_2\text{S}}$ becomes unity upon saturation. Using the values of ΔG_R^{o} calculated above and the data in Table II, the mole fraction of FeCl₂ in Li₂S saturated LiCl-KCl eutectic melts were calculated to be 7 x 10⁻¹⁰, 2 x 10⁻⁹ and 4.5 x 10⁻⁹ at 673, 723 and 773 K respectively. These mole fractions which are equivalent to the solubilities of FeS at the respective temperatures are about three orders of magnitude smaller than those in the unsaturated melt.

SOLUBILITIES OF OTHER IRON SULFIDE CONTAINING COMPOUNDS

The determination of the solubilities of the compounds, Li₂S •FeS (13), $Li_2Fe_2S_4$ (13) and $Li_{2+x}Fe_{1-x}S_2$ (13) in the eutectic electrolyte is not possible, because at equilibrium, most of the Li2S is leached out of these compounds by the electrolyte leaving behind iron compounds in the solid state. In this situation, final iron sulfide concentration in the electrolyte will be that of the electrolyte saturated with Li2S. Under the assumption that there is an equilibrium between the compound and the electrolyte, then the concentrations of iron sulfide and Li2S in the electrolyte will correspond to their activities in the compound. These concentrations should be smaller than those in the electrolyte in equilibrium with the pure phases of unit activities. The compound Li3Fe2S4 coexists with FeS2, so the iron concentration and sulfur concentration or species in the electrolyte should be the same whether the compound is equilibrated with FeS_2 or $Li_3Fe_2S_4$. That means if there is no polysulfide in the electrolyte in equilibrium with FeS2 or Li2S, then there should not be any polysulfide in the electrolyte in equilibrium with Li3Fe2S4. The same reasoning can be extended to discount the presence of polysulfide in the electrolyte in equilibrium with $Li_{2+X}Fe_{1-x}S_2$, etc.

REFERENCES

- Chemical Engineering Division, "Progress Report for the Period, April-June, 1976," Argonne National Laboratory, Argonne, Illinois, Report No. ANL-76-81, July 1976.
- J. S. Dunning, T. G. Bradley, and E. J. Zeitner, <u>Proc. 11th</u> IECEC, p. 491 (1976).
- 3. L. R. McCoy and L. A. Heredy, Proc. 11th IECEC, p. 485 (1976).
- 4. R. A. Murie, Proc. 12th IECEC, p. 349 (1977).
- R. A. Sharma and R. N. Seefurth, <u>Extended Abstracts</u>, Vol. 82-2, Electrochemical Society Fall Meeting, Detroit, Michigan, Oct. 17-21 (1982).
- S. I. Berezina, A. G. Bergman, and E. L. Bakumskoya, <u>Russ. J.</u> Inorg. Chem. (English Translation), 1120 (1963).
- J. E. Hall, Argonne National Laboratory, Argonne, Illinois, Private communication.
- M. L. Saboungi, J. J. Marr, and M. Blander, J. Electrochem. Soc., 125, 1567 (1978).
- R. N. Seefurth and R. A. Sharma, J. Electrochem. Soc., <u>122</u>, 1049 (1975).
- Z. Tomczuk, M. F. Roche, and D. R. Vissers, J. Electrochem. Soc., <u>128</u>, 2255 (1981).
- R. A. Sharma and R. N. Seefurth, J. Electrochem. Soc., <u>123</u>, 1763 (1976).

- 12. JANAF Thermochemical Tables, Second Edition, NSRDA-NBS-37 (1971).
- 13. R. A. Sharma, J. Electrochem. Soc. 123, 448 (1976).
- 14. R. A. Sharma, to be published.
- M. Hansen, "Constitution of Binary Alloys," McGraw-Hill Book Co., New York, 1958, p. 704.
- H. A. Laitinen and C. H. Liu, J. of Am. Chem. Soc., <u>80</u>, 1015 (1958).
- 17. C. E. Wicks and F. E. Block, "Thermodynamic Properties of 65 Elements -- Their Oxides, Halides, Carbides and Nitrides," Bureau of Mines Bulletin 605, U.S. Govt. Printing Office, Washington, DC, 1963.
- 18. T. Rosenqvist, J. Iron and Steel Inst., 179, 37 (1954).
- F. D. Richardson and J. H. E. Jeffes, J. Iron and Steel Inst., <u>171</u>, 165 (1952).

TABLE I

Solubility of FeS₂ (Pyrite) in LiCl-KCl Eutectic Melts

Sample	FeS ₂ Weight (µg)	Eutectic Weight (g)	Mole Fraction FeS ₂	Dissolution Temperature (K)
1	26	11.15	1.09×10^{-6}	782
2	45	12.51	1.68×10^{-6}	808
3	14	10.57	6.17 x 10^{-7}	764
4	9	11.70	3.58×10^{-7}	721
5	800	40.0	9.32 x 10^{-6}	893
6	245	40.0	2.85 x 10^{-6}	824
7	62	30.0	9.63 x 10^{-7}	783
8	171	30.0	2.66 x 10^{-6}	828
9	73	30.0	1.13×10^{-6}	783
10	117	30.0	1.82×10^{-6}	800
11	40	30.0	6.21 x 10^{-7}	745
12	10	10.0	4.66×10^{-7}	727

TABLE II

Pertinent Thermodynamic Data Used for Calculating the Equilibrium Constant for Reaction [7] and the FeS Concentration in LiCl-KCl Melts

Temp.		XSat	ΔG^0 , cal per mole, for			
K	^a LiCl	<u> </u>	LiCl	FeS	Li ₂ S	FeC12*
673	0.865	0.000655	-84409	-24143	-99650	-65402
723	0.753	0.00132	-83425	-24317	-98950	-63985
773	0.668	0.00204	-82450			-62568
800	0.635	0.00309	-81923	-24600	-97850	-61803

 a_{LiCl} from Ref. (9). $X_{Li_2S}^{Sat}$ from Ref. (5). ΔG^0 for LiCl from Ref. (12). ΔG^0 for FeS was calculated using the data from Refs. (18) and (19). ΔG^0 for Li₂S from Ref. (14). ΔG^* for FeCl₂ from Appendix.



Fig. I Schematic representation of the silica capsules used for solubility measurements (chemical technique).



Fig. 2 Schematic diagram of the solubility apparatus (optical technique).



Fig. 3 Solubility of FeS₂ (pyrite) in LiCl-KCl eutectic electrolyte melts, where Δ - optical technique, \square - chemical technique and \Diamond - Hall (7).



Fig. 4 Solubility of FeS in LiCI-KCl eutectic electrolyte melts, where \Box - chemical technique, Δ - Saboungi, et.al.,(8), \diamond - Hall (7) and χ - present calculated values.

APPENDIX

Calculation of
$$\Delta G_{FeCl_2}^{*}$$
 for FeCl_2

The standard potential, E^0 , of a Fe/FeCl₂ electrode versus a Pt(II)-Pt(0) reference electrode in a LiCl-KCl eutectic melt at 723 K has been reported to be 1.171 V by Laitinen and Liu (16). This is for an infinitely dilute solution as the standard state such that $a_{FeCl_2}/X_{FeCl_2} = 1$ when $X_{FeCl_2} \rightarrow 0$. They have also reported E° for a Cl₂/Cl⁻ electrode versus the reference in the eutectic at 723 K to be 0.216 V (16). Therefore, the standard formation potential of FeCl₂ with infinite dilution as the standard state can be calculated by combining the following reactions,

$$(FeCl_2) + Pt \rightarrow (PtCl_2) + Fe \qquad E_1^0 = -1.171 V [A1]$$

n

$$C1_2 + Pt \rightarrow (PtC1_2)$$
 $E_2^0 = 0.216 V$ [A2]

and obtaining,

$$(FeCl_2) \rightarrow Fe + Cl_2$$
 $E_3^{\circ} = -1.387 V$ [A3]

Since

$$\Delta G_{FeC1_2}^* = -nFE_3^0, \qquad [A4]$$

where a is the number of equivalents and F is the Faraday constant, then $\Delta G^{\star}_{FeCl_2}$ is calculated to be -63,985 cal/mole at 723 K.

The value of $\Delta G_{FeCl_2}^{\star}$ at other temperatures (673 and 800 K) was calculated using the temperature coefficient of the standard free energy of formation of pure solid FeCl₂. This temperature coefficient was calcualted to be 28.335 cal/K from the data reported in the JANAF

tables (12). The values of $\Delta G_{FeCl_2}^*$ at 673 and 800 K were calculated to be -65402 and -61803 cal/mole, respectively.

A second check of the $\Delta G_{FeCl_2}^{\star}$ calculations can be made using the work of Saboungi, et al., (8). They report the potential, E, of a Fe/FeCl_2 electrode versus a AgCl/Ag electrode (8.4 x 10^{-3} mole fraction AgCl) in a LiCl-KCl eutectic melt to be 256.66, 231.58 and 209.09 mV at 673, 723 and 773 K, respectively. The potential of the Fe/FeCl_2 electrode versus a standard AgCl/Ag electrode (standard state such that $a_{Ag}/X_{Ag} = 1$ when $X_{Ag} \neq 0$) was calculated to be 0.5339, 0.5294 and 0.5275 V at the respective temperatures, and the corresponding standard free energies were found to be 024630, 024422 and 024335 cal/mole at the same temperatures. The standard formation potential of a Fe/FeCl_2 electrode versus a Cl⁻/Cl_2 electrode was then calculated by combining the reactions

$$2(AgC1) + Fe \rightarrow (FeC1_2) + 2Ag$$
[A5]

$$(PtCl_2) + 2Ag \rightarrow 2(AgCl) + Pt$$
[A6]

and

$$Pt + Cl_2 \rightarrow (PtCl_2)$$
 [A7]

to obtain

$$Fe + Cl_2 \rightarrow (FeCl_2)$$
 [A8]

Using the potentials 0.637 and 0.216 V for reactions [A6] and [A7] reported by Laitinen and Liu (16), and 0.5294 V for reaction [A5] (derived above), the potential of reaction [A8] was calculated to be 1.382 V at 723 K. Proceeding as above, $\Delta G_{FeC1_2}^{\star}$ was then calculated to be -63754 cal/mole at 723 K, once again in good agreement with the value derived above.

A second method was also used to check the values of $\Delta G_{FeCL_2}^{*}$ at other temperatures. The standard free energy of formation of AgCl, ΔG_{AgCl}^{*} , was calculated using the $\Delta G_{FeCL_2}^{*}$ value and the standard free energy change of reaction [A5] (-24422 cal/mole reported above). It was found to be -19666 cal/mole at 723 K. The values of ΔG_{AgCl}^{*} at 673 and 773 K were then calculated using the temperature coefficient of the standard free energy of formation of pure solid AgCl (17). The temperature coefficient was found to be 11 cal/K between 600 and 700 K, and 8 cal/K between 700 and 800 K (17). The ΔG_{AgCl}^{*} was calculated to be -20216 and -19266 cal/mole at 673 and 773 K, respectively. Using these values and the standard free energy changes for reaction [A5] (-24630 and -24335 cal/mole reported above), the values of $\Delta G_{FeCl_2}^{*}$ were calculated to be -65062 and -62867 cal/mole at 673 K and 773²K, respectively. These values are once again in very good agreement with the values of $\Delta G_{FeCl_2}^{*}$ calculated above.

MEASUREMENTS OF THE PARTIAL ELECTRONIC CONDUCTIVITY IN LITHIUM CHLORIDE - POTASSIUM CHLORIDE MOLTEN SALTS

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ABSTRACT

The partial electronic conductivity of the lithium chloride-potassium chloride eutectic molten salt electrolyte has been studied as a function of lithium activity, temperature and melt composition using the Wagner asymmetric d-c polarization technique (1). Measurements were made over the temperature range $383-465^{\circ}C$ and at lithium activities extending from 1.95×10^{-7} to unity.

The results confirmed the applicability of this technique to molten salt systems. The partial electronic conductivity was shown to be much greater than the partial hole conductivity over the range of lithium activities investigated, and was found to increase monotonically with temperature and lithium activity, but decreased on addition of excess LiCl to the eutectic composition.

Approximate values of self-discharge currents for cells utilizing an "Al/LiAl" negative electrode and a LiCl-KCl molten salt electrolyte have been calculated.

Introduction

It is well known that a number of practical difficulties are found in the use of lithium chloride - potassium chloride molten salts as electrolytes in the presence of high lithium activities. Lithium dissolves in the salt in the form of positive lithium ions and itinerant electrons. The presence of these electronic species leads to self-discharge, and the transport and deposition of lithium and various lithium compounds within high temperature battery systems.

These problems are reduced if the negative electrode contains lithium-rich alloys with a lower lithium activity, instead of pure lithium. Because of the lowered lithium activity the solubility of lithium in this family of salts is reduced, and some of these practical problems are alleviated. Very little is known, however, about the fundamental and quantitative aspects of this problem and about the influence of both temperature and salt composition on these phenomena. In this work, the Wagner asymmetrical d-c polarization technique (1) was used to determine the partial electronic conductivity, σ_e , of the lithium chloride - potassium chloride molten salt electrolyte as a function of lithium activity, temperature and melt composition.

The schematic asymmetrical cell arrangement required for the Wagner d-c polarization technique is shown in Fig. 1. In this cell configuration, one of the electrodes is inert and ionically-blocking: only electronic species can cross this electrode-electrolyte interface. The other electrode must be reversible to both ionic and electronic species, and should fix the value of the chemical potential of lithium and also the electron concentration in the adjacent electrolyte.

The theoretical basis for this experimental technique has been given by Wagner (1) and reviewed more recently by others (2,3). If one can assume that, under steady state conditions: (i) the driving force for ionic transport across the cell is everywhere zero and that no ionic current flows in the electrolyte; (ii) local equilibrium exists everywhere in the electrolyte; (iii) the total electronic current density across the cell is constant; and (iv) no chemical reactions occur in the electrolyte or at either interface, i.e. the electrode potentials must both be kept within the stability regime of the electrolyte (to prevent decompositon or electrolysis), then one obtains the equations:

$$I_{t} = I_{e} + I_{h}$$

$$= \frac{RT}{FG} \left\{ \sigma_{e}^{\circ} \left(1 - \exp\left[\frac{-F(E-E^{\circ})}{RT}\right] \right) + \sigma_{h}^{\circ} \left(\exp\left[\frac{F(E-E^{\circ})}{RT}\right] - 1 \right) \right\}$$
(1)

and

$$\sigma_{t}(L) = \sigma_{e}(L) + \sigma_{h}(L) = G \frac{\partial I}{\partial E(L)}$$
(2)

where:	${\bf I}_t$ = total steady state current due to both electrons and holes	
I _e ,	<pre>I_h = steady state current due to electrons and holes, respectively</pre>	
	σ_t = total electron and hole conductivity	
σ _e ,	o _h = electron and hole conductivities, respectively	
	E = potential difference across cell	
	G = cell constant	
	F = Faraday constant	

- R = gas constant
- T = absolute temperature
 - indicates that these values correspond to some standard reference state

and

(L) is used to denote the conductivities and local potential occurring at the ionically-blocking electrode/electrolyte interface.

Thus measurement of the steady state d-c current vs. potential difference across the cell enables the direct determination of the partial electronic and hole conductivities.

Data Analysis Techniques

Examination of equation (1) shows that the total current that flows between such electrodes under steady state conditions varies with interelectrode voltage as the sum of two contributions. The electronic contribution increases rapidly with positive values of $(E-E^{\circ})$ at first, but eventually approaches a plateau value. The hole contribution, on the other hand, increases exponentially with positive values of $(E-E^{\circ})$. These two contributions and their sum are shown schematically in Fig. 2.

A. In cases where the concentration of electronic defects, [e'], is much greater than that of holes, [h°], one may assume that $\sigma_e^{>>}$ σ_h° , and equation (1) may be written as

$$I_{t} = B \sigma_{e}^{\circ} [1-exp(-W)]$$
(3)

where the substitutions

$$B = \frac{RT}{FG}$$
(4)

and

$$W = \frac{F(E-E^{\circ})}{RT}$$
(5)

have been made.

(i) A plot of (I/B) vs. $[1-\exp(-W)]$ thus yields a straight line of slope σ°_{e} and intercept zero. Similarly, plotting of $\ln(I/B)$ vs. $\ln[1-\exp(-W)]$ gives a straight line of slope unity and intercept σ°_{e} .

(ii) When $\sigma_e(L) \gg \sigma_h(L)$, then equation (2) becomes

$$\sigma_{e}(L) = G \frac{\partial I}{\partial E(L)}$$
(6)

Thus a graphical differentiation of the current vs. potential plot gives σ_p for a range of activities.

B. Under different conditions it is possible to make appropriate approximations which both simplify the data analysis and provide means to calculate σ_{α} independently.

Furthermore, if we can assume that $\sigma_e^{\circ} \gg \sigma_h^{\circ}$, then we can consider equation (3) in the following limiting cases:

(i) W is small, i.e. $(E-E^{\circ}) \ll RT/F$

Then

$$\exp(-W) \rightarrow 1 - W \tag{7}$$

and

$$[1 - \exp(-W)] \rightarrow W \tag{8}$$

thus

and a plot of I vs. W should be linear, with a slope of $B\sigma^\circ_e$ and a zero intercept.

(ii) $(E-E^{\circ}) \gg RT/F$ and W is large.

Then

$$exp(-W) \ll 1$$
 (10)

and

$$\left[1 - \exp(-W)\right] \neq 1 \tag{11}$$

so that

$$I \approx B \sigma^{\circ}_{e}$$
 (12)

Thus the electronic current is seen to reach a saturation value as the imposed current increases.

(iii) (E-E°) is negative and, in magnitude, much greater than RT/F. W is negative and

$$[1 - \exp(-W)] \rightarrow \exp(-W)$$
(13)

so that

$$I \approx B \sigma^{\circ}_{\rho} \exp(-W)$$
 (14)

and

$$\ln(-I) = \ln(B \sigma_{e}^{\circ}) - W,$$
 (15)

i.e. a plot of ln(-I) vs. (-W) should be linear with a slope of unity and an intercept of $ln(B\sigma_{e}^{\circ})$.

In the general case, for the electrolyte MX, this condition (negative I, negative E) can only be met if the reversible reference electrode is at some potential which is positive of unit activity of M. Otherwise, a negative applied potential difference would cause M metal to be deposited at the ionicallyblocking electrode and an ionic current would flow in the electrolyte. In practice, in the LiCl-KCl molten salt electrolyte, this method of analysis is convenient when an "Al/LiAl" reference electrode is used.

Experimental Arrangement and Procedures

Polarization experiments were conducted over the temperature range $383-465^{\circ}C$ on samples of the eutectic composition (41 mol % KC1 and 59 mol % LiC1) obtained from Anderson Physics Laboratory and Lithium Corporation of America. They were used as supplied without further purification. In addition, an experiment was performed at 430°C on a composition containing more lithium chloride than is present in the eutectic composition (39 mol % KC1 and 61 mol % LiC1). In this case Baker reagent grade LiC1, which was dried in vacuo overnight at 400°C was added to the Lithcoa eutectic composition in a helium filled dry-box.

Prior to running the polarization experiments, cyclic voltammetry was performed on a series of candidate ionically-blocking electrode materials. This technique performs a potential sweep at a constant rate (typically 5 mVs⁻¹) and measures the current flowing in the cell as a function of potential relative to some fixed reference electrode (here $\text{Li}_{0.75}\text{Al}$ was used). As the presence of peaks on the I - V plot indicates that reactions are taking place which involve the transfer of electrons at the electrodes, an effective ionically-block-ing electrode should exhibit an absence of these peaks, indicating electrochemical stability, over a wide potential range.

The results of these experiments demonstrated the deleterious influence of any oxide layer existing on the surface of the electrode and also that graphite and platinum electrodes reacted at high lithium activities. Molybdenum, nickel and tantalum were found to be suitable materials. Removal of the oxide film on the surface of these metals resulted in their satisfactory and reproducible performance as ionically-blocking electrodes.

A schematic representation of the apparatus used is shown in Fig. 3. The fused salt was contained in a high density alumina crucible, into which the electrodes were inserted. The reference electrode consisted of a loop of .002 inches thick Mo (or Ni) foil, firmly wound around a pellet 1/4" in diameter and of nominal composition Li0.75Al. This two-phase (and hence constant lithium activity) reference material was prepared by chemically reacting the stoichiometric quantities of Li foil (Lithcoa) with Al shot (Alfa) in a molybdenum bucket above 600°C. The ionically-blocking electrode was a strip of .010 inch Mo (or Ni) foil, the surface of which was previously cleaned with fine emery paper and by etching in a dilute solution of $HNO_3 - HF$. Both electrodes were held in place by a teflon sleeve, which also held firm a chromel-alumel thermocouple protected by an The alumina crucible was placed inside a nickel alumina tube. crucible and lowered into the hot zone of a furnace sited in a helium filled Vacuum Atmospheres dry-box equipped with commercial de-oxygenation and de-nitrogenation systems. A PAR 173 potentiostat plus 179 digital coulometer were used to control the current in the external circuit. Cell potentials were monitored though the high impedance electrometer probe using a Keithley multimeter, and recorded on a strip chart recorder.

In order to prepare a clean surface on the ionically-blocking molybdenum electrode, a current was imposed which eventually plated out lithium metal on the electrode surface; the electrode was then removed from the melt and scraped clean.

A constant current was passed through the cell and the potential was allowed to reach a steady value (usually requiring about 15 minutes, although sometimes drift occurred for several hours). The current was set so that the Mo electrode was always negative with respect to the $\rm Li_{0.75}Al$ reference electrode, as the data obtained in this region were more reproducible and less subject to experimental noise. At the end of each experiments, the cell constant, G, was determined by a-c impedance measurements. An interesting observation was made under open circuit, i.e. zero current, conditions: a

potential of between 0.7 and 1 V vs. $\rm Li_{0.75}Al$ was observed at the Mo electrode. This potential decreased slowly with time and varied as the distance between the electrodes was changed. It is believed that this phenomenon arose due to the loss of potassium vapor from the system.

Results

Methods A(i), A(ii) and B(iii) were used to analyze the experimental data, and representative plots are shown in Figs. 4, 5, and 6. Reasonable agreement was observed (within an order of magnitude) between the different modes of analysis. Fig. 7 shows a plot of log σ_e vs. log a_{Li} for a series of temperatures. As expected, σ_e was found to increase monotonically with increasing temperature. The slopes of the lines in Fig. 7 are close to unity, thus verifying the theoretical relationship (1):

$$\sigma_{e} = \sigma_{e}^{\circ} \cdot \frac{a_{\text{Li}}^{\circ}}{a_{\text{Li}}^{\circ}}$$
(16)

The dotted line in Fig. 7 denotes the data obtained for the melt containing 61 mole % LiC1. The partial electronic conductivity of this melt composition at 430°C is less than that of the eutectic composition at 415°C. This indicates that increasing the LiC1 content of the electrolyte significantly decreases the partial electronic conductivity.

Discussion

The magnitudes of σ_e found here are significantly lower than those originally given by Heus and Egan (4) in the first work on this subject. However, these values were later retracted (5) and these authors quoted a new value of $\sigma_e = 5.6 \times 10^{-3}$ at $a_{\rm Li} =$ 5.7×10^{-3} and T = 450° C, but did not include experimental details. This value corresponds reasonably well with the results reported here.

Our values range from a maximum of approximately 0.18 ohm⁻¹cm⁻¹ at 465°C and unit activity Li to about $\sigma_e = 8 \times 10^{-5}$ ohm⁻¹cm⁻¹ at 383°C and at $a_{Li} = 5.6 \times 10^{-2}$ (corresponding to the activity of lithium in Li_{0.75}Al at this temperature). An additional experiment in which Sb/Li₂Sb (E vs. Li = 0.912 V) was used as a reference electrode gave a value of $\sigma_e = 1.8 \times 10^{-9}$ ohm⁻¹cm⁻¹ at $a_{Li} = 1.95 \times 10^{-7}$ and T = 412°C.

In their earlier work (4), Heus and Egan paid great attention to the possibility of problems associated with convection and took special precautions to eliminate any such effects. Although little attempt was made in these experiments to prevent convection currents, the alumina crucible was surrounded by nickel, and kept in the hot zone of the furnace to minimize temperature gradients within the melt. Any significant convection currents would cause the measured value of σ_e to be larger than the actual value. The overall reproducibility of the results implies that neglecting convection effects does not lead to significant error.

If the value of σ_e at a particular temperature and activity of lithium is known, then the self-discharge current under these conditions can be calculated. This is an important parameter relating to the shelf-life and faradiac efficiency of a practical energy storage device. For such a device, based on lithium as the active electrochemical species, the activity of lithium at the positive electrode is very small compared to that at the negative electrode, and the self-discharge current can be approximated by the equation (5):

$$i_e = \frac{-RT}{EC} \sigma_e$$
 (at the negative electrode) (17)

For a cell with an interelectrode distance of 1 cm and an "A1/LiA1" negative electrode, then, using the data illustrated in Fig. 7, the self-discharge current due to electronic conductivity in the LiC1-KC1 eutectic molten salt is 34 μ A cm⁻² at 405°C, rising to 200 μ A cm⁻² at 465°C. The magnitude of i_e is seen to be strongly temperature dependent, and it is clearly advantageous to operate any cell using this molten salt electrolyte at the lowest possible temperature compatible with the kinetic requirements of the electrochemical system.

Wagner (6) has shown that the emf of any galvanic cell is given by the expression:

$$E = \frac{1}{zF} \int_{\mu_{i}}^{\mu_{i}} t_{ion} d\mu_{i}$$
(18)

where μ_i is the chemical potential of neutral species i, z is the charge number of the i ions, and t_{ion} is the ionic transference number:

$$t_{ion} = \frac{\sigma_{ion}}{\sigma_{ion} + \sigma_{e}}$$
(19)

i.e., that fraction of the cell current which is transported by ionic species. In the case of a galvanic cell in which lithium is the electro-active species, one can write:

$$E = \frac{RT}{F} \ln \frac{a_{Li}^{II}}{a_{Li}^{I}} - \frac{RT}{F} \ln \frac{t_{ion}^{I}}{t_{ion}^{II}}$$
(20)

where superscripts I and II refer to the positive and negative electrodes, respectively.

The first term in the above equation relates the emf of a galvanic cell to the difference in the activity of the neutral mobile species at the two electrodes. However, equation (20) demonstrates that one can use equilibrium voltage measurements to determine accurate activities only when the second term is vanishingly small. In the case of the cell

for example, using a value for the ionic conductivity of 1.36 $ohm^{-1}cm^{-1}$ (7) and the electronic conductivity data determined here, then at 405°C, the second term in equation (20) is equal to 3.7 mV, i.e. the Li activity in the "Al/LiAl" two-phase region measured using the LiCl-KCl eutectic molten salt electrolyte and a lithium reference electrode would be approximately 1% higher than the true value. The use of an "Al/LiAl" reference electrode for the determination of (lower) lithium activities in other alloys, would lead to no detectable error at temperatures below 460°C.

The LiCl-KCl fused salt has been used as an electrolyte by many workers and it has been established that, at high lithium activities, potassium evaporates from the melt (8,9). The mechanism for this reaction is dependent on the transport of electrons from the negative electrode to the potassium ions in the electrolyte, and thus the reaction rate will increase with increasing electronic conductivity of the molten salt. This phenomenon can also explain why, at zero current, i.e. on open circuit, a steady state zero voltage is not observed. When an external potential measurement is made, one actually measures the difference in the electrochemical potential of the electrons in the electrodes. In the Wagner asymmetric polarization cell, the electrochemical potential of the electrons in the electrolyte must everywhere reach a constant value identical to that in the reversible reference electrode in order for no potential difference to exist across the cell. However, in an unsealed system at high lithium activities, the continuous process of potassium evaporation prevents the attainment of equilibrium everywhere in the electrolyte. This gives rise to a lower electrochemical potential of electrons at the ionically-blocking electrode than exists at the reference electrode. Thus a finite positive potential difference is measured between the electrodes on open circuit.

The evaporation of potassium also provides a driving force for the continued dissolution of lithium ions and electrons from the reference electrode into the electrolyte, a process which eventually leads to the exhaustion of the electrode. In addition, the ionic current which flows due to potassium loss causes a systematic deviation from the ideal steady state current vs. voltage behavior predicted by the Wagner model. Wherever the local activity of Li is high, the rate of potassium evaporation, according to the equation

$$Li (eut) + K^{+} (eut) = Li^{+} (eut) + K (g)$$
 (21)

will be correspondingly larger. However, this ionic contribution to the total current will be less dependent on potential than the electronic contribution (which has an exponential dependence - see Fig. 2). Therefore more reliable data are obtained at high current densities. Use of a sealed system should also greatly reduce this problem, and also enable experiments to determine the hole conductivity, σ_h , at very low lithium activities, and correspondingly higher partial pressures of chlorine gas.

It is interesting to note that, at sufficiently low activities of Li, and when clean molybdenum is used as an ionically-blocking electrode, an equilibrium open circuit voltage which is very close to zero is observed. This supports the hypothesis that potassium vapor loss from the melt causes a non-zero open circuit voltage.

The experimental arrangement used in these experiments could be further improved if the high density alumina crucible were replaced with magnesia or yttria. It is known (10) that Al_2O_3 is thermodynamically unstable with respect to unit activity lithium. At the high activities of lithium and potassium present in these experiments, a blackening of the surface of the alumina components was observed. On addition of an oxidizing agent, such as LiNO₃, this surface layer was bleached to its original color. It is conceivable that Al_2O_3 could provide a sink for lithium ions and electrons; however, due to the insulating nature of the product, diffusion into the bulk cannot occur at an appreciable rate.

Finally, it has been demonstrated that the addition of excess LiCl to the eutectic composition causes a decrease in the electronic contribution to the total conductivity. This can readily be explained in terms of the relative solubilities of the alkali metals in their respective halides, which increases with atomic number. This increase in solubility gives rise to a higher concentration of electrons, which, in turn, leads to a higher σ_e value. Thus decreasing the mole fraction of potassium chloride by addition of lithium chloride to the eutectic composition results in a lowering of the total alkali metal content, and hence of the electronic defect concentration in the molten salt.

Conclusions

Our experimental results demonstrate the general applicability of the Wagner asymmetric polarization technique to molten salt electrolyte systems. Anomalous effects due to convection were not encountered, and better data were obtained under galvanostatic conditions at higher current densities.

The data obtained were analyzed in three different ways: good overall agreement between the various modes of analysis was observed.

A monotonic increase of σ_e with increasing temperature was found, and the theoretical expression relating σ_e to a li (equation (16)) was confirmed.

The partial electronic conductivity of the LiCl-KCl molten salt electrolyte was found to decrease upon addition of excess lithium chloride. It is thus advantageous to work in a molten halide system in which the concentrations of heavier alkali metals are kept to a minimum, although this necessitates the use of higher temperatures.

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REFERENCES

- (1) C. Wagner, Proc. CITCE 7, 361 (1957).
- (2) F.A. Kröger, in "<u>The Chemistry of Imperfect Crystals</u>", North-Holland, New York, Vol. 2 (1974).
- (3) J. Mizusaki and K Fueki, Rev. Chim. Min. 17, 364 (1980).
- (4) R.J. Heus and J.J. Egan, J. Phys. Chem. 77, 1989 (1973).
- (5) R.J. Heus and J.J. Egan, in "Proceedings of the International Symposium on Molten Salts", Washington DC, Electrochem. Soc., Pennington, NJ (1976), p. 523.
- (6) C. Wagner, Z. phys. Chem. (B) 21, 25 (1933).
- (7) G.J. Janz, C.B. Allen, N.P. Bansal, R.M. Murphy and R.P.T. Tomkins, "Physical Properties Data Compilations Relevant to Energy Storage. II. Molten Salts", <u>NSRDS-NBS 61</u>, Part II, (1979), p. 228.
- (8) M.S. Foster, S.E. Wood and C.E. Crouthamel, Inorg. Chem. <u>3</u>, 1428 (1964).
- (9) R.N. Seefurth and R.A. Sharma, J. Electrochem. Soc. <u>122</u>, 1049 (1975).
- (10) I. Barin, O. Knacke and O. Kubaschewski, "<u>Thermochemical</u> <u>Properties of Inorganic Substances</u>", Springer-Verlag, Berlin (1977).



Fig. 1. Schematic representation of d-c asymmetric polarization cell.



Currents due to electrons and holes in the polarisation experiment





Currents due to electrons and holes in the polarization experi-An "Al/LiAl" reference ment. electrode (whose potential relative to pure lithium is indicated by the vertical dotted line) was used so that the ionically-blocking electrode could be made to negative with respect the reference electrode without depositing Li at the ionicallyblocking electrode/electrolyte interface.



Fig. 3. Experimental apparatus.







Fig. 6. Plot of log(-I) vs. E for LiCl - KCl eutectic molten salt at 738 K.



Fig. 7. Plot of log σ_e vs. log a_{Li} for LiCl - KCl molten salt at different temperatures.

CELL DESIGN PRINCIPLES FOR THE MEASUREMENT OF KINETICS OF FAST ELECTRODE REACTIONS

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ABSTRACT

The rates of electrode processes in high temperature molten salts are often very fast and special precautions are needed in their measurement. The measurement methods are invariably some sort of relaxation technique where a fast perturbation of the current (or the potential) is applied and the resulting potential (or current) relaxation is recorded. The measuring cells used in these experiments have to be carefully designed so that the distortion of the fast electrical signals and the introduction of spurious signals are avoided. The two requirements of a good cell design can be simply stated as (i) the assurance of uniform current distribution on the working electrode (ii) small impedance. The latter requirement includes surface and small stray capacitances and small inductances, which is necessary to avoid detrimental phase shifts and inductive spikes in the signal. In addition, one requires a small ohmic resistance of the solution between the reference and the working electrodes. Three cell designs, aimed at fulfilling these requirements, are described.

The rates of electrode processes in high temperature molten salts are often very fast and special precautions are needed in their measurement. The measurement technique is invariably some sort of relaxation technique; that is, a fast perturbation of the the current (or potential) is applied and the resulting potential (or current) relaxation is recorded. The measuring systems used in these experiments have to be carefully designed so that distortion of the fast electrical signals and introduction of spurious signals are avoided. The measuring system includes the cell, the electronic instrumentation, and the connecting leads. In this communication, a review will be presented of some cells which were designed for the measurement. primary current distribution (but, see below). Uniform primary current distribution can be obtained with relatively simple geometric arrangements, *e.g.*, parallel plate electrodes or concentric cylinders. Edge effects can be minimized by a large ratio of electrode dimension to interelectrode separation, or can be completely eliminated by employing nonconducting walls that contain the solution between the electrodes. On the other hand, the shape of the auxiliary electrode will have little effect on the current distribution if it is far enough removed from the working electrode.

The secondary current distribution is generally more uniform than the primary, but this smoothing effect is of little help in the case of fast electrode reactions since the charge transfer resistance will be generally very small. It should also be realized that, for the case of the relaxation techniques, the tertiary current distribution will be a function of time: while it may be nonuniform under steady state conditions, the nonuniformity may be negligible within the time frame of the measurements. For example, a circular disk inlaid electrode will have a contribution from spherical diffusion at the edges, in addition to the dominating effect of linear diffusion; this edge effect depends on the radius of the electrode and the time frame of the measurement. Specifically, if the electrode radius is not smaller than 0.01 cm and the diffusion coefficients are 1×10^{-5} cm² sec⁻¹. the error caused by the spherical diffusion component is less than 2% for a galvanostatic transient lasting for up to 1 msec (10-12). In this respect, another effect should also be considered. In calculating the tertiary current distribution, one usually assumes that the true area of the electrode is equal to the geometric area, that is, that the roughness factor of the working electrode surface is unity. This is a fair assumption, as long as the penetration of the diffusion layer is considerably larger than the scale of the surface roughness. For a transient of 10 μ sec, the penetration of the diffusion layer, approximated as \sqrt{Dt} , will be about 1×10^{-5} cm, which suggests that a very careful surface preparation is required. The primary and secondary current distributions will, of course, also be distorted by a rough surface; for a general review of the effect of surface roughness see reference (13).

The impedance requirements include (i) small stray capacitance of all components, (ii) small, or compensating, self- and mutual-inductance of all components, and (iii) small ohmic resistance of the solution between the reference and working electrodes. These are needed to avoid (i) the slowing of the signal and detrimental phase shifts, (ii) inductive voltage spikes and phase shifts, and (iii) errors in the potential measurements or control. The overall ohmic resistance of the cell is usually of lesser importance, unless an unusually large voltage capability is required of the instrumentation. While the uniformity of current distribution is a general requirement, the emphasis on the impedance requirement depends on the experimental technique used, as discussed below. of fast electrode reactions. Instrumentation is usually commercially available and only some mention will be made of the requirements for leads. However, it should be emphasized that for best results the whole measuring system has to be considered as a design unit, because one part will often influence the requirements of the other. Detailed descriptions of general cell design principles for measuring the kinetics of electrochemical reactions are available in books (1,2) and so is a review on molten salt electrochemical techniques (3). Therefore, many important, but general design requirements for the cell (such as separation of electrode compartments, protection from the atmosphere, ease of operation, price, materials of construction, etc.) will not be discussed here. Emphasis will be placed on the special requirements due to the high rate of reactions.

DESIGN REQUIREMENTS

The requirements can be broadly classified in two groups: uniform current distribution on the working electrode surface and low impedance for the cell components. These requirements will be discussed below. Not all requirements are equally important in every instance, depending on the characteristics of the electrode reaction and on the measuring technique used. Furthermore, the requirements are sometimes contradictory; therefore, the best cell design for a given system is often a compromise. For example, the close placement of the classical Luggin capillary to the working electrode will assure a small resistance between the working and reference electrodes, but will considerably distort the current distribution on the face of the working electrode (4).

Uniform current distribution is a tacit assumption in the theories of all relaxation techniques. It is always assumed that the measured electrode potential is representative of the whole surface of the electrode and does not vary with the location of the measurement. The results will be distorted if this condition is not fulfilled during the experiments, introducing a spurious frequency dependence of the electrode impedance. Kasper (5–7) has given the current distributions for many useful geometries, and recent reviews are available on the subject (8,9). For a measuring cell under consideration, the main concern is to achieve a uniform primary current distribution. The primary current distribution is calculated from the cell geometry and solution resistance, with the effect of surface processes on the working electrode surface being neglected. It is, of course, assumed that the preparation of the electrode will produce a uniform surface; consequently, the secondary current distribution (which includes the effect of the charge transfer resistance) and the tertiary current distribution (which also includes the effect of the mass transport impedance) will be identical to, or more uniform than, the

GALVANOSTATIC AND COULOSTATIC TECHNIQUES

The cell inductance is critical for relaxation methods using a fast-rising current pulse as the perturbing signal. In these cases, the inductive emf generated even in a straight piece of wire can be much larger than the overpotential to be measured (14), especially for fast reactions when one is forced to use large currents and very fast rising pulses (15–17). Thus, an inductive voltage spike will distort the potential relaxation at short times, creating a certain "dead-time" when meaningful potential measurements are not possible. On the other hand, it is desirable to minimize this dead-time and to carry out the measurements at short times when the diffusional effects are not yet overwhelming. One could deliberately slow down the rise of the current pulse to diminish this effect, and use a computerized curvefitting data evaluation which corrects for the rise time (15–17). But, this will be of little help for fast reactions and/or low concentrations when the diffusional effects are significant at short times. Therefore, the requirement for small inductance cell will remain.

The leads connecting the cell to the instrumentation are very important with respect to the inductance. Widely separated, long leads will create a large inductive loop. Very short, parallel-running or twisted leads will minimize this problem, but the best solution is to use coaxial cables because then much of the mutual inductances of the conductors cancel. Coaxial cables will introduce considerable capacitance, but this can be minimized by using driven shields. The effect of leads is especially important for high-temperature work, because the instrumentation and the cell are often separated by long distances. To minimize this effect, Blomgren and coworkers (18) suggested a coaxial cable-like cell design, shown schematically in Fig. 1. The high-temperature coaxial connector is built around a glass capillary, the conductors being a thin wire in the capillary hole and a metal tube surrounding the capillary. With this design, coaxial conductors are used from the instrumentation and into the furnace leading very close to the electrodes. Therefore, most of the inductance of the leads is eliminated (14,18) and the overall inductance is practically that of the loop A-B-C. This loop can be made very small by using microelectrodes sealed in glass. One of the electrodes is a working micro-electrode, while the other is a large-area ("unpolarizable") auxiliary electrode, which also serves as a reference electrode. Several varieties of this cell design have been used for molten-salt electrode kinetic studies, and dead-times as short as 40 nsec were achieved (14,18,19). A third (reference) electrode can also be used with this design, but it will increase the dead-time. This design can easily be used in a sealed cell arrangement. Uniformity of the current distribution and minimization of solution resistance were not emphasized with this design. The stray capacitances were kept small by using coaxial cables as short as possible.

Uniform current distribution and very small solution resistances can be achieved with the cell design shown on Fig. 2 (20). This is a two-electrode, thin-layer cell consisting of two identical working electrodes and no reference electrode. One of the working electrodes is polarized anodically and the other cathodically, while the sum of the two overpotentials and the IR-drop in the solution between the two electrodes is measured. This arrangement is favorable in the linear current density-overpotential range, because it considerably extends the applicability of the linearization approximation due to cancellation of errors (21.22). This arrangement also restricts the use of the cell to the linear range; this restriction is not a serious disadvantage for very fast reactions because the current limitations of the instrumentation and the early onset of diffusion will often restrict the experiments anyhow to a few millivolts. The electrodes are press fit into boron nitride holders and polished. By polishing the electrodes together in a common holder, any misalignment of the working faces from perfectly perpendicular will be corrected in assembly and the electrodes will be parallel. The gap thickness is controlled by a metal spacer between the electrode holders. This spacer and the alignment pins are fabricated from the same material as the working electrodes to avoid contamination of the melt. Gap thickness as small as 1.25×10^{-2} cm has been achieved, assuring small interelectrode resistance. The cell also has a large ratio between the electrode radius and the interelectrode distance, minimizing edge effects of the current distribution. The overall cell arrangement is like a micrometer: the top electrode is vertically movable, facilitating the introduction of electrolyte melt into the interelectrode gap. Because of the need to move the upper electrode, this design is not readily usable in a sealed-cell arrangement. It was designed to be used in a furnace well which is attached to a glovebox, with the melt exposed to the box atmosphere (20). Coaxial connectors of the type shown in Fig. 1 were also used with this cell. A disadvantage of this design is that the inductive loop, consisting of the electrodes and their leads connected to the high temperature coaxial cable, is larger than that achievable with microelectrodes sealed in glass; thus, the dead-time increases to at least 200 nsec, and typically to around 400 nsec. This cell design has been used to study the kinetics of metal deposition/dissolution reactions in molten alkali halides (23).

POTENTIOSTATIC TECHNIQUE

For potentiostatic measurements a three-electrode cell is needed. In this case, the cell impedance is important for two reasons: (i) the cell is in the control loop of a feedback amplifier system, thus, phase lags introduced by the cell may cause instability of the potential control, and (ii) the solution resistance between the reference and working electrodes will distort the potential control. General discussions on the interaction between the cell and the potentiostat, and discussions of stability criteria of the measuring system are available elsewhere (24-27) and

only the cell design will be discussed here. The usual Luggin capillary cannot be placed very close to the working electrode (to decrease the solution resistance) without causing nonuniformity in the current distribution (4). Furthermore, exact positioning of the capillary is usually difficult in molten salt cells. A Luggin capillary has further disadvantages when used in potentiostatic investigations of very fast electrode reactions: its high frequency characteristics are rather poor. The capillary usually has a high ohmic resistance, since it is made thin enough to allow close placement to the working electrode, and there is also a large capacitive coupling between the solutions inside and outside the capillary. These characteristics are highly undesirable for fast potentiostatic measurements (27).

Several modifications of the Luggin capillary have been suggested. Piontelli et al. (28,29) proposed the use of a flat-ended glass tube pressed against the electrode surface, with the electrical connection to the main solution achieved by a hole near the electrode surface, as shown in Fig. 3. This design can result in small solution resistance between the reference and the working electrodes, but there still can be some distortion of the current distribution (especially if there is solution leakage under the flat glass surface), and the high frequency characteristics are unimproved. Cahan et al. (30) used a side-hole electrode, which is an inside-out version of the Piontelli electrode, as shown in Fig. 4. A flat working electrode is pressed against an insulator cell body made of a heavy walled tube. The large hole (perpendicular to the working electrode surface) leads to the auxiliary electrode compartment, and a small capillary hole is drilled into the body, close to the surface of the working electrode, which leads to the reference electrode compartment. This design results in a small solution resistance between the working and reference electrodes because the capillary hole can be drilled very close the the working electrode surface. The high frequency characteristics are also improved: the stray capacitances are small because of the thick walls separating the reference compartment from the other compartments. The internal resistance of the reference electrode connection can also be made smaller than that of a conventional Luggin because the hole can be widened a short distance from the electrode surface. This design also provides a uniform current distribution on the face of the working electrode, independent of the shape of the auxiliary electrode, as long as there is a straight, long channel leading to the auxiliary electrode compartment, with a length-to-diameter ratio of at least six (5,31); however, leakage between the cell body and the working electrode surfaces must be avoided.

The side-hole electrode concept was further extended by Cahan *et al.* (27) to the designs shown schematically in Fig. 5 and 6. In the first design (Fig. 5), the "side hole" was extended 360° around to form a conical slot with the two body pieces held apart by suitable spacers. This design considerably reduces the internal resistance of the reference electrode connection, further improving the

high frequency characteristics. It can be used advantageously when a limited area of a large electrode is to be studied; however, the seal between the cell body and the large-area metal surface may be a problem. The design shown in Fig. 6 eliminates this problem. The cell body consists of two parts made of insulating materials. The working electrode is press fit into the bottom piece, so as to provide a flush surface with the cell body. The top portion has a cylindrical hole corresponding exactly in position and dimension to the working electrode; this hole leads to the auxiliary electrode compartment. A thin gap between the pieces, controlled by a suitable spacer, leads to the reference electrode compartment, which surrounds (360°) the working electrode. The latter extension of the side-hole concept was used in aqueous electrode kinetic studies (32,33) and a detailed design is shown in Fig. 7. Although this specific embodiment of the design is not suitable for molten salt studies, the concept of the extended side-hole reference electrode could be utilized as a basis for a molten-salt cell design. It results in a cell having uniform current distribution, very small resistance between the working and reference electrodes, and good high frequency characteristics, but with a somewhat larger inductive loop than the design shown in Fig. 1.

SUMMARY

The two main requirements for a measuring cell, to be used in the determination of kinetics of fast electrochemical reactions, were identified as the assurance of (i) uniform current distribution on the working electrode surface and (ii) small impedance for the cell components. These requirements were discussed and their implementations demonstrated with three specific cells used previously for fast electrode kinetic studies. The first cell was designed to provide extremely small cell inductance, which mininizes disturbing inductive spikes associated with fast current pulses. This was achieved by using a coaxial cable-like construction. The second cell aimed at very small solution ohmic drop and uniform current distribution. These were achieved by a two-working electrode, thin-layer design. The third cell was designed for potentiostatic work, aimed at small solution resistance between the working and reference electrodes and good high frequency characteristics. These were achieved by eliminating the classical Luggin capillary and using a slot connection to the reference compartment.

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REFERENCES

- 1. D. T. Sawyer and J. L. Roberts, "Experimental Electrochemistry for Chemists," Wiley-Interscience, New York (1974).
- 2. D. D. Macdonald, "Transient Techniques in Electrochemistry," Plenum Press, New York (1977).
- A. D. Graves, G. J. Hills, and D. Inman, in "Advances in Electrochemistry and Electrochemical Engineering," P. Delahay and C. W. Tobias, Editors, Vol. 4, p. 117, Wiley-Interscience, New York (1966).
- 4. S. Barnartt, J. Electrochem. Soc., 99, 549 (1952).
- 5. C. Kasper, Trans. Electrochem. Soc., 77, 353 (1940).
- 6. C. Kasper, Trans. Electrochem. Soc., 77, 365 (1940).
- 7. C. Kasper, Trans. Electrochem. Soc., 78, 131 (1940).
- J. Newman, "Electrochemical Systems," Prentice-Hall, Englewood Cliffs, N.J. (1973).
- 9. G. A. Prentice and C. W. Tobias, J. Electrochem. Soc., 129, 72 (1982).
- 10. K. B. Oldham, J. Electroanal. Chem. Interfacial Electrochem., 122, 1 (1981).
- K. Aoki and J. Osteryoung, J. Electroanal. Chem. Interfacial Electrochem., 122, 19 (1981).
- S. Sarangapani and R. de Levie, J. Electroanal. Chem. Interfacial Electrochem., 102 165 (1979).
- R. deLevie, in "Advances in Electrochemistry and Electrochemical Engineering," P. Delahay and C. W. Tobias, Editors, Vol. 6, p. 329, Wiley-Interscience, New York (1967).
- 14. W. E. Triaca, C. Solomons, and J. O'M. Bockris, *Electrochim. Acta*, 13, 1949 (1968).
- 15. Z. Nagy, Electrochim. Acta, 26, 671 (1981).
- 16. Z. Nagy, J. Electrochem. Soc., 128, 786 (1981).
- 17. Z. Nagy and J. T. Arden J. Electrochem. Soc., 130, 815 (1983).
- 18. E. Blomgren, D. Inman, and J. O'M. Bockris, Rev. Sci. Instr., 32, 11 (1961).
- A. D. Graves and D. Inman, in "Electromotive Force Measurements in Hightemperature Systems," C. B. Alcock, Editor, p. 183, American Elsevier, New York (1968).
- 20. Z. Nagy and J. L. Settle, Abstract 158, p. 408, The Electrochemical Society Extended Abstracts, Los Angeles, California, October 14-19, 1979.
- D. J. Kooijman, M. Sluyters-Rehbach, and J. H. Sluyters, *Electrochim. Acta*, 11, 1197 (1966).

- Z. Nagy, R. H. Land, G. K. Leaf, and M. Minkoff, Abstract 321, p. 516, The Electrochemical Society Extended Abstracts, Detroit, Michigan, October 17-21, 1982.
- 23. J. L. Settle and Z. Nagy, to be published.
- 24. G. L. Booman and W. B. Holbrook, Anal. Chem., 37, 795 (1965).
- 25. R. R. Schroeder and I. Shain, Chem. Instr., 1, 233 (1969).
- 26. Z. Nagy, PhD Thesis, University of Pennsylvania, Philadelphia (1972).
- 27. B. D. Cahan, Z. Nagy, and M. A. Genshaw, J. Electrochem. Soc., 119, 64 (1972).
- 28. R. Piontelli and G. Bianchi, Gazz. Chim. Ital., 80, 581 (1950).
- 29. R. Piontelli, G. Bianchi, and R. Aletti, Z. Elektrochem., 56, 86 (1952).
- B. D. Cahan, J. B. Ockerman, R. F. Amlie, and P. Ruetschi, J. Electrochem. Soc., 107, 725 (1960).
- 31. S. Barnartt, J. Electrochem. Soc., 106, 722 (1959).
- 32. J. O'M. Bockris, Z. Nagy, and A. Damjanovic, J. Electrochem. Soc., 119, 285 (1972).
- 33. B. D. Cahan and C. T. Chen, J. Electrochem. Soc., 129, 474 (1982).



Fig. 1. Cell design with small inductive loop.



Fig. 3. Piontelli electrode.



Fig. 4. Side-hole electrode.



Fig. 2. Cell design with small solution resistance. A-to coaxial electrical leads, B-steel support rod, C-metal electrode contacts, D-boron nitride housing, E-metal electrodes, F-boron nitride electrode holders, G-Grafoil gasket, H-metal alignment pins, I-metal spacer, J-steel adapter, K-steel universal joint, L-steel rod connecting to micrometer head.



Fig. 5. Extension of the sidehole electrode concept, conical slot reference.



Fig. 6. Extension of the sidehole electrode concept, horizontal slot reference.



Fig. 7. Exploded cross sectional view of a cell built with horizontal slot reference. 1-Teflon bottom piece, 2-KEL-F top piece, 3-working electrode, 4-nylon bushing, 5-adjusting screw, 6-stainless steel contacts, 7-stainless steel spacer, 8-stainless steel locating pins, 9-reference electrode groove, 10-reference electrode connection, 11-auxiliary electrode compartment, 12-connections for auxiliary electrode, solution inlet, etc., 13hole for illuminating fiber light guide, 14-observation window, 15part of stainless steel frame, 16-Viton O-rings.

THE ELECTROCRYSTALLISATION OF CHROMIUM FROM MOLTEN L1C1-KC1 AT 450°C

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The ion Cr^{2+} is stable in molten LiCl-KCl at 450°C and chromium metal can be deposited from it by a two-electron charge transfer process.

The electrocrystallisation of chromium has been studied both by electrochemical, e.g. chronoamperometry, and structural, e.g. scanning electron microscopy techniques, in the latter case both at the initial nucleation stage and after the growth of the electrodeposit. The results indicated that the initial stage of deposition involved progressive three-dimensional nucleation with the growth of the nuclei controlled by diffusion of ions in the melt. The nucleation rate is well described according to classical nucleation theory. The electro-nucleation rate constant is proportional to η^{-2} (η is overpotential) and increases with the concentration of Cr^{2+} in the melt.

On this basis, high quality deposits have been obtained by the use of a double-pulse potentiostatic procedure.

Introduction

The electroanalytical chemistry and the electrochemistry of chromium and its ions in molten chlorides have been the subject of several previous investigations (1-5). In the previous work in this laboratory (5), chronopotentiometric and steady-state voltammetric techniques were employed to study the electrochemical processes

 $Cr(III) + e \rightarrow Cr(II)$ and $Cr(II) + 2e \rightarrow Cr(0)$

separately, using the LiCl-KCl eutectic as the solvent at 500° C. The adsorption of ions on the electrode surface appeared to play a role in the overall electrode processes.

The general aim of the present study has been to relate the forms, structures, constitution and properties of chromium deposits prepared under well defined electrochemical conditions to the controlled parameters, and use this to optimise the properties of electroplates. In particular, attention has been focused on the mechanism of formation of the deposit in the initial stages of deposition, under potentiostatic conditions, and its effect on the morphologies of subsequent chromium electroplates.

The present study was carried out in the LiCl-KCl eutectic melt at 450° C. The chromium, present in the electrolyte as chromium (II) ions in concentrations ranging from 0.04 to 0.9 M.1⁻¹, was introduced by anodic dissolution of aqueous electrolytic chromium or by addition of anhydrous CrCl₂. The system was studied by various electrochemical methods, e.g. sweep voltammetry and chronoamperometry, complemented with scanning electron microscopic examinations of the electrode surfaces at different stages of the deposition. The basic aspects of electrocrystallisation were studied on tungsten and platinum electrodes and the preparation of thicker deposits was attempted on stainless and low-carbon alloy steels.

Experimental

Full details of the equipment and electrodes employed and the experimental procedure are given elsewhere(6) or are referred to in the results and discussion section below.

Results and Discussion

<u>Electroanalytical aspects</u>. Figure 1 shows a typical cyclic voltammogram obtained at a sweep rate of 100mV sec⁻¹ for the reduction of chromous (Cr^{2+}) ions on platinum. The small pair of waves on the right hand side corresponds to Cr^{3+}/Cr^{2+} , while the large pair on the left corresponds to Cr^{2+}/Cr^{0} ; as expected, the anodic (stripping) wave is much sharper than the cathodic (deposition) wave. The linear sweep voltammogram obtained at much lower sweep rates (1 mV sec⁻¹) is more revealing (Fig. 2) The shift of the cathodic wave corresponding to the process $Cr^{2+} + 2e \Rightarrow Cr^{0}$ in the cathodic direction and the consequent hysteresis after potential reversal, indicate that nucleation phenomena are involved. Similar sweep voltammograms were obtained for every substrate investigated in this study.

<u>Electrocrystallisation phenomena</u>. Chronoamperometry (I - t transients at constant potential) was employed to study the nucleation and growth phenomena per se. I - t transients, typical of those obtained on all substrates, are shown in Figure 3. The transients depend on the applied overpotential $(n_7 > n_6 > n_7$ etc.). The current first rises to very high values due to double layer charging and initial cluster formation without the clusters reaching the critical size for growth. The current then decays during the induction time and then increases again due to the formation and growth of isolated stable nuclei which increase the area for deposition. As the diffusion zones for each nucleus eventually meet each other and start to form a uniform diffusional plane, the current reaches a maximum and then decays according to the usual $t^{-\frac{1}{2}}$ dependence.

The I-t relations for the rising parts of these curves were examined in more detail. Log I - log t plots are shown in Figure 4. The middle portions of these plots are parallel straight lines, the slopes of which are 3/2. This indicates that nucleation and growth phenomena are occurring simultaneously.

The expression for the current to a single nucleus growing under mass transfer control and assuming a hemispherical diffusive flux, is given by (7)

$$I_{1} = Z F \Pi M^{\frac{1}{2}} (2 C D)^{\frac{3}{2}} t^{\frac{1}{2}} / \rho^{\frac{1}{2}}$$
(1)

If nucleation and growth occur simultaneously, assuming that there is no overlap of diffusion zones, the resulting current is given by

$$I = \int_{0}^{t} I_{1}(u) (d N/dt)_{t=t-u} du$$
(2)

where u is the age of a nucleus and N is the number of nuclei at any time during the process of nucleation.

Assuming a steady state nucleation rate (J_0) , we can write:

$$d N / d t = J$$
(3)

and, substituting u for t in the expression (1), the resulting current obtained by integrating (2) is:

I = 2 J₀ Z F I
$$M^{\frac{1}{2}}$$
 (2 C D) $^{\frac{5}{2}}$ $t^{\frac{5}{2}}$ / $3\rho^{\frac{1}{2}}$ (4)

This expression is valid for high overpotentials (C_g \rightarrow o); however if the overpotential is low, the surface concentration C_g is not negligible but given by the Nernst relation:

$$\mathbf{C} = \mathbf{C} \exp \mathbf{Z} \mathbf{F} \eta / \mathbf{R} \mathbf{T}$$

In these circumstances, (4) becomes

I = 2
$$J_0 Z F I M^{\frac{1}{2}} (2 C D)^{\frac{3}{2}} \left[1 - \exp \frac{Z F \eta}{RT} \right]^{\frac{3}{2}} t^{\frac{3}{2}} \sqrt{3\rho^{\frac{1}{2}}}$$
 (5)

According to the classical theory of nucleation, the expression for the steady-state rate of three-dimensional electrochemical nucleation is

$$J_{0} = K_{1} \exp(-K_{2}/\eta^{2})$$
 (6)

(8)

where η is the overpotential and K_1 , K_2 are constants.

Introducing this expression in equation (5) we obtain:

$$\mathbf{r} = \mathbf{K}_{3} \begin{bmatrix} 1 - \exp \frac{Z + \eta}{RT} \end{bmatrix}^{\frac{3}{2}} \exp (-\mathbf{K}_{2}/\eta^{2}) t^{\frac{3}{2}}$$
(7)
$$\mathbf{K}_{3} = 2 \mathbf{K}_{1} Z + \Pi M^{\frac{1}{2}} (2 C D)^{\frac{3}{2}} / 3\rho^{\frac{1}{2}}$$
(8)

where

Rearranging and taking logs

$$\ln \left[I/t^{3/2} (1 - \exp Z F \eta/RT)^{3/2} \right] = \ln K_3 - K_2/\eta^2$$
(9)

The description of the nucleation of chromium according to the classical theory is shown here for the specific case of the deposition on to a tungsten substrate.

Figure 5 shows the expected linear dependency of I versus $t^{\frac{3}{2}}$ (equation 7) and Figure 6 confirms the applicability of equation 9 to the present case.

It was expected that the nuclei densities on the substrate would increase with increasing applied overpotential and this was confirmed by the scanning electronmicrographs (Fig. 7) of the substrate obtained after 100s of potentiostatic deposition at four different applied overpotentials.

<u>Macro-electrodeposition</u>. Our electrocrystallisation studies have demonstrated that the nucleation of chromium occurs via a progressive nucleation mechanism and that an increase in overpotential increases the surface density of chromium nuclei . However, complete coverage of the electrode surface cannot be achieved (irrespective of the magnitude of the overpotential) due to the inherent formation of nucleation exclusion zones (9).

Clearly, the growth of the highest number of nuclei possible is ultimately desirable for producing complete coverage of the substrate and the formation of a dense macrodeposit.

A schematic representation of the effect of the initial nucleation mechanism and the growth of nuclei at different levels of overpotential upon the 'nature' of the final macro-deposit is shown in Figure 8. Continued growth of isolated nuclei at high overpotential results in a dendritic macrodeposit, having a relatively high porosity. However, if growth is continued at a low overpotential, then smooth dense and coherent macrodeposits are generally produced.

Figure 9 shows the surface structure (topography) of a typical chromium deposit obtained as a result of applying an initial high overpotential pulse to force 'instantaneous nucleation', followed by a low growth overpotential. Deposits were grown at low overpotentials for several hours. The scanning electron micrograph, Figure 9, shows clearly that a fine, dense structure may be obtained with no indication of dendritic or nodular growth.

The purity of the deposit may be qualitatively evaluated using a microprobe analysis technique (a JOEL T-200 SEM was used). Figure 10 shows the microprobe results corresponding to the area of chromium deposit shown in Figure 9. Two X-ray peaks are shown, corresponding

to those for α -Cr and β -Cr; no impurity elements were detected using this technique. Thus it may be concluded that the deposits obtained were of high-purity chromium.

Transverse sections of the deposits are shown in Figures 11 and 12. The low magnification micrograph (Figure 11) of a 36 μ m thick coating, further shows that smooth, coherent coatings may be obtained, and that good adhesion to the substrate occurs over the entire surface. Both the low and the high magnification micrographs, and particularly the latter, show a distinct absence of any inclusions, voids or cracks within the deposit, even at high stress areas such as the edge of the electrode (figure 12).

In addition to a microscopic structural investigation, microhardness profiles of the transverse sections have been undertaken, using a Reichert MeF2 microscope with a microhardness attachment. The micrographs of the transverse sections and hardness profiles are shown for two samples in Figures 13 and 14. Typical hardness values of the chromium deposit ranged from a minimum value of 240 VHN to a maximum value of 383 VHN. This provides further evidence of the purity of the chromium deposit.

The predominant factor in determining the use of a chromiumdeposited, low carbon alloy steel, is the inherent strength of the chromium/ low carbon alloy steels interfacial bond. An intimate bond between the two metals may be obtained by an annealing process to produce a diffusion layer.

Figure 15 shows the transverse sections of the Cr/low carbon alloy steels interface before annealing. Table 1 shows the concentration of chromium as a function of the distance from the interface to the low carbon alloy steels substrate as obtained by a spot analysis technique using a JEQL JSM-35 SEM instrument. The results show that, even during an electrodeposition process at 470°C, a small but distinct chromium concentration gradient exists within the substrate, extending approximately 25 μ m from the interface.

Conclusions

In this study, we have clearly shown that it is possible to optimise the properties of electroplates by the use of double-pulse potentiostatic procedures. These procedures are based on studies of the fundamental electrocrystallisation phenomena underlying the macro-deposition process.

Nomenclature

C bulk solute concentration, mol. $\rm cm^{-3}$

C _s	solute concentration at the electrode surface, mol. ${\rm cm}^{-3}$
D	diffusion coefficient of electrodepositing species, ${ m cm}^2~{ m sec}^{-1}$
F	Faraday constant C mol ⁻¹
Jo	steady-state nucleation rate, nuclei \sec^{-1} cm $^{-2}$
M	molecular weight of depositing material
N	number of nuclei at any time
t	time, sec
R	molar gas content, J. $mol^{-1} K^{-1}$
Т	absolute temperature, K
z	valence number
η	overvoltage, V
ρ	density of deposited metal, gr. ${ m cm}^{-3}$
u	age of nucleus
I, I ₁	current, A
к ₁ , н	^K 2, K ₃ constants

References.

1.	H.A. Laitinen and W.S. Ferguson, Anal. Chem., 30, 1266 (1958)
2.	I.I. Naryshkin, V.P. Yurinskii and P.T. Stangrit, Elektrokhimiya
	5, 1043 (1969).
3.	K. Cho and T. Kuroda, Denki Kagaku, <u>39</u> , 206 (1971)
4.	S.C. Levy and W. Reinhart, J. Electrochem. Soc., 122, 200 (1975).
5.	D. Inman, J.C.L. Legey and R. Spencer, J. Electroanal. Chem.
	Interfac. Electrochem., <u>61</u> , 289 (1975).
6.	T. Vargas, PhD Thesis, London, 1983.
7.	G.J. Hills, D.J. Schiffrin and J. Thompson, Electrochim. Acta
	19, 657 (1974)
8.	I. Markov, Thin. Solia, Films, 35, 11 (1976).
9.	I. Markov, A. Boynov and S. Toschev, Electrochim. Acta, 18,
	377 (1973).

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- Fig. 1. Cyclic voltanmogram for the reduction of chromous ions on platinum. 39 mM CrCl₂, 100mV/ sec, 0.39 cm²
- Fig. 2. Cyclic voltammogram for the reduction of chromous ions on platinum.Conditions as Fig. 1 but sweep rate: lmV/sec.



Fig. 3. Typical current-time profiles Fig. 4. Plots of log I vs log t for chronoamperometric experiments for the potentiostatic current at low concentrations (~40mM) transients obtained on tungster



'ig. 4. Plots of log I vs log t for the potentiostatic current transients obtained on tungsten electrodes at the overpotentials indicated (in mV). Cr^{2+} concn: 42mM, area electrode: 0.045 cm².



Fig. 5. I vs t plot for the nucleation and growth of Cr nuclei on tungsten electrode at the overpotentials indicated (in mV). Cr^{+2} concn.: 42mM, area electrode: 0.045 cm⁻²



Fig. 6. Test of equation (9) for the nucleation and growth of Cr deposited on tungsten electrode (data from figure 5).



Fig. 7. Scanning electron micrograph series corresponding to 100 sec of deposition under potentiostatic conditions, showing the increase of the nucleus saturation number with higher overpotentials. Working electrode: stainless steel EN58B, Cr²⁺ concn.: 39mM, a:45mV, b:54mV, c:64mV, d:74mV.



Fig. 8. Scheme showing possible alternative paths followed during the formation of an electrodeposit under potentiostatic conditions.



Fig. 9 Scanning electron micrograph of the surface of a chromium deposit, mag x180. Nucleation: three, -500, 5s pulses. Growth: -20mV, 100 min.



Fig. 10. Corresponding X-ray analysis of Figure 9.



Fig. 11. Low magnification (x104) transverse section of chromium plate, Cr4 El2. Anodic cleaning: +300, 20s; +200, 20s. Nucleation: three -500, 5s pulses. Growth: -20mV, 75 min.



Fig. 12. High magnification (x1040) of the above figure 11.



Fig. 13. Transverse section of a chromium plate and hardness profile (Mag. x 180), Cr4 E24. Anodic cleaning +500 5s; +300, 25s; +200, 25s. Nucleation: three -500, 5s pulses. Growth: -30mV 103 min.



Fig. 14 Transverse section (Mag. x180) of a chromium plate and hardness profile Cr4 El2. Anodic cleaning: +300, 20s. +200, 20s. Nucleation: three -500, 5s pulses, at 1 minute intervals. Growth: -20 mV, 75 min.



Fig. 15. Transverse section of chromium plate Cr-4 E24 before heat treatment. Anodic cleaning +500, 5 sec.; +300, 25 sec. +200, 25 sec. Nucleation: three -500mV, 5 sec. pulses. Growth: -30 mV.

Table 1. Spot analysis (JSM-35)

Sample	Position	Cr%
Cr-4 E-24 before	2.5μm from interface between chromium coating and substrate (in substrate)	2.269
heat	8µm (as above)	1.54
treatment	12μm (as above)	1.362
	17µm (as above	1.073
	24μ m (as above)	0.918
	36µm (as above)	0.651
	in substrate	0,809
	н н	0.806

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THE ELECTROCHEMICAL DEPOSITION OF REFRACTORY METALS FROM CHLORIDE MELTS

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ABSTRACT

The deposition of refractory metals such as chromium and molybdenum is discussed from the standpoint of the solution chemistry and the electrocrystallization phenomena involved in forming coherent metal.

INTRODUCTION

The precious metals, the refractory metals, and other transition elements which are required for use in the advanced technologies of aerospace and the nuclear industry have been plated from molten salt solutions. Molten alkali metal fluorides were proposed as general media from which the majority of the refractory metals might be obtained in coherent form (1). However, there are limitations to these electrolytes, not the least of which concerns the high temperatures required (1,2). On the other hand, control of the morphology of the depositing metal is achieved albeit without a detailed understanding of the associated chemistry and electrochemistry involved. The interrelationship between the electrolyte solution chemistry and the electrode processes is an important feature of these systems, and in the studies reported here, these two aspects are being examined to enable the development of low temperature baths from which the more noble refractory metals can be plated.

EXPERIMENTAL

The LiCl-KCl and the ZnCl₂ based melts were prepared by vacuum drying, hydrogen chloride gas treatment, preelectrolysis with a tungsten cathode and graphite anode, followed by filtration (3). The products were stored and handled in a dry box. The cell design, experimental details, and electrochemical instrumentation were similar to those described earlier (4). The data were recorded on a BT microprocessor/ recorder and data analysis was carried out on this instrument and with an Apple computer.

RESULTS AND DISCUSSION

The importance of the acid-base chemistry in relation to refractory metal plating can be deduced from the recent results relating to molybdenum (5,6) in alkali metal chloride-aluminum chloride mixtures in which the pCl is in the range 3 to 5, and measurements (7) in the LiCl-KCl where the pCl is less than 1. The formation of metal in melts of high pCl is inhibited by the more favorable reactions to form metal bonded compounds of oxidation state greater than zero. Even at higher temperatures, the low pCl melts may induce this reduction pathway (8). Thus, one of the major problems associated with the development of low temperature, nonfluoride electrolytes, is to understand and then control the solution chemistry in such a way that the reduction pathway to metal avoids the intervention of these intermediates.

Zinc chloride is a weaker acid than aluminum chloride and when mixed with alkali metal chlorides reduces the melting points to less than 300°C. Highly pure, water free melts have an electrochemical window of 1.5V at around 300°C, on appropriate substrates and thus can be employed with the more noble metals. Figure 1 shows that in the acidic composition region of such mixtures the pCl is still too high for successful metal deposition. Compositions excluding zinc chloride at 550°C show good indications that metal is produced, still in coherent form, in contrast to the suggestions of earlier workers (9).

Chromium metal can be plated from the basic LiCl-KCl melt (7,10) in the temperature range 400-500°C in contrast to the 800-1000°C required in the fluoride melts (11). Figure 2 shows the redox behavior of chromium (II) ions, soluble in the LiCl-KCl melt. The oxidation reaction:

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$$Cr^{2+} \neq Cr^{3+} + e \tag{1}$$

provides a convenient means of determining the diffusion coefficient for the Cr^{2+} species, which in turn enables the chromium content of the bath to be monitored. Cyclic voltammetry, chronoamperometry, chronopotentiometry and normal pulse voltammetry have been employed to determine the diffusion coefficient, but the measurements indicate that the chromium (II) concentration in the solution is a little unstable, especially at the lower concentrations. This is in agreement with the variation in the open circuit potentials of a chromium electrode with time. The cells were leak tight as demonstrated by the absence of oxidation of a piece of chromium suspended just above the melt. The stability of Cr_2O_3 and the presence of oxidic materials in the cell components may contribute to this behavior. Table 1 compares the results from this work with those of earlier studies (12,13). The diffusion coefficient is typical for that of a transition metal in this medium (13). The availability of this value is helpful in developing an understanding of the phenomena associated with the metal deposition process (14,15).

The evolution of a diffusion coefficient from the reduction of chromium (II) species studied by current pulse, linear sweep, and normal pulse voltammetry gives diffusion coefficients in poor agreement with those from the anodic measurements, under the same conditions (which excludes the concentration variation as a factor). Closer examination of the resultant transients at higher resolution show features at shorter times which can be attributed to the influence of the electrocrystallization process. Examples of these features on different substrates can be seen in Figures 3-5. Furthermore, the $E_D/2$ and the $E_T/4$ for the cathodic voltammograms and chronopotentiograms were shifted in the cathodic sense some 50 to 100 mV from the Cr/Cr²⁺ potential measured simultaneously. Crossover of the return cathodic current after the switching potential was observed at any scan rate, especially if the switching occurred prior to the peak potential.

The previous analytical procedure for voltammograms and chronopotentiograms has involved the assumption that the metal is depositing at an activity of unity and it might be expected, at the early stages of metal formation on foreign substrates, that this condition is not satisfied (16). Conversely, this means that the early stages of the galvanostatic transients or the prepeak region of the voltammograms contain information about the deposition process. The deposition of metal (excluding alloy formation) is a heterogeneous process which disturbs the surface state so that techniques, in which the experimental variables such as voltage and current density can become time dependent simultaneously (7), are not so simple to resolve as the case of potential step measurements where only the time dependent current density reflects the details of the crystallization and growth processes.

Figures 6 and 7 show the potentiostatic transients obtained at gold and nickel electrodes resulting from the application of a single cathodic potential step of decreasing magnitude. The usual monotonous decay of current with time is only observed at the longer times. The initial charging current density decay is followed by an increase in current density reflecting the nucleation and subsequent growth of nuclei, ultimately passing through a maximum and decaying monotonously under diffusion control. The data from the region where the current density is increasing enables some insight to be gained into the way in which nuclei are formed and grow. Qualitatively, the rate of change of this growth current density is rather small, particularly on the nickel electrode. By selecting the digital data recorded in the region, analyses were made by plotting log(i) versus log(t) to obtain the time dependence of the current density. The results for different overpotentials (vs. Cr/Cr²⁺) show that the current depends on the half power of time which suggests that for Cr deposition on gold the nucleation process is instantaneous and the rate controlling step is probably the diffusion controlled growth at the hemispherical nuclei formed. Such a current is given (8) by:

$$I(t) = 3.14 z F N_0 M^{1/2} (2 D C_0)^{3/2} \rho^{-1/2} (1 - exp z F n/RT) t^{1/2}$$
(2)

and the potential dependence of the intercept is seen in Figure 8. The number of nuclei were calculated and the relevant results are shown in Table 2. The post-maxima currents were analyzed in the same manner using the digital data and showed a $t^{-\frac{1}{2}}$ dependence, with an intercept of the log-log plot independent of the potential step. The diffusion coefficient calculated from the values of the intercept shows agreement with the diffusion coefficient obtained from the anodic oxidation of Cr^{2+} . The spherical diffusion to the nuclei, initially formed, translates into a linear regime at the longer times, consistent with the presence of the current maximum.

The correspondence between the properties of the potential maxima and current maxima from the galvanostatic and potentiostatic pulse measurements on gold is seen by comparison of data in Tables 2 and 3. Using a simple model to relate the charge under the galvanostatic maxima with the charge required to create the nuclei, the radius of the individual nuclei can be calculated (Table 3) for the extremes of nuclei density, measured in the potentiostatic experiment. The results suggest nuclei with radii in the region of 0.2 to 0.3 micrometer. These values are consistent with those reported for aqueous solution (19) and for first row transition metals (14) in the LiCl-KCl at 450° C. Control of the nuclear density and size is clearly possible and may lead to the preparation of coherent deposits of refractory metals with selected grain sizes.

The interpretation of the data obtained so far has ignored the influence of specific substrate metal-deposit metal interactions, as certainly can occur in the case of chromium deposition on gold, platinum, and tungsten. Figure 9 shows cyclic voltammograms that contain oxidation peaks which suggest alloy formation in the case of gold and nickel. Such interactions must be accounted for in any detailed consideration of the deposition process. Finally, the coverage (after the passage of a small amount of charge at low current density) of the less noble electrodes seems such that the conditions referred to earlier concerning the simple theoretical treatments are met, since potential-time analyses of the galvanostatic transients, Figure 10, show excellent fits to the equation:

$$E(t) = E^{\circ} + RT/ZFlnC + RT/ZFln (1-(t/\tau)^{1/2})$$
(3)

showing that on copper and nickel at least the base metal is uniformly covered.

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REFERENCES

- 1. G. W. Mellors and S. Senderoff, Plating (1964).
- 2. D. Inman and S. H. White, J. Appl. Electrochem., 8, 357 (1978).
- 3. S. H. White, in <u>Ionic Liquids</u>, D. Inman and G. Lovering, eds (London: Plenum, 1981).

- S. H. White and U. M. Twardoch, in <u>Proceedings 3rd Intern. Symposium</u> on <u>Molten Salts</u> (New Jersey: The Electrochemical Society, Inc., 1981), p. 284.
- 5. S. H. White, D. Inman, R. Huq, T. Mukherjee and G. F. Warren, I.S.E. Zurich, Extended Abstract No. 254 (1976).
- J. Phillips and R. A. Osteryoung, J. Electrochem. Soc., <u>124</u>, 1465 (1977).
- 7. S. H. White and U. M. Twardoch, unpublished work, 1982.
- G. F. Warren, S. H. White and D. Inman, in <u>Proceedings 1st Intern</u>. <u>Symposium on Molten Salts</u> (New Jersey: The Electrochemical Society, Inc., 1976), p. 218.
- 9. S. Senderoff and A. Brenner, J. Electrochem. Soc., 101, 16 (1954).
- 10. T. Vargas and D. Inman, Euchem Conf., Abstract B2 (1982).
- 11. I. Ahmed, W. A. Spiak and G. J. Janz, J. Appl. Electrochem., <u>11</u>, 291 (1981).
- D. Inman, J. C. L. Legey and R. Spencer, Electroanal. Chem., <u>61</u>, 289 (1975).
- D. Inman, Dj. Jovanovic and S. H. White, Electroanal. Chem., <u>43</u>, 37 (1973).
- 14. F. Lantelme, J-P. Hanselin and M. Chemla, Electroanal. Chem., <u>97</u>, 49 (1979).
- 15. S. H. White, C. Bernard and D. Inman, unpublished work, 1978.
- 16. T. Berzins and P. Delahay, J. Amer. Chem. Soc., 75, 555 (1953).
- F. Lantelme, J-P. Hanselin and M. Chemla, Electrochim. Acta, <u>22</u>, 1113 (1977).
- G. J. Hills, D. J. Schiffrin and J. Thompson, Electrochim. Acta, <u>19</u>, 657 (1974).
- G. A. Gunawardena, G. J. Hills and I. Montenegro, Discussions of the Faraday Soc., 12 (1977).

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TABLE 1

DATA FOR DIFFUSION OF Cr(II) IONS IN LiCl-KCl EUTECTIC MIXTURE

Method	Electrode <u>Materials</u>	Temperature °C	10 ⁵ D _{Cr(II)} 	References
Calculated	_	450	1.78	13
Reduction CP	Cr Coated	500	1.53	12
Oxidation CP	Tungsten	500	2.53	12
Oxidation CA	Gold	425	1.00	This Work
Oxidation CV	Vitreous Carbon	425	1.50	This Work
Oxidation NPV	Gold	425	1.25	This Work

CP = Chronopotentiometry; CA = Single Potential Step;

CV = Cyclic Voltammetry; NPV = Normal Pulse Voltammetry

TABLE 2

POTENTIOSTATIC TRANSIENT ANALYSIS VIA LOG LOG PLOTS OF THE PRE-MAXIMA AND POST-MAXIMUM REGIONS AT 425°C

Gold Electrode	=	0.4 cm^2
Concentration of Cr ²⁺	=	8.75 x 10-6
Potential of Cr/Cr ⁺ Electrode	=	-0.751 vs. Ag/Ag+

	P	re-Peak	Data		Post-Peak Data			
 Pot. Step <u>mV</u>	J(max) <u>mA/cm²</u>	t(max) 	Slope/ Intercept	No. of Nuclei 10 ⁶ cm ⁻²	Time Range sec	Slope/ Intercept	10 ⁶ D <u>cm² sec</u>	
-0.139	16.875	98	0.329 -2.114	1.52	0.25-0.50	-0.518 -2.961	8.25	
-0.129	13.5	140	0.424 -2.18	1.30	0.30-0.50	-0.525 -2.969	7.96	
-0.124	11.5	175	0.528 -2.211	1.20	0.35-0.50	-0.513 -2.971	7.88	
-0.119	9.5	250	0.603 -2.311	0.95	0.30-0.50	-0.427 -2.954	8.52	
-0.109	5.625	500	0.538 -2.793	0.31	-	-	-	

TABLE 3

CALCULATION OF THE NUCLEAR RADIUS FROM GALVANOSTATIC CHARGING CURVES

Gold Substrate Electrode Area = 0.4 cm² Double Layer Capacitance = $30 \ \mu\text{F/cm}^2$ Atomic Wt Metal = 51.996 Density of Metal = 7.1 gm/cm³ at 20°C

					No. of Nuclei = (see Table 2)	310000	1510000
Eff. Over- Potential	i <u>mA</u>	t(max) msec	it(max) μCb 10 ⁶	Nuclear Charge Corr. <u>10⁶ µCb</u>	Nr ³ cm ³	Radius 10 ⁵ cm	Radius <u>10⁵ cm</u>
-0.154 -0.146 -0.139 -0.126	10 8 6 4	59 69 102 170	588 552 612 680	577.1 541.2 601.3 669.5	1.046 0.981 1.090 1.214	3.23 3.16 3.28 3.40	1.91 1.87 1.94 2.00
-0.109	2	420	840	829.7	1.504	3.65	2.15


Fig. 1. Cyclic voltammograms for the reduction of K3MoCl₆ on gold electrodes, scan rate 50 mV/sec in molten: a) ZnCl₂-KCl (67-33 mol%), temp. 350°C, C = 2.61 x 10^{-2} mol/kg, A = 0.57 cm²; b) LiCl-KCl (59-41 mol%), temp. 550°C, C = 5.06 x 10^{-4} mol/kg, A = 0.4 cm². Potential vs. the Ag/Ag⁺ (0.16 mol/kg) reference electrode.



Fig. 2. Cyclic voltammogram (scan rate 100 mV/sec) for reduction-oxidation of Cr(II) (C = $4.99 \times 10^{-3} \text{ mol/kg}$) in molten LiCl-KCl (51.49 mol%) at a gold electrode (0.4 cm² at 425°C. Potential vs. the Ag/Ag⁺ (0.16 mol/kg) reference electrode.



Fig. 3. A series of cyclic voltammograms acquired on three different substrates for the reduction of Cr(II) ions at three different concentrations at 500 mV/sec: a) gold flag, CP -751 vs. Ag/Ag(I) ref. at 425° C, C2; b) copper flag(I), CP -738 vs. Ag/Ag(I) ref. at 425° C, C3; c) copper flag(2), CP -723 vs. Ag/Ag(I) ref. at flag(2), CF -723 vs. Ag/Ag(I) ref. at Ag/Ag(I) ref. at 450° C, C4; d) nickel flag, CP -723 vs. Ag/Ag(I) ref. at 450° C, C4;



Fig. 4. Current reveral chronopotentiograms acquired for the reduction of Cr^{2+} at two different concentrations on a gold electrode: a) conc $Cr^{2+} \approx 9 \times 10^{-3}M$; b) conc $Cr^{2+} \approx 6 \times 10^{-3}M$. Applied current density 5 mA cm⁻²; t = 425°C.



Fig. 5. The influence of applied current density on the initial stages of the potential-time transients observed at a gold electrode during the reduction of Cr^{2+} ions. a) $i_{\rm C} = 25 \text{ mA cm}^{-2}$; b) $i_{\rm C} = 15 \text{ mA cm}^{-2}$; c) $i_{\rm C} = 5 \text{ mA cm}^{-2}$.



Fig. 6. Cathodic chronoamperograms for gold electrode deposition of Cr at increasingly negative potential steps: 1 = -139, 2 = -129, 3 = -124, 4 = -119, 5 = -109 mV vs. Cr/Cr(II). RP is 0 mV vs. Ag/AgCl (0.163m) in LiCl-KCl at 450°C.



Fig. 7. Potentiostatic transients for the reduction of Cr(II) ions on a Ni electrode at 450 °C. Potential steps: 1 = -67 mV; 2 = -77 mV; 3 = -87 mV; 4 = -107 mV; 5 = -127 mV vs. Cr/Cr(II) potential.



Fig. 8. Analysis of potentiostatic growth transients for Cr deposition on gold substrates.



Fig. 9. Cyclic voltammograms acquired on different electrode substrates showing the interaction of deposited Cr with the base metal. (a) Gold substrate at 425° C; (b)-(c) Nickel substrate at 450° C. Scan rate = 0.5 V sec⁻¹.



Fig. 10. Potential time analysis of galvanostatic transient for Cr deposited on chromium coated copper. The slope gives n = 1.999 and from the intercept $E_{T}/4$ is calculated to be -0.811 mV vs. reference. $E_{T}/4 = -0.763V$ based upon E° and concentration.

THE ELECTROCHEMISTRY OF TUNGSTEN (V), (IV) AND (III) IN MOLTEN LiC1-KC1 EUTECTIC

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ABSTRACT

The electrochemistry of tungsten (V), (IV) and (III) in molten LiC1-KC1 eutectic was studied using cyclic voltammetry.

Tungsten (V) exhibited a reversible one electron reduction, $W(V) + e \longrightarrow W(IV)$, an irreversible reduction, $W(IV) + 2e \longrightarrow W(II)$, and a broad reduction wave near the cathodic limit, $W(II) + 2e \longrightarrow W(0)$. A disproportionation, $W(II) \longrightarrow W(IV) + W(0)$ occurred, as shown by the deposition of powdery tungsten at any potential beyond that leading to the formation of W(II).

Tungsten (IV), added as K WCl, exhibited oxidation to W(V), reduction to W(II), and other W(II) related peaks. However on continued electrolysis, a continuous tungsten "mirror" was deposited on all cell surfaces. This was apparently due to the effect of the high W(IV) concentration on the disproportionation of W(II).

Tungsten (III), added as $K_{3}W_{2}Cl_{3}$, exhibited a complex electrochemical behavior. Electrolysis at a platinum flag resulted in the formation of resistive film which prevented the deposition of tungsten metal. Electrolysis at a tungsten flag yielded a dendritic tungsten deposit.

INTRODUCTION

The purpose of this work was to elucidate the electrochemistry of tungsten (III), (IV), and (V) in molten LiCl-KCl eutectic. Information of this type is central in the development of new tungsten electroplating and electrowinning techniques and furthers the understanding of the chemistry of tungsten halides as well. While this has been attempted before, first by Balko (1), and then by Johnston (2), the results have been neither complete nor conclusive. Balko's work relied mostly on chronopotentiometry as the electroanalytical tool, a technique whose results are often difficult to interpret. He also often suggested that further study was needed. Several of his products were either unidentifiable or admittedly produced under less than rigorous conditions. The later study, by Johnston, was of a narrower scope. It included only studies of tungsten (III). To further complicate matters, some of his results were in direct contradiction of earlier, carefully performed work (3). These difficulties indicated that further study was necessary to clarify the electrochemistry of this important chemical system.

EXPERIMENTAL

The LiCl-KCl eutectic was prepared by pre-drying the components at 150° in a vacuum oven. After mixing, the eutectic was ball-milled and redried. The mixture was then purified and made anhydrous by sparging with dry HCl as the temperature was raised to 425° over four hours. The melt was then sparged with nitrogen to remove the HCl. Magnesium turnings were added to remove the last trace of HCl, and the melt was then filtered and solidified. Remelting under vacuum completed the process and routinely gave melts having low residual currents. Background voltammograms were recorded to ascertain melt purity and the melt was disacarded if these were unsatisfactory.

The electrochemical cell used in this study is shown schematically in Figure 1. A head (not shown) was clamped on the top of the cell to provide a hermetic seal as well as the necessary pass-throughs for gasses, electrical leads and sample addition. Measurements were made at 450°C.

The tungsten species studied were prepared as follows: Tungsten (V) was added as WBr, as obtained from Alpha Products. Tungsten (IV) was added as K_3 WC1, prepared by the method of Kennedy and Peacock (4). Tungsten (III) was added as K_3 W_2C1, prepared by the method of Saillant et. al. (5)

RESULTS AND DISCUSSION

<u>Tungsten</u> (<u>V</u>)

Tungsten (V) was added to the melt as WBr_s . The bromide was chosen over the chloride due to its higher boiling point (333° vs. 276°). It was added as pellets pressed in a die in a glove box filled with dry nitrogen. It was felt that the slight amount of bromide present would not affect the electrochemistry due to the five hundredfold excess of chloride in the melt. The pellets dissolved rapidly to form a blue green solution which later became yellow green, particularly at higher concentration. Measurements on the W(V) system were complicated by its high volatility at 450° C. Brown vapor was often noted above the melt. While the solubility of W(V) in the melt was sufficient to allow electrochemical measurements, the conclusion was reached that the concentration of W(V) in the melt for tungsten after cooling have been of any use. Similarly, peak heights from the voltammograms would be of only qualitative use when compared with other such measurements.

Pure WC1 was shown to be stable with respect to disproportionation into WC1 and WC1 by Drobot and Nikolaev (6). This was determined from measurements leading to a WC1 -WC1 phase diagram. While extrapolation of this information from the pure system to a dilute molten salt solution may have been risky, the results of this study did not indicate W(V) disproportionation.

A sample voltammogram of W(V) is given in Figure 2. The results indicated a reversible couple believed to be $W(V) + e \longrightarrow W(IV)$. The average potential of the cathodic and anodic peaks were $0.86\pm.04$ and $1.02\pm.04V$ respectively*. Neither peak, nor obviously, their separation, $0.15\pm.03V$, changed with varying scan rate. From this value, n, the number of electrons transferred can be calculated from the equation:

$$E_{pc} - E_{pa} = -(.059/n)(T/298)$$

The resulting value, n =0.9±.2, clearly indicated a one electron transfer. It must be noted that the reduced species appeared to be insoluble because $i_{pa} > i_{pc}$. This agreed with the observation that K_2 WCl₆, a plausible analog to an electrochemically produced W(IV) species, dissolved slowly and incompletely, even with agitation of the melt.

An irreversible cathodic peak was observed at $E_p = 0.40V$ at a scan rate of 0.867V/sec. This peak shifted anodically with decreasing scan rate. When E_p was plotted versus log v, a value for the product an can be determined from the slope according to the equation:

an = (30/m)(T/298)

where v was the scan rate in mV/sec and m was the slope in mV/decade,

*all potentials given vs. mole fraction Ag/Ag⁺

A broad peak of variable shape and position occurred at negative potentials near the cathodic limit of the scan. The potential range of this peak was from -0.70 to -1.00V. While this peak could not be well characterized numerically, it was common to all tungsten halide species studied and has been assigned to be $W(II) + 2e^{----} W(0)$ for reasons discussed below.

Two other peaks were found, a cathodic peak at 0.10V and a broad anodic peak at -0.02V. These could not simply be the reverse of each other and may involve various tungsten cluster ions of compounds such as WC1, or WC1, (7).

Controlled potential electrolysis was performed at two potentials to identify the products of the respective cathodic reactions. In the first case, the potential was controlled at a value just above the cathodic limit. A platinum flag was used as the working electrode. A black deposit was collected after overnight electrolysis. The deposit was insoluble in water. X-ray diffraction showed that the product was tungsten metal (8) with an impurity of β -tungsten (9). The β -tungsten was probably formed due to the presence of oxide or oxygen from atmospheric contamination of the melt overnight. While the melt initially was oxygen and oxide free, as shown by a background voltammogram, slow contamination was inevitable unless the cell was totally sealed. In the second case, the potential was controlled at +0.47V, just past the potential necessary for the reaction assigned to be W(IV) + 2e ----- W(II). A black material was produced which was denser than the melt and insoluble in water and also appeared to be tungsten metal. The formation of the same product from both reduction steps is accounted for by a disproportionation of W(II) as discussed later. Analyses of the product were not made.

Tungsten (IV)

Tungsten (IV) was added to the melt as K WCl. This was found to be more practical than the addition of WCl², the next most likely source. It was assumed that the electrochemical behavior of K WCl was identical with that of WCl₄, due to the favorable chloride ion affinity of WCl₄ (10). Thus any WCl₄ added to the large excess of chloride present in the melt would have reacted to form WCl².

 K_{2} WCl did not dissolve as readily as the other tungsten species studied. Upon mixing with bubbling nitrogen, a yellow green solution was produced. Complete dissolution of the material added was not always

achieved.

electrochemical results for this system were striking. The Voltammetry at first appeared to give normal results. Subsequent scans showed the current growing rapidly to values above the capabilities of the potentiostat. Upon disassembly, the working electrode invariably had a conductive coating on the glass surrounding the platinum microelectrode. This increased the area of the electrode so greatly that voltammetry was no longer possible. The initial voltammogram, for example Figure 3, indicated a pattern of two cathodic peaks and two anodic peaks. The first cathodic peak was an irreversible reduction occuring at about +0.5V. This was believed to be the result of the reaction $W(IV) + 2e^{-} W(II)$. The second peak occurred at about -1.0V and was believed to show the reaction $W(II) + 2e^{-} \longrightarrow W(0)$. These two cathodic peaks were common to all the tungsten halide systems studied. The anodic peak which occurred around +1.0V was believed to indicate the reaction $W(IV) \longrightarrow W(V) + e^{-}$. Another anodic wave at +0.32V probably indicated oxidation of W(II) to a tungsten species with a valence around 3. These peaks were also common to all the tungsten halide voltammograms. The exact peak currents associated with the various reactions could not be determined due to the rapid increase in electrode size with time. This size increase also tended to reduce the resolution of the technique thus making the potential of the peak difficult to estimate.

Ey far, the most striking result of the study of this system came from controlled potential electrolysis. Electrolysis of the solution on a platinum flag at $\pm 0.46V$ gave an initial current of about $3mA/cm^2$. After overnight electrolysis, the current had increased to $6mA/cm^2$. When the cell was shaken gently, the current dropped to $1mA/cm^2$ and then began to increase again. The electrolysis was carried on for another half hour and then was stopped. Upon solidification the melt was white and a metallic mirror was deposited on all the glass surfaces. Explanation of this behavior, which was unique to the W(IV) system, was the key to understanding the electrochemistry of tungsten halides in the melt.

The widespread deposition of tungsten on all surfaces in contact with the melt suggested a chemical reaction rather than a purely electrochemical deposition process. Electrodeposition would be expected to produce a smooth coating, dendrites or a powder only on the electrode surface. Some means of transport of a reduced tungsten species must be postulated in this actual case. To explain the phenomenon, it was proposed that disproportionation of W(II) gave rise to the tungsten film on all cell surfaces. This reaction was well documented (7). A film was formed instead of powder or dendrites due apparently to the equilibrium:

 $2 W(II) \longrightarrow W(C) + W(IV)$

Tungsten (IV) was in much higher concentration here than in any of the other systems in this study. This would allow a higher equilibrium concentration of soluble W(II) which could migrate further from the electrode before disproportionating. Thus an extensive film was formed rather than a local product. The film was continuous, conductive, grew out from the electrode, and was fragile, as shown by the sudden decrease in current when the cell was shaken, followed by the gradual increase in current as the film was reestablished. In the absence of an electrolysis current, no film formed and no metallic deposit or precipitate was observed.

Balko also found a 2-step reduction for this system by chronopotentiometry, though on the basis of less data he believed that the first product was W(III). This species seems unlikely to exist without disproportionating. He found no evidence of film formation but the use of a platinum flag electrode for the relatively short period of time necessary to record a chronopotentiogram would have made the additional area due to film formation, less apparent in the electrochemical results.

<u>Tungsten</u> (III)

Tungsten (III) was added to the melt as $K_{3}W_{2}Cl_{3}$. This cluster compound was chosen because no simple W(III) halide or alkali metal halide was stable under the conditions of this study. Attempts to synthesize WCl₃ by disproportionation of other tungsten halides have yielded only WCl_{2.6} (11) or WCl_{3.5} (7). These non-stoichiometric halides probably have a cluster structure as well.

The K₃W₂Cl₂ dissolved rapidly in the melt to give a tan-orange solution. In the absence of electrolysis, a reaction slowly occurred leading to an orange precipitate, which turned brown overnight at 450°C. After this solution was frozen, it was leached with water. No heavy metallic particles were observed and only a yellow precipitate remained insoluble. Thus, while K₃W₂Cl₂ may have disproportionated or reacted with the melt at 450°C, the final product was not observed to be tungsten metal.

Johnston did not agree with this (2). He found that solid $K_y W_2 Cl_y$ was thermally unstable at this temperature. He postulated that;

K W C1 ----- 3KC1 + WC1 + WC1

This was based on the observation that a sample of the alkali tungsten halide held at 450° C in an argon atmosphere decomposed to leave only a KCl residue. This was odd because a thermogravimetric study has shown that solid WCl₂ is stable to 600° in an inert atmosphere. WCl₂ was not

stable at 450° but decomposed to WCl and WCl (7). He did not note any condensation of volatile tungsten species on the cooler portions of the cell. Poor temperature control or high rates of inert gas purge may have driven the above reaction to the right, but in this study, this decomposition did not appear to be a problem. Johnston also claimed that K.W.Cl disproportionated in the melt to form tungsten metal and higher tungsten halides. His X-ray diffraction pattern of the insoluble reaction product did not indicate tungsten, nor did those of Balko for a similar experiment. Johnston noted the formation of a tungsten mirror on cell surfaces similar to that formed by W(IV) in this study. This phenomenon did not occur during any experiment with W(III) in this study. No mention of WCl evolution was made during any of these disproportionation experiments. While this study suggested that disproportionation occurred, it is doubtful that it proceded to the ultimately stable products, WC1, and tungsten metal. Neither a metallic precipitate nor distillation of volatile tungsten species were ever noted. It was more likely that insoluble tungsten cluster compounds of valence less than three were formed along with soluble WCl_{2}^{2} . The electrochemical evidence supports this rather than the conclusions reached by Johnston.

The electrochemical investigation of $\mathbb{W} Cl_{p}^{3-}$ began with cyclic voltammetry performed on a platinum microelectrode. This resulted in a complicated pattern of peaks which changed greatly with scan rate. The slow disproportionation of $W_2 Cl_3^{3-1}$ into insoluble products prevented accurate knowledge of the concentration of various tungsten species in the melt. A typical voltammogram of $\mathbb{W}_2 Cl_2^{3-}$ at various scan rates is shown in Figure 4. The cathodic portion of the scan showed only one irreversible peak at E_p = +0.45V at a scan rate of 100mV/sec. The peak shifted cathodically with increasing scan rate. The value of an was determined from a plot of E_p versus log v to be -2.3±.2. The similarity of potential between this peak and those present in other systems has the other systems, controlled potential electrolysis at a potential slightly cathodic of this peak did not produce tungsten metal on a platinum flag electrode. A dependence of i on v also suggested something other than a simple charge transfer. Instead, it appeared that an insoluble film, probably composed of lower tungsten halide clusters, was formed. This essentially insulated the platinum and stopped continued reduction to tungsten metal, even at the cathodic limit of the melt. It was therefore assumed that the W(II) produced at the electrode reacts with some lower tungsten species not found in the other systems. Otherwise, it would have disproportionated to tungsten as it did in every other case. Johnston also found that a resistive film formed on his platinum electrodes under some conditions while studying $K_{3} \times C_1$. He found that the film could be produced in quantities sufficient for analysis and that it was actually tungsten metal (which should not be resistive). The results of this study do not agree with this. While sufficient product was not collected for chemical analysis, when voltammetry was performed on a tungsten

electrode, the results were far different from the simple ohmic curve which Johnston obtained on his platinum, film covered electrode. These results will be discussed later in this section.

The anodic sweep of the cyclic voltammogram displayed a complicated pattern of oxidations. The first anodic wave was often resolved into two peaks, particularly at low scan rates. The peaks tended to shrink with increasing scan rate, suggesting that this was an oxidation of a species produced by the reaction of W(II) with another tungsten species present in the melt. It could not, however, simply be the reverse of $W(IV) + 2e^{-}$ W(II) because the peak occurred at a potential cathodic to this reaction. "Window opening" experiments with an increasingly cathodic vertex potential, E_{λ} , showed an increase in i_p as E_{λ} became more negative. A more cathodic E_{λ} , or a slower scan rate would have allowed more time at potentials cathodic of the production of W(II). Thus more reactant for the oxidation indicated would be present, allowing a higher peak current and easier resolution of the peaks. The peaks did not shift significantly with scan rate; $E_{pi} = +0.30$, $E_{p2} = +0.37$, and $i_{p1} > i_{p2}$. Two peaks of similar potential in this case indicated either that two similar oxidations were taking place or that an adsorption of either the product or reactant occurred. The existence of non-stoichiometric lower tungsten chlorides gave credence to the former, while the lack of a continued high reduction current at very cathodic potentials supported the latter, whereby an adsorbed species may "poison" the platinum surface preventing electrodeposition of tungsten metal. Sufficient information was not available to discrimintate between these two mechanisms and subtle changes could cause the peaks to merge in either case as was occasionally observed. Due to the similarity in potential to the peak observed in the study of $WC1^{2-}$, which was characterized by a high concentration of W(II), the peaks have been assigned as:

The concentration of W(II) in this case must have been low due to its reaction with other tungsten components in the melt, or tungsten metal deposition would have occurred. This would also account for the low peak currents observed for the above reactions.

The next anodic peak also did not correspond to any cathodic peak. It was characterized by narrow width and high peak current compared to all other peaks recorded by this study. The high peak current suggested the oxidation of an insoluble reduced species that was adherent to the electrode. The peak potential, E_p , shifted anodically with increasing scan rate. At a 100nV/sec scan rate, $E_p = 0.85V$. The slope of a plot of E_p versus log v was $43\pm3mV/decade$. This corresponded to a value of an $1.7\pm.1$. As no independent evaluation of a was available, the value of n could not be determined. Window opening experiments were performed to evaluate the effect of varying E_λ on the peak current. The behavior

clearly indicated that this oxidation involved the product of the cathodic reaction which occurred at +0.47V when scanned at 33mV/sec. When E_{λ} was anodic of 0.47V, the anodic peak disappeared. The anodic peak grew steadily as E_{λ} was made more cathodic. In light of this information about the reactant for the oxidation, and the existence of still more anodic waves at higher potentials, the peak has been assigned to the reaction:

W(II) + W(III) ----- W(II-III) clusters W(II-III) clusters ----- W(IV) + (1-2)e

The next anodic peak was present only when the potential scan included the region at or near the cathodic limit of the melt. The peak vanished in scans with a more anodic E_{λ} . The peak occurred at around +1.01V at a scan rate of 33mV/sec. Faster scan rates tended to shrink the peak and the peak was never observed at 1000mV/sec. This could have been due to slight variations of E_{λ} with different settings of v due to imperfect instrumentation, but more likely was a result of the minimal time spent in the region at the cathodic limit at high scan rates. It may represent oxidation of a different insoluble tungsten halide cluster, perhaps even one incorporating lithium generated at the cathodic limit. The data obtained were too variable to make a more rigorous mathematical analysis for camparison with the diagnostic criteria for peak identification.

The most anodic voltammetric peak observed in the system occurred in the potential range of $\pm 1.17 - \pm 1.24$ V. Its closeness to the anodic limit sometimes prevented an adequate identification. It was felt that, in view of its similarity in potential with peaks in other systems, that it can be assigned to the reaction $W(IV) \longrightarrow W(V) + e^-$. It must be noted that no corresponding cathodic reaction has been recorded. This could have been due to the presence of a high concentration of reduced tungsten species which would quickly reduce any W(V) formed i.e. $W(V) + W(III) \longrightarrow W(IV)$.

The electrochemical investigation included a set of experiments similar to those above except that they were performed on a tungsten wire microelectrode or flag electrode instead of platinum. The resulting pattern of voltammetric peaks was far less complicated than those described above. Controlled potential electrolysis gave a nonadherent product which consisted of tungsten dendrites. Electrolysis at +0.21V gave a steady state current density of 0.26mA/cm^2 , while at +0.01V, the current density was 2.3mA/cm^2 . The voltammogram of W_{cl}^{3-} on a tungsten electrode is given in Figure 5. It showed one irreversible reduction, a reversible couple with an insoluble product and an irreversible oxidation. The irreversible cathodic wave occurred at a potential of +0.5V at 1000 mV/sec scan rate. The peak current was very strongly dependent on scan rate, and tended to disappear at the lowest available rate (33 mV/sec.) This suggested weak adsorption of the reactant because $i_p/v^{1/2}$ increased with increasing v (12). The peak current also tended to increase with time as the experiment proceded. The potential shifted cathodically with increasing scan rate, as would be expected for an irreversible reduction. Insufficient data prevented a reliable determination of an. Due to the similarity in potential between this peak and peaks observed in other systems, this peak has been assigned to the reaction:

The increasing peak current suggested an increasing concentration of W(IV) in the melt due to continued disproportionation of $W_2Cl_9^{3-}$. Electrolysis at +0.21V yielded a steady but small current.

The next reaction was a reversible one. The peak anodic current was much greater than the peak cathodic current which indicated that the reduced species was insoluble. The peak potential did not display a significant shift with scan rate and occurred at $+0.12\pm.02V$. The corresponding anodic wave occurred at $+0.22\pm.02V$. The average value of $E_{pa}-E_{pc}=102\pm4mV$, which corresponded to n=1.4 electrons transferred. This reaction was believed to be:

W(III) + e⁻→→ W(II) W(II) + W(III) →→ insoluble clusters

This case differed markedly from that observed at the platinum microelectrode. The corresponding reduction was irreversible. Moreover, on a tungsten electrode, tungsten metal was produced at a potential of +0.3V in quantities sufficient for analysis. On a platinum electrode, the electrolysis current was too low at accessable potentials to produce a significant amount of product. This may be due to some participation of the tungsten metal in the final disproportionation of W(II) to W(C) and W(IV). Perhaps the tungsten catalyzed the disproportionation by providing low-energy nucleation sites for tungsten crystallization. Or, alternatively, the following mechanism could be proposed:

 $\begin{array}{c} \mathbb{W}(\mathrm{III}) + e^{-} & \mathbb{W}(\mathrm{II}) \\ \mathbb{W}(\mathrm{II}) + 2 \ \mathbb{W}(\mathrm{III}) & \text{insoluble clusters} \\ \text{insoluble clusters} + \mathbb{W}(0) & - 4 \ \mathbb{W}(\mathrm{II}) \\ 4 \ \mathbb{W}(\mathrm{II}) & - 2 \ \mathbb{W}(0) + 2 \ \mathbb{W}(\mathrm{IV}) \\ \hline \\ 3 \ \mathbb{W}(\mathrm{III}) + e^{-} & \mathbb{W} & \mathbb{W}(0) + 2 \ \mathbb{W}(\mathrm{IV}) \end{array}$

Further study of this system must be made to determine the complicated

electrochemical mechanisms governing the reduction of $W_2 C l_9^{3-}$ to the metal.

The last voltammetric peak observed for $\mathbb{W}_{2}Cl_{3}^{3-}$ on a tungsten electrode was an irreversible oxidation which occurred at a potential of +1.10V. The peak appeared only late in the run, probably due to the increased concentration of reaction products of the disproportionation of \mathbb{W} Cl_{3}^{3-}. $\mathbb{W}(IV)$ has been postulated as one of these products as well as a product of the disproportionation of $\mathbb{W}(II)$ to tungsten metal. The potential of the peak was similar to the irreversible oxidation assigned to the reaction $\mathbb{W}(IV) \longrightarrow \mathbb{W}(V) + e^{-}$ in other, previously discussed systems, and may be assigned to the above reaction.

Both Balko and Johnston observed the disproportionation of $\mathbb{W}_{2}Cl_{9}^{2-}$. Johnston found one irreversible cathodic peak and no anodic peaks. This did not seem plausible because disproportionation products should surely show their voltammetry pattern as well. Also, a substance which disproportionates should also be oxidizable, but he found no anodic peaks. Balko observed the presence of $\mathbb{W}(IV)$ and $\mathbb{W}(V)$ in the melt by spectroscopy as well as by electrochemical measurements, although he differed with this study on some of the peak assignments.

CONCLUSION

The electrochemical results obtained for tungsten (V), (IV) and (III) are summarized in the table below. The reaction scheme below agreed with the known chemical behavior of the various tungsten species and accounted for the various voltammetric peaks and types of tungsten deposits obtained through electrolysis.

Summary of Electrochemical Results for Tungsten (III), (IV), (V)

Reaction	Pot.	<u>ws+</u>	W4 +	₩ ^{3 +}	<u>W³ +**</u>
W(IV)+2e W(II)	+0.5	+	+	+	+
$W(II) \longrightarrow W(IV) + W(0)$	-	+	1	2	3
W(II)→→W(II-III)+(0-1)e ⁻	+0.3	+	+	4	5
$W(II) + 2e^{ r} W(0)$	-1.0	+	+	-	-
W(II-III)	+0.9	-	-	+	-
$W(II-III) \xrightarrow{Li} W(IV) + (1-2)e^{-1}$	+1.0	-	-	+	-
$W(IV) \longrightarrow W(V) + e^{-1}$	+1.1	5	+	+	+

1. tungsten mirror deposited on cell surfaces 2. no tungsten deposited, only resistive film

******tungsten electrode

 complicated mechanism including tungsten clusters and tungsten participation
resolved into two peaks
reversible

The most significant finding of the study on tungsten halides was that tungsten was deposited at positive potentials by disproportionation of tungsten (II) rather than by direct reduction. However, further work, including product identification, is needed to bolster this conclusion. The disproportionation mechanism of tungsten deposition explains why tungsten deposited at a potential just cathodic of +0.5V when other reduction peaks were observed at potentials far more cathodic. It accounted for normal deposition of tungsten from W(V) via an unhindered disproportionation of W(II), the tungsten mirror from W(IV) via a hindered disproportionation which permitted W(II) diffusion, and the lack of deposition from W(III) due to a reaction of W(II) with tungsten species in the melt, except when a tungsten electrode was used whereby the deposition was catalyzed. The overall reaction scheme agreed with many documented disproportionation reactions and the formation of insoluble non-stoichiometric halide complexes. Direct reduction to tungsten as proposed by others does not explain the differences in tungsten deposition behavior.

REFERENCES

- E. N. Balko, <u>Electrochemical and Electronic Studies of Transition</u> <u>Metal Ions in Fused Salt Solvents</u>, PhD dissertation, Rensselaer Polytechnic Institute, 1971.
- R. O. Johnston Jr., <u>Electrochemical Studies of Selected Tungsten</u> <u>Compounds in Lithium Chloride-Potassium Chloride Eutectic</u>, PhD dissertation, University of Illinois, 1974.
- 3. K. E. Johnson, J. R. Mackenzie, Anal. Chem., 1969, pp. 1843.
- 4. C. R. Kennedy, R. D. Peacock, J. Chem. Soc., 1963, pp. 3392.
- R. Saillant, J. L. Hayden, R. A. Wentworth, <u>Inorg. Chem.</u>, Vol. 6, 1967, pp. 1497.
- D. V. Drobot, A. V. Nikolaev, <u>Russian Journal of Inorganic Chemistry</u>, Vol. 22, 8 1977, pp. 1217-8.
- 7. T. Takuma and S. Kawakubo, <u>Nippon Kagaku Kaishi</u>, Vol. 4, 1973, pp. 700-6.
- 2. "X-ray Diffraction Powder File, op. cit.," Card #4-806
- 9. "ibid.," Card #2-1138
- J. Eurgess, S. J. Cartwright, I. M. Haigh, R. D. Peacock, P. Taylor, H. D. B. Jenkins, K. F. Pratt, J. <u>Chem. Soc.</u>, <u>Dalton</u> <u>Trans</u>., Vol. 7, 1979, pp. 1043-9.
- 11. R. Matsuzaki, Y. Saeki, Nippon Kagaku, Kaishi, 7 1972, pp. 1226-9.
- 12. R. H. Wopschall, I. Shain, Anal. Chem., Vol. 39, 1967, pp. 1514.

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Figure 1: The Electrochemical Cell

The Electrochemical Cell; A-addition chute/gas bubbler, Bmelt container, C-reference electrode compartment/working electrode, D-fill hole, E-silver flag reference electrode, F-10mm. fine porosity frit, G-flag type working electrode, Hthermocouple well, I-microelectrode type working electrode, Jplatinum flag auxilliary electrode, K-level of melt, Lauxilliary electrode compartment/working electrode





STUDY ON ELECTROWINNING OF SOLID LANTHANUM-NICKEL ALLOYS IN LICI-KCI EUTECTIC MELT

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ABSTRACT

The variation of the e.m.f. of the cell La/La^{3+} in LiCl-KCl eut/La₂Ni was measured over the whole composition range of lanthanum-nickel alloys, at a temperature of 450°C. The alloys were formed by intermetallic diffusion from either chemical deposits of nickel or lanthanum, or electrochemical deposits of lanthanum on nickel. Seven intermediate alloys LaNi₅, La₂Ni₇, LaNi₂, LaNi₃, La₂Ni₃, LaNi and La₃Ni were observed. Moreover, our results suggest the existence of metastable compounds. Coulometric titration technique for a composition range from pure lanthanum to LaNi alloy confirmed these results. The determination of the composition dependence of the chemical diffusion coefficient for that composition range is included. The Gibbs free energies of formation of the La-Ni alloys have been deduced from these measurements.

INTRODUCTION

Some rare earth-transition metal alloys have the ability to absorb and desorb hydrogen reversibly. At room temperature, and for a pressure range of 1-10 atm, the absorbing capacity reaches a maximum at a composition close to ReM_5 (1) (Re = Rare earth ; M = 2d Metal); in particular, the compound LaNi_5 absorbs hydrogen_up to a density_of nearly twice that of liquid hydrogen (up to 6 x 10⁻² atoms per cm⁻³). Thus, the hydride LaNi_5H_6 is of considerable interest for hydrogen storage purposes and for fuel technology (2).

As the rare earth metal cannot be readily obtained, the melting processes (direct fusion of rare earth and 2d metals mixed together in convenient proportions) are of little interest for large-scale production. The present procedure is a metallothermic reduction (3) which can be applied to the production of alloys with relatively fine particle size; the rare earth oxide is reduced by calcium in the presence of the 2d metal powder or metal oxide, at high temperature (over 1000°C). This process is a simple and low-cost method for the production of alloys, but is subject to various drawbacks :

calcium is an expensive reactant, and the alloys have high oxygen contents and a heterogenous microstructure.

An electrolytic process was described in 1968 by Morrice <u>et al.</u> (4). According to it, a liquid alloy is obtained by electrodeposition of the rare earth metal on a 2d metal cathode, by electrolysis of Re_2O_3 dissolved in a molten fluoride mixture at about 900°C. This process may be easily controlled and monitored, but is yet more expensive than the former. The composition of the alloy, determined by the temperature is close to ReM_2 . Therefore, it must be melted again with additional 2d metal to reach the convenient composition (ReM_r , for instance).

The use of a molten chloride electrolyte instead of the fluoride + oxide mixture leads to a less expensive process at a rather low working temperature (400-500°C), with less difficulty for material selection and cell design.

We intended to obtain fundamental data which would help us to define clearly the practicability of such a process in the case of La-Ni alloys.

We have first studied the behavior of lanthanum and its ions in LiCI-KCI eutectic at 400-500°C, and then attempted to obtain the La-Ni alloys by electrodeposition of solid lanthanum on a nickel cathode at 450°C. We have determined the thermodynamic parameters of the alloys so produced, as well as the kinetic parameters of the lanthanum diffusion in the nickel electrode.

EXPERIMENTAL PART

Equipment and Procedure

Apparatus.

The cell consisted of a 150 ml pyrex crucible placed in an insulated pyrex body (Bercauverre) already described (5).

A gaseous atmosphere of fixed composition or vacuum could be imposed on the cell. High vacuum was obtained by means of an ALCATEL 1004 AC vacuum pump. The temperature was maintained constant within 2°C by means of a furnace and a programmable device described elsewhere (6). Temperature was measured with a chromel-alumel thermocouple inside a closed pyrex tube submerged in the melt. It was recorded with a SEFRAM Servofram recorder connected to a high impedance AOIP millivoltmeter.

E.m.f. measurements were carried out by means of a high impedance TACUSSEL Minisis 6000 voltmeter connected to a SEFRAM model Servofram recorder. A TACUSSEL PRT 10 potentiostat was used as a coulometer by means of a calibrated resistance (4.7Ω). This potentiostat was controlled by a periodical triangular signal generator TASCUSSEL model GSTP 3.

Melts.

Lithium chloride and potassium chloride were PROLABO (R.P. normapur quality) products. The procedure for the preparation and purification of the eutectic mixture has been previously described (7). Lanthanum chloride (LaCl₃, 7H₂O) was supplied by Rhône-Poulenc. It was dehydrated using a procedure similar to that described by Johnson and Mackenzie (8). The hydrous salt was placed on a sintered glass (porosity 0) assembly in a pyrex vessel. The chloride was heated under vacuum for two hours at 180°C, then ground and placed at 250° C under an hydrogen chloride atmosphere for one hour and a half. The salt was then weighed and transfered into the eutectic mixture.

The dehydrated salt dissolved in water yielded a clear solution; it may be considered as pure lanthanum chloride (less than 5% oxychloride detected by analysis). The possible oxy-chloride was removed by hydrogen chloride bubbling through the melt for one hour.

Electrodes.

a). The working electrodes (cathodes) used were the following : (i) Ø 1 mm nickel wire (Johson-Matthey), grade 1), (ii) Ø 1 mm tungsten wire (Sochibo, Koch-light, 99,9%), (iii) Ø 1mm lanthanum wire (Johnson Matthey, grade 1, delivered in a vacuum sealed tube) set up in an inert atmosphere, (iv) electrode constituted of a glassy carbon (Le Carbone Lorraine) rod : quality V 25 of 3 mm diameter, material which is non-oxidizable but forms interaction compounds with lithium (9).

b). The auxiliary electrode (anode) was glassy carbon (3 mm diameter, le Carbone Lorraine, quality V 25) in a pyrex compartment connected to a sintered pyrex capsule (porosity 4).

c). The reference electrode was made from a silver wire (1 mm diameter) dipped in a pyrex glass tube containing silver chloride 0.65 mol.kg⁻¹ dissolved in LiCl-KCl eutectic. All potentials measured with this reference electrode are given versus the chlorine reference ($Cl_2(1 \text{ atm})/Cl^-$) whose potential is 1.060 V versus our experimental reference electrode.

Preliminary determinations.

1. Voltammetric curves.

The reduction of Ni²⁺ on a glassy carbon electrode has been studied by cyclic voltammetry at 450°C. Fig. 1 shows a voltammogram obtained (curve 1). The reaction on the electrode is a reversible deposit of metallic nickel under diffusion controlled conditions. The peak potential value Ep does not depend on the voltage sweep rates, nor does the ratio $ip/v^{1/2}$ (ip = peak current; v = sweep rate). The peak current ip (Amperes) obeys the formula (10):

$$ip = 0.61 (zF)^{3/2} (RT)^{-1/2} AD^{1/2} [Ni^{2+}]v^{1/2}$$
(1)

where z is the number of electrons (z = 2 for Ni²⁺), R the gas constant, F the Faraday, T the temperature (K), A the area of the electrode (7.07 10^{-2} cm²), D the diffusion coefficient (cm² s⁻¹), [Ni²⁺] the concentration of Ni²⁺ ions (mol.cm⁻³) and v the voltage sweep rate (V s⁻¹). The concentrations in mol.cm⁻³ are calculated by considering the density of the bath as equal to 1.65 g.cm⁻³ (11). The diffusion coefficient of nickel ion was determined to be D_{Ni} = 2.12 10⁻⁵ cm² s⁻¹ which is in good agreement with the values given by several authors (12-14).

On a glassy carbon electrode the reduction of lithium ions appears at a potential of -2.3 V versus the chlorine reference electrode. Therefore it is impossible to use this electrode to study the lanthanum system. We have made La deposits on a tungsten electrode (0.15 cm²) and on a nickel electrode (0.13 cm²).

Typical voltammograms are shown in Fig. 1. The deposition on the tungsten electrode may be considered as reversible. Relation analogous to (1) was therefore used to determine the diffusion coefficient of lanthanum ion. Our value, $D_{La} = 8.76 \ 10^{-6} \text{cm}^2 \text{s}^{-1}$, is slightly lower than the one determined by Smirnov et al. ($D_{La} = 1.28 \ 10^{-5} \ \text{cm}^2 \ \text{s}^{-1}$) (15).

The voltammograms obtained on a nickel electrode show several current peaks for potential values located between the peak potential of lanthanum ion on the tungsten electrode and the peak potential of nickel ion on the glassy carbon electrode. Those peaks are characteristic of the formation of intermetallic compounds between nickel and lanthanum. La-Ni alloys can therefore be obtained by a deposit of lanthanum on nickel at 450°C.

 Standard potentials of the electrochemical systems La³⁺/La and Ni²⁺/Ni.

In order to determine the standard potential of Ni²⁺/Ni, a nickel deposit was formed on a planar glassy carbon electrode and the equilibrium potential of this electrode, dipped into a mixture of LiCl-KCl eutectic and NiCl₂, was measured for several concentrations of nickel chloride, at various temperatures (Table 1). The observed slope is in accordance with a two electron-exchange per nickel ion. The standard potential measured at 450°C (E =-1.084 V versus the chlorine reference electrode) is higher by 15 mV⁶ than the

value determined by Liu et al. (16) E = -1.1 V ; these authors measured directly the potential of a nickel wire dipped into LiCI-KCI eutectic .

In a similar manner, the equilibrium potential of a lanthanum electrode (1 mm diameter wire) in presence of dissolved LaCl₂ at various concentrations was measured.

This potential became stabilized in a few minutes (potential variation less than 1 mV/10 min). After each measurement the electrode was removed from the bath, and replaced by a new one, before the next measurement for a new concentration of lanthanum chloride. The Nernst relation :

$$E_{La} = E^{\circ} (La^{3+}/La) + \frac{2.3RT}{3F} \log La^{3+}$$

followed for temperatures 400, 450 and 510°C, and Table 1 indicates the corresponding values of E°(La 1 /La). The standard potential as a function of temperature is given (in V versus the chlorine reference electrode) by :

$$E^{\circ}(La^{3+}/La) = -3.474 + 4.3 10^{-4} T$$

(T = temperature in Kelvin). This result agrees well with the value given by Lesourd and Plambeck at 450°C (17) :

$$E^{\circ}(La^{3+}/La) = -3.159 V$$

Study of the lanthanum-nickel alloys formation.

Two sorts of experiments based on intermetallic diffusion were carried out. The first one corresponds to a chemical deposition of nickel on a lanthanum electrode, and the second one to an electrochemical deposition of lanthanum on a nickel electrode. In both sorts of experiments we have measured the variation of the potential of the electrode just after the metallic deposition. This potential is expressed in the following as the e.m.f. ε of the cell:

by using the value of $E(La^{3+}/La)$ previously determined. This procedure makes easier the analysis of the results.

1. Experiments with chemical deposition.

Chemical deposits of nickel on a lanthanum electrode have been achieved under an argon atmosphere from an electrolytic bath containing lanthanum trichloride ($[La^{+}] = 0.24 \text{ mol.kg}^{-1}$) and nickel chloride ($[Ni^{+}] = 0.18 \text{ mol.kg}^{-1}$). Nickel cations react spontaneously with metallic lanthanum according to the following general reaction :

$$(2/3 + y)$$
 La + Ni²⁺ $\rightarrow 2/3$ La³⁺ + La_yNi

A lanthanum-nickel alloy is therefore produced on the surface of the electrode, and we measured the variation of the potential of this

electrode as a function of time. A typical chronopotentiogram obtained during this sort of experiment is given in Fig. 2. We can observe, before the complete corrosion of the electrode, two plateaus whose potentials are indicated in Table 2.

2. Experiments with electrochemical deposition.

Electrochemical deposits, either at a controlled potential or at a controlled current, of lanthanum on a nickel electrode result in the formation of alloys in the whole range of composition (from pure lanthanum to almost pure nickel).

- Deposits realized at a controlled potential.

The discharge curve 1 of Fig. 3 was obtained under an argon atmosphere after a lanthanum deposit realized at E = -3.230V ($\varepsilon = -0.070V$) during 100 s. We can observe 9 plateaus before reaching the rest-potential of nickel in the melt. The potential of some plateaus varies (up to 50 mV) with the duration of the electrochemical deposition, especially for the plateau h (Fig. 3).

In such experiments, only $1.5.10^{-6}$ mole of lanthanum was deposited on the nickel electrode. So, oxide (or hydroxide) anions can interfere because the equilibrium concentration of O^{2^-} is about 10^{-5} mol.kg⁻¹ after purification of the eutectic melt (18, 19). Therefore we have carried out numerous experiments under a low HCI pressure which permits to reach a pO^{2^-} value close to 8, for which no lanthanum oxychloride is formed (20). In the course of these experiments, HCI oxidized the lanthanum very slowly and the duration of the relaxation has practically been the same as the one observed for experiments performed under an argon atmosphere.

The curve 2 of Fig. 3 was obtained after deposition of lanthanum at E = -3.230 V ($\varepsilon = -0.070$ V) during 100 s. We observe 9 plateaus of potential corresponding to the formation of La-Ni alloys by diffusion of La inside the nickel electrode, and one more relative to the rest-potential of nickel in melt ($\varepsilon \approx 1.860 \pm 0.005$ V). We remark that the plateaus are very close to those obtained under argon. The most noticeable differences correspond (i) to the existence of a plateau at $\varepsilon = 0.088$ V, (ii) to the disappearance of the two plateaus a' and e' (observed on the curve 1), and (iii) to the shift of the potential of the 8th plateau (h).

In the case of lanthanum deposition at E = -3.330 V ($\varepsilon = -0.170 V$), the discharge curve 3 of Fig. 3 made clear the appearance of two supplementary plateaus (i and j), the others being similar to those of the preceding experiment achieved at E = -3.230 V.

In order to determine the influence of the preelectrolyze potential upon the nature of the alloys formed, we obtained lanthanum deposits at potentials whose values varied between E = -3.100 V ($\varepsilon = 0.060 V$) and -2.700 V ($\varepsilon = 0.460 V$). For E = -3.100 V (curve 4, Fig. 3), only the last three plateaus (f,g,h) are observed. For -3.05 V \leq E \leq -2.95 V (curves 5 to 7), only the plateaus g and h, corresponding to the two nickel rich alloys, appear (for g, the more reductive is the preelectrolysis potential, the larger is the plateau). When we preelectrolyze at E \geq -2.700 V ($\epsilon \geq 0.460$ V) no alloy formation is observed (curve 9), and we reach the rest-potential of nickel directly.

- Deposits realized at a controlled current.

The preceding experiments only give the variation of the e.m.f. ϵ as a function of time, but do not allow us to establish experimentally the relation between the e.m.f. and the composition of the alloys formed. We therefore made coulometric titrations using the method called "Electrochemical Galvanostatic Intermittent Titration Technique" or GITT, developped by Weppner et al. (21-24). Very small amounts of lanthanum are deposited by means of pulses at a controlled current, and after each pulse, the equilibrium potential is measured at the end of the relaxation time. Thus, it was possible to know the exact composition of the alloy relative to the e.m.f. ϵ measured.

In these experiments, the cathode used was a 0.1 cm diameter nickel wire, dipped by 0.7 cm in the bath. The value of the coulometric current I was 20 mA. With each pulse of current (duration $\tau = 60$ s), the variation in alloy composition is given by the formula :

$$\Delta y = \frac{I_o \tau}{zE} \cdot \frac{M_{Ni}}{m_{VV}}$$

where z is the number of electrons exchanged, F the Faraday constant, M_{Ni} the molecular weight of nickel, and m_{Ni} the weight of nickel in the alloy. With our experimental conditions Δy is 5.10^{-3} . After each pulse, therefore, it is possible to calculate the theoretical composition of the alloy, assuming total interdiffusion. The duration of relaxation (between two pulses of current) was 1000 s, which appeared sufficient to reach equilibrium. In our experiments we applied the coulometric signal 200 times, in order to reach a final composition corresponding to LaNi.

Fig. 4a shows a typical curve which was experimentally obtained under an HCl atmosphere and which gives the relation between the e.m.f. ε and the alloy composition. This curve has the same general from as the curves shown in Fig. 3. The equilibrium potential of the nickel-richest part of the curve has a value near that of plateau h of curve 1 in Fig. 3. It occurs after a shift of potential at a composition close to LaNi₁₀.

INTERPRETATION OF THE RESULTS AND CONCLUSION Lanthanum-nickel intermetallic compounds.

Fig. 5 gives the phase diagram of the lanthanumnickel system which was determined by Bushow and Van Mal (25). This diagram shows the existence of seven lanthanum-nickel alloys of definite compositions. Moreover, all these alloys are solid at our working temperature (450°C) because the La₃Ni alloy, which has the lower melting point, melts at 485°C. So after having coated a nickel electrode with lanthanum, this last metal diffuses inside nickel and the surface composition varies from pure lanthanum to an alloy very rich in nickel (the supporting metal).

Theoretical variation of the e.m.f. ε as a function of the surface composition of the working electrode (lanthanum-nickel alloy).

The e.m.f. g(y) corresponding to a chemical composition of the alloy (formed at the surface of the electrode) is related to the activity of lanthanum, by the expression :

$$\varepsilon(\mathbf{y}) = -(\mathbf{RT}/\mathbf{3F}) \ln a(\mathbf{La}) \tag{2}$$

where a(La) is the activity of the rare earth in the alloy (taking the pure lanthanum as the standard state). When the electrode surface is composed of a mixture of alloys of definite compositions Lay₁Ni and Lay₂Ni, the activity of the lanthanum is fixed by the equilibrium :

$$Lay_1Ni + (y_2 - y_1)La \neq Lay_2Ni \qquad (3)$$

and so the e.m.f. ε has a constant value during the complete transformation of the definite alloy Lay₁Ni into the definite alloy Lay₂Ni. For the exact composition of a definite alloy, Lay₂Ni for example, we observe a sudden variation of ε from the value of the two phase plateau corresponding to the mixture of Lay₁Ni and Lay₂Ni, to the value of the two phase plateau of Lay₂Ni and Lay₂Ni mixture. Such sharp variations, however, are not observed when solid solutions exist; in that case the e.m.f. varies slowly from one two phase plateau to another. So, the plateaus observed in an e.m.f. - composition diagram are related to the two plateau areas in the phase diagram (Fig. 5 and 6).

Analysis of experimental curves.

The e.m.f. corresponding to the two phase plateaus observed with our experimental conditions, are listed in Table 2. The values obtained from the chemical deposits of nickel on a lanthanum wire (Fig. 2), can be assigned to the lanthanum-rich alloys La_3Ni and LaNi mentionned in the phase-diagram of Fig. 5. The measurements achieved under a low HCI partial pressure, and after an electrochemical deposition of lanthanum on a nickel electrode at a controlled potential of -3.230 V (curve 2; Fig. 3) are the most reliable because the experimental conditions minimize the possibility of a codeposition of lithium and of the influence of dissolved O^{2-} ions. The plateaus a,b,c,d,e,f,g, may be clearly related to the successive two phase domains obtained with the lanthanum and its seven alloys with nickel (Table 2). The plateaus d' and h also observed for $\varepsilon = 0.110$ V and $\varepsilon = 0.648$ seem to be due to metastable phases : the plateau d' observed in curve 2 (Fig. 3) does not appear in curve 3, and the plateau h corresponds to different values of ε in curve 2 and curve 3. The plateausi and j (curve 3, Fig. 3) may be assigned to lanthanum-lithium alloys. In fact, no nickel-lithium alloys can be formed because no plateau appears after an electrochemical deposit of lithium alone on a nickel electrode, the potential varying from that of lithium to that of nickel in the bath (26) (Experiment performed with no lanthanum chloride in the bath) Besides, the analysis of the obtained deposits (X rays, backscattered electrons) does not indicate the presence of lithium.

The plateau e' which appears in curve 1 (Fig.3) may be due to the influence of oxide ion. It is not observed in curves obtained under an HCI atmosphere, and the analysis of the compound formed indicates the presence of lanthanum oxychloride.

The preceding assignment of the plateaus is confirmed by our results by the GITT method giving the relation between the e.m.f. ε and the compositions of the alloys (Fig. 4a).

Our values agree very well with those calculated from values of Rezukhina and Kutsev (27) obtained at higher temperatures in molten fluorides (Table 2). These authors didn't study the alloys whose composition is included between LaNi and pure lanthanum.

Our results allow us to calculate the Gibbs free energies of formation of the lanthanum-nickel alloys at 450°C. The Gibbs free energy of formation ${}^{\Delta}G_{p}^{\circ}$ of an alloy of composition La $_{y\,2}Ni$ is related to that of a La $_{y\,1}Ni$ alloy by the relation :

$$\Delta G_{f}^{o}(La_{\gamma 2}Ni) = -3F \int_{\gamma_{1}}^{\gamma_{2}} \varepsilon(\gamma) d\gamma + \Delta G_{f}^{o}(La_{\gamma_{1}}Ni)$$
(4)

The values obtained are collected in Table 3 and are corroborated by values derived from literature data (27,28) as shown in Table 3.

The kinetic parameters of metallic interdiffusion, the chemical diffusion coefficient \tilde{D} , may be obtained from results of the GITT method as it was described by Weppner and Huggins (21-23). The chemical diffusion coefficient \tilde{D} expresses the variation of the concentration of one species at the surface of the electrode, according to Fick's second law :

$$\frac{\partial C_{La}}{\partial t} = \widetilde{D} \frac{\partial^2 C_{La}}{\partial x^2}$$
(5)

where t is the time, C_{La} the local concentration of lanthanum, and x the distance into the solid form the electrode/electrolyte interface. A solution of equation (5) gives the concentration C_{La} of lanthanum at the surface of the working electrode as a function of time for small total currents i.e. $\tau << r^2/D$ (τ = duration of the current pulse; r = radius of the electrode) (24) :

$$C_{1a}(t) - C_{1a}(0) = 2 I_0 \sqrt{t} (z F A \sqrt{r} \tilde{D})^{-1}$$
 (6)

with $C_{1,2}(t)$ and $C_{1,2}(0)$ being respectively the surface concentration of lanthanum at time t and at the origin of time, I the current for the coulometry and A the area of the interface electrolyte/electrode.

Equation (6) may be related to the variation $\Delta \varepsilon_{c}$ of the cell voltage during the current pulse (neglecting the IR drop) and to the variation $\Delta \varepsilon$ of the equilibrium potential between two successive relaxations (assuming that $\Delta \varepsilon$ is small and that the variation of ε_{c} is linear as a function \sqrt{t} during the coulometric pulse, which is verified for our experimental conditions):

$$\vec{D} = \frac{4}{\pi\tau} \left(\frac{V}{A}\right)^2 \left(\frac{\Delta\varepsilon}{\Delta\varepsilon_c}\right)^2 \tag{7}$$

(V is the volume of the electrode). With our experimental conditions (r = 60 s, V = 6.10^{-3} cm³), the relation (7) becomes :

$$\widetilde{D} = 1.33.10^{-5} (\Delta \varepsilon / \Delta \varepsilon_c)^2$$

The maximum values of the chemical diffusion coefficient reported in Fig. 4b correspond to sudden variations of the concentration of lanthanum at the surface of the electrode, i.e for single phase components. Related to Fig. 4a, this curve gives the composition of the definite alloys observed. The values of the coefficient vary from $1.8.10^{-6}$ cm² s⁻¹ for the LaNi₅ phase to $1.33.10^{-7}$ cm²s⁻¹ for the La₂Ni₇.

Conclusion

In this study we have determined the Gibbs free energies of the seven lanthanum-nickel alloys. It was found that the presence of oxide ions must be carefully avoided, and that metastable phases might be formed, especially for a composition close to LaNi₁₀. Further investigations are needed to better understand the phenomena that occur. At the present time experiments are carried out as a function of temperature in order to obtain the temperature dependence of the thermodynamic parameters of La-Ni alloys.

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REFERENCES

- 1. R.A. Guidotti, G.B. Atkinson and M.M. Wong, J. Less Common Metals, 52, 13 (1977).
- 2. D.P. Gregory "The Rare Earths in Modern Science and Technology", G.J. Mc Carthy Ed, Plenum Press, N.Y. (1978), p. 1.

- 3. C. Herget and H.G. Domazer, Goldschmidt Informiert, 35, 4(1975).
- E. Morrice, E.S. Shedd and T.A. Henrie, Direct Electrolysis of Rare Earth Oxides to Metals and Alloys in Fluoride Melts, U.S. Bureau of Mines, R.I. 7146, 1968.
- 5. F. Séon, G. Picard and B. Trémillon, J. Electroanal. Chem., <u>138</u>, 315 (1982).
- 6. R. Combes, J. Vedel and B. Trémillon, Electrochim. Acta. <u>20</u>,19 (1975).
- 7. G. Picard, F. Séon and B. Trémillon, J. Electroanal. Chem., <u>102</u>, 65 (1979).
- K.E. Johnson and J.R. Mackenzie, J. Inorg. Nucl. Chem., <u>32</u>, 43 (1970).
- 9. J.R. Selman, "Electrochemistry of Lithium Carbide", ANL-75-46, 33 (1975).
- 10. G. Ting, Ph. D. Thesis, University of Tennessee (1973).
- 11. E.R. Van Artsdalen and I.S. Jaffe, J. Phys. Chem., <u>59</u>, 118 (1955).
- 12. W.K. Behl, J. Electrochem. Soc., 118, 889 (1971).
- 13. J. Bouteillon and M.J. Barbier, J. Electroanal. Chem., <u>56</u>, 399 (1974).
- 14. E. Schmidt, Electrochim. Acta, 8, 23 (1963).
- M.V. Smirnov, Yu.N. Krasnov, V.E. Komarov and V.N. Alekseev, Tr. Inst. Elektrokhim. Akad. Nauk. SSSR., Ural'sk filial, N° 9, 59 (1966).
- C.H. Liu, A.J. Zielen and D.M. Gruen, J. Electrochem. Soc., <u>120</u>, 67 (1973).
- 17. J.B.Lesourd and J.A. Plambeck, can. J. Chem., 47, 3387 (1969).
- 18. F. Séon, Doct. Etat Thesis, Paris 1981.
- B. Trémillon and G. Picard, "Proc. 1st Internat. Symposium on Molten Salt Chemistry and Technology", Kyoto (1983) p. 93.
- 20. G. Picard, Y. Mottot, C. Duval and B. Trémillon, to be published.
- W. Weppner and R.A. Huggins, "Proceedings on the Symposium on Electrode Materials and Process for Energy Conversion and Storage", The Electrochemical Society, 833 (1977).
- 22. W. Weppner and R.A. Huggins, J. Electrochem. Soc., <u>124</u>, 1569 (1977).
- 23. W. Weppner and R.A. Huggins, J. Electrochem. Soc., <u>125</u>, 7 (1978).
- 24. G.J. Wen, B.A. Boukamp, R.A. Huggins and W. Weppner, J. Electrochem. Soc., 126, 2258 (1979).

- 25. K.H. J. Buschow and H.H. Van Mal, J. Less. Common Metals, 29, 203 (1972).
- 26. Y. Mottot, unpublished results.
- 27. T.N. Rezukhina and S.V. Kutsev, Zh. Fiz. Khim., 56, 1 (1982).
- C. Chatillon-Colinet, H. Diaz, J.C. Mathieu, A. Percheron-Guegan and J.C. Achard, Ann. Chim., <u>8</u>, 657 (1979).

	Lanthanum			Nickel			
Temperature T/°C	2.3 RT/3F, mV exp. Theor.		standard potential/V	2.3 RT/2F, mV Exp. Theor.		standard potential/V	
400	45	46	- 3.185				
435				. 77	74	- 1.083	
450	45	49	- 3.164	80	75	- 1.084	
500				81	80	- 1.086	
510	54	53	- 3.137				

Table 1 : Verification of the Nernst relation for the La³⁺/La and Ni²⁺/Ni electrochemical systems in LiCI-KCI eutectic.

lantha	lanthanum deposit on a nickel cathode		N. deposit on a L a electrode	Alloys in molten fluoride	observations	
plateaus	curve(1) Fig.3	curve(2) Fig.3	curve(3) Fig.3	curve Fig.2	REZUKHINA et al 27	
i			- 0.056			La-Li alloys
j			- 0.030			La-Li alloys
a	0	0	0	0	0	La on a Ni wire La/La ₃ Ni alloys
a'	0.015					alloys+oxychlorides
Ъ.		0.042	0.042	0.041		La ₃ Ni/LaNi alloys
c	0.070	0.072	0.075	0.071		La2Ni/La2Ni3alloys
d		0.088	0.085		0.094	La ₂ Ni3/LaNi2 alloys
d'	0.109	0.110				metastable phase
e	0.131	0.136	0.130		0.137	LaNi ₂ /LaNi3 alloys
e'	0.153					oxychloride influence
f	0.215	0.206	0.204		0.204 0.206	LaNi ₃ /La ₂ Ni ₇ / LaNi ₅ alloys
g	0.425	0.478	0.471			LaNi ₅ /Ni alloys
h	0.608	0.648	0.700			Metastable phase
	1.860	1.860	1.865			N, wire electrode potential

Table	2	:	Relation between	experimental	e.m.f. (see	text)	and
			lanthanum-nickel	phases. (T =	= 450°C).		

Reaction of formation	e.m.f. & /volt	- $G_f^{\circ}/KJ.mol^{-1}$			
of alloys		This work	From litterature		
La + 5 Ni = LaNi ₅	0.475	136.2	143 (27);130(28)		
La + 3.5 Ni = La Ni _{3.5}	0.205	111	114 (27)		
La + 3 Ni = La Ni ₃	0.205	112	115 (27)		
La + 2 Ni = La Ni $_2$	0.133	81	88 (27)		
La + 1.5 Ni = La Ni	0.087	68	68 (27)		
La + Ni = LaNi	0.071	56	-		
La +.33 Ni = La Ni.33	0.041	23	-		

Table 3 : Gibbs free energies of formation of the La-Ni alloys.

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Figure 2 : e.m.f. variation (see text) as a function of time observed when a lanthanum electrode is dipped into LiCI-KCl eutectic melt containing Ni^{2+} (0.18 mol.kg⁻¹) at T = 450°C.












Figure 5 : Phase diagram of the La-Ni system from Buschow and Van Mal (25).



Figure 6 : e.m.f. - composition diagram for La-Ni system at 450°C.

FURTHER DEVELOPMENTS IN MOLTEN SALT ANODISING

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ABSTRACT

Samples of aluminium, titanium, niobium, tungsten and molybdenum have been anodised in a low melting urea-ammonium nitrate eutetic between $45^{\circ}-85^{\circ}C$. The presence of dissolved water in the melt significantly influences the oxide growth process and breakdown voltage. Previous claims concerning the desirability of anodising in anhydrous media may need to be re-examined, as water would appear to be a necessary component of the electrolyte. Results for aluminium and niobium show some promise for commercial exploitation.

INTRODUCTION

In a previous report¹, important commercial and military applications of anodised films were suggested; these include corrosion inhibiting coatings, adhesive bonding keying surfaces, electronic devices and solar conversion cells as well as decorative finishing. With the exception of the latter, it was considered¹ that anodising in molten salts might confer advantages. Work to date in this area is limited and has been critically reviewed¹⁻⁴. One claimed advantage of working in melts has been that they offer a non-aqueous medium. However, it was apparent¹, in most cases, that dissolved water was present in the melts employed by previous workers. Furthermore, it has recently been established⁴ the presence or absence of water significantly influences the nature of anodised films formed in molten salts. New interpretations of data presented here suggest that the presence of water in melts may be necessary in order to grow reasonably thick, especially porous, films.

Another factor influencing film type appears to be the melt temperature⁵, such that lowering the temperature may produce thicker or more adherent films. As a result, the adoption of low melting nitrate and organic amide systems has been preferred. Frequently, these have included ammonium nitrate leading to ionisation of the strong Lux-Flood acid, NH_4^+ ; this entity could promote the growth of porous films if there were some interaction with the oxide. In this

case, the appearence of porous films might be explained in terms of sparing solubility of the oxide according to accepted theory for aqueous anodising, but vide infra.

Certainly, anodised films produced in molten salts may be rather different to oxide films formed by other techniques or in other media Thus, their electronic, mechanical and chemical properties deserve investigation. Most studies have been concerned with aluminium and its alloys $^{4,7},$ although titanium 8, tantalum 9 and zirconium 10 alloys have also been anodised in melts; invariably the molten medium has consisted of alkali metal nitrates above 140°C. In the present programme, the eutectic system urea-40.4 mole% ammonium nitrate (M.Pt. 44.5°C) has been employed in the temperature range 45°-85°C. Samples of aluminium, titanium, tungsten, niobium and molybdenum have been anodised at constant voltage both in anhydrous melts and those containing water. Films have been characterised by electron microscopy, optical microscopy and interferometry, photoelectrochemically, as well as by in situ electrochemical and chemical analysis. In some cases comparison with thermally grown oxide specimens has been possible. Tentative explanations of the electrochemical processes occurring are offered in some instances and the possible role of water assessed. It is possible to predict the most promising direction for future investigations.

EXPERIMENTAL

Metals:

<u>Aluminium</u> - strips of 0.15mm thick, super-pure (>99.99%) aluminium, 4mm wide and several centimetres long were electropolished and then bolted into a stainless steel chuck mounted on tungsten pins. The area contacted by the melt was determined after each experiment.

<u>Titanium</u> - lcm squares of lmm thick, 99.2% pure titanium sheet were polished on one face to $\frac{1}{4}$ micron on diamond wheels. Titanium wires were spot welded to one corner to act as conductors. The reverse face, sides and contact wires were coated with epoxide resin as a mask. These specimens were then attached to tungsten pins via stainless steel chucks.

<u>Niobium</u> - 1cm squares of 0.5mm thick, 99.9% niobium sheet were mounted and finished as for titanium samples.

<u>Tungsten</u> - lcm squares of 0.5mm thick "pure" tungsten, kindly provided by Murex, were similarly prepared.

<u>Molybdenum</u> - similar samples of 0.125mm molybdenum, also provided by Murex, of unknown purity, were also prepared. The Nb, W, and Mo specimens were provided with Nichrome wire contacts, great care being taken to adequately mask the joints. Samples were degreased and stored in a desicator prior to use. Large platinum foil counter electrodes were used.

Melts:

Eutectic melts of pre-dried BDH 'Analar' urea + 40.4 mole% ammonium nitrate were prepared in situ in the experimental cell. In some cases melts were further dried by melting under vacuum and sparging with dry N_2 or Ar overnight.

Cells:

All-glass, borosilicate cells were used. A 52.5cm flanged cup, carried a flanged cell-head onto which were joined ground-glass joints. These were fitted with screw-cap joints through which plain glass tubes carrying electrodes, gas inlet/outlet and other accessories passed. The melt was contained within an inner glass cell. The assembly was placed in an aluminium block thermostat which was generally maintained at $63.5^{\circ} \pm 0.5^{\circ}C$; the temperature was varied in the range $45^{\circ} - 85^{\circ}C$ for some experiments. Water was injected via a microlitre syringe. Gas samples were collected in evacuated glass capsules fitted with taps and assembled directly into the cell heads.

Equipment:

Samples were polarised in incremental steps of 2V using a stabilised power supply; currents were continuously recorded by monitoring the iR drop across standard resistors with a y-t recorder and a digital voltmeter. Samples were examined by a range of microscopical techniques, by interferomtry and surface profiling. The photoresponse of some specimens was determined potentiostatically in aqueous 0.1M Na₂SO₄ at 20°C using a 2kW high-pressure mercury source and monochromator.

RESULTS AND DISCUSSION

Only a few specimens of aluminium were anodised in these melts. However, thick, white adherent films were formed in both anhydrous and "wet" melts over a range of voltages and temperatures. Visual inspection suggested that these films were similar to those formed in LiNO₃ - NH₄NO₃ melts at 110^oC, and, therefore would be of commerical interest.

Two different types of anodising behaviour were apparent for titanium specimens, depending upon the dryness of the melt. When quite small quantities of water were present, the anodising voltage could be raised, gradually, to the breakdown value of 83 as shown in Figure 1(b). Scanning electron microscopy evidenced local "punch-through" and melting, characterising dielectric failure at this voltage. Some gassing occurred at >76V - probably NO₂, judging by its colour. For anhydrous melts, an infinite current rise commencing at ~12V and accompanied by the evolution of a colourless gas, was observed (see Figure 1(a)). Mass spectometric analysis of this gas indicated that it was predominately NO, with minor amounts of O₂, N₂, CO₂ and NO₂. Ammonia was absent implying stability of the urea component of the melt. The gas was colourless at all times suggesting that NO₂ is not involved in the reaction scheme, and that equations including this species would be difficult to justify. An overall reaction involving co-oxidation of the electrode by both the melt and the applied potential might be:

$$Ti + NO_3 - e \rightarrow TiO_2 + NO$$

Figure 1 compares the I vs. V curves for titanium with those for aluminium, obtained in eutectic $\text{LiNO}_3-\text{KNO}_3$ melts at 140°C . In anhydrous melts only thin barrier films are generally formed in each case. For aluminium low currents are observed in anhydrous melts (Figure 1(c)) up to a breakdown voltage of $\sim 85^6$, indicating that the film is sufficiently insulating and coherent as to prevent melt decomposition at the outer oxide-melt interface. In the case of titanium, however, sufficient potential does seem to appear at this interface, for quite low applied voltages, such that massive melt elctro-oxidation occurs. This suggests that the thin, anhydrous oxide films on titanium are extensively flawed when formed under these conditions i.e. there is a considerable leakage current. In contrast, in the presence of water, porous (nonadherent) films can be grown between ~15-40V on aluminium as shown by the larger currents in Figure 1(d). Although, films of only ~ 2000Å are indicated in "wet" melts for titanium, the current continues to rise, with a peak at ~18V, up to the limit of dielectric integrity, Figure 1(b). Taken together, these results might suggest that the presence of water in melts actually promotes the growth of porous films and is a necessary co-reactant in the overall mechanism. In view of the uncertain levels of water present in the melts of previous investigators and various claims concerning the desirability of anodising in anhydrous media, it may be worth emphasising the apparent requirement for water dissolved in the melt, if porous films are sought. If this is so, then mechanisms envisaged for aqueous anodising may pertain to melts also.

In order to assess the suitability of melt-anodised TiO₂ for photoelectrochemical devices, their photoresponses were recorded at 1.0V and 1.6V vs. s.c.e. in aqueous 0.1M Na₂SO₄ solutions at 20^oC, in the range 300-450nm. Figure 2 shows the variation of maximum photoresponse, occurring at ~360nm, with polarisation to 1.0V vs. s.c.e., as a function of film anodising voltage. At low formation voltages, \pounds 2, first order interference colours, yellow \rightarrow blue, suggest a linear thickness voltage relationship¹¹ and a linear photoresponse is evident in Figure 2. Second order interference colours were progressively observed between 12-60V, parallelled by the photoresponse again, but obeying a different law. The anomaly occuring for films grown at \sim 12V was reproducible, is unexplained, but may be associated with film rearrangement or with melt decomposition, film cracking and product inclusion as observed in anhydrous melts.

Definitive film thickness measurements proved illusive for titanium. However, comparisons with well characterised interference colours obtained for tantalum suggest¹² that the first order, completed at ~12V corresponds to ~500 Å and that the second order completed at ~60V corresponds to ~1300 Å . Probably 2,000 Å represents an upper limit for films prepared in this way. Certainly, photoresponses were weak when compared with those resulting from thermally grown specimens.

No previous reports have appeared concerning the anodising of niobium in melts, even though this refactory, transition metal and its oxides exhibit interesting electronic, physical and chemical properties¹³. For this metal, anodising in the urea-ammonium nitrate melt was possible up to at least 103V without evidence of dielectric breakdown. However, a colourless gas (probably NO) was evolved in copious quantities between ~50 - 60V, corresponding to the large current peak shown in Figure 3. The effect of the presence of water in the melt was less marked for niobium anodising, but this might have been due to the use of inadequately dried melts. Nevertheless, scanning electron microscopical examination of sectioned samples indicated two disticntly different layer structures between the substrate and bulk oxide on specimens anodised in "wet" melts. All films were barrier-type with a maximum probable thickness of $\sim 3,000$ Å, as determined by interferometry under illumination with a sodium lamp, $\lambda = 5,400$ Å . The photoresponses of these anodised films under a range of conditions were relatively low. ~100 μ A.cm⁻², as shown in Figure 2.

Although a few reports have been concerned with low voltage oxide films on tungsten in melts, no previous studies appear to have been concerned with molten salt anodising the metal to higher forming voltages. Results obtained in this study show, Figure 3, that an infinite current rise occurs at ~28-32V and is accompanied by the evolution of a colourless gas (NO?). Up to this voltage, barrier films were evident, with a maximum probable thickness of ~1400 Å, as determined by interferometry ($\lambda = 5,400$ Å), obtained in "wet" melts. As for niobium, the influence of the presence of water in the melt was less apparent. The photoresponses of these films were also small, <100 μ A.cm⁻², as shown in Figure 2. Of particular interest for this metal, is the stability of its oxide films as a function of pH. Unfortunately no benefit appeared to be conferred by the molten salt anodising procedure; films were unstable in aqueous solutions at all pH's above ~4.

Molybdenum may not normally be anodised in aqueous solution due to the solubility and conductivity of its oxide. Apparently the same pertains in melts, since brown dinitrogen tetroxide gas was evolved, with infinite current rise at applied voltages \ge 2.

CONCLUSIONS

Anodising of aluminium, titanium and niobium in low melting salts can lead to the production of a wide range of barrier and, for aluminium, porous oxide films. The presence of water in the melt critically influences the structure of these films and the breakdown voltage. Water appears to be a pre-requisite for the formation of porous films on aluminium, and appears to be involved in the mechanism of growth of the thicker films on all metals. The ammonium cation may also influence film formation. Low temperature, molten salt anodising procedures may be of commercial interest for aluminium and niobium, although further investigations, especially of the role of dissolved water in the melt, are desirable. Detailed microscopical studies of films formed on aluminium, titanium and niobium are also called for.

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REFERENCES

 D.G. Lovering, A.K. Turner and K.P.D. Clark, Proc. 3rd. Int. Molten Salt Symp. Eds. G. Mamantov, M. Blander, & G.P. Smith. <u>81-9</u>, 539 (1981), The Electrochemical Society Inc., Pennington, N.J.

2. D.H. Kerridge and D.G. Lovering in "Molten Salt Technology" Ed. D.G. Lovering, Plenum, N.Y. (1982).

3. D. Inman and D.G. Lovering in "Comprehensive Treatise of Electrochemistry" Vol. 7, eds. J.O'M. Bockris, B.E. Conway, E. Yeager and S.U.M. Khan, Plenum, N.Y. (1983).

4. D.G. Lovering Trans. Inst. Met. Finish. 61, in press (1983).

5. A.K. Turner and D.G. Lovering, Trans. Inst. Met. Finish. <u>58</u>, 109, (1980).

6. A.K. Turner, thesis, London (1978).

7. See, for example, L. Campanella and A. Conte, J. Electrochem. Soc. <u>116</u>, 144 (1969); F.H. Cocks, D.R. Cogley, G.H. Holleck, G.F. Hurley and C.R. Mitchell Corrosion 32, 135 (1976). 8. See, for example, K. Hirata, H. Yoneyama and H. Tamura Electrochem. Acta <u>17</u>, 793 and 803(1972); E.L. Krongauz, V.D. Kascheev and V.D. Busse-Machukas Soviet Electrochem. <u>8</u>, 1219 (1972); V.P. Yurinskii, N.B. Vorob'eva, A.G. Morachevskii, A.E. Ivanov and E. Yu. Riskina Zhur. Priklad. Khim. 52, 221 (1979).

9. R.K. Nigam and R.S. Chaudhary Electrochim. Acta 17, 1765 (1972).

10. A. Conte, A. Borello and A. Cabrini J. Appl. Electrochem. <u>6</u>, 293 (1976).

11. A. Charlesbey Proc. Phys. Soc. B66, 317 (1953).

12. J.W. Diggle, T.C. Downie and C.W. Goulding Chem. Rev. <u>69</u>, 365 (1969).

13. "Transition Metal Oxides: Crystal Chemistry, Phase Transitions and Related Aspects" C.N.R. Rao and G.V. Subba Rao, U.S. Dept. Commerce, Nat. Bur. Stds. NSRDS - NBS 49, June (1974).





Formation Voltage,V

Figure 1. Current-voltage curves for anodising (a) titanium in anhydrous $(NH_2)_2CO-NH_4NO_3$ at 63.5°C (b) titanium in "wet" (NH₂)₂CO-NH₄NO₃ at 63.5°C, all curves, steady currents after 3 mins. (c) aluminium in anhydrous $LiNO_3-KNO_3$ at $140^{\circ}C$ (d) aluminium in "wet" LiNO3-KNO3 at 140°C Figure 2. Photoresponse curves at

360mm under 1V polarisation vs. s.c.e. in aqueous 0.1M Na₂SO₄ at 20°C.

Figure 3. Current-voltage curves for anodising niobium and tungsten in $(NH_2)_2CO-NH_4NO_3$ at 63.5°C. Nb in anhydrous melt, current after 3 mins, W in "wet" melt after 1 min. NOTE: current density scale for tungsten shown X4.



Figure 3

ELECTRODEPOSITION OF TUNGSTEN CARBIDE COATINGS FROM MOLTEN SALTS

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Dense, adherent coatings of tungsten carbide have been electrodeposited on nickel substrates from the ternary (Li, Na, K)F eutectic at 750-800°C. The source of tungsten was Na₂WO₄; the source of carbon was K_2CO_3 . The concentration of both solutes was less than 10 wt%. By applying a voltage between a tungsten anode and the nickel cathode, the anions are reduced to the elements and react on the cathode to form the carbide. Current efficiencies of up to 50% have been achieved for the deposition of W_2C . The dependence of surface structure on melt composition is shown.

Introduction

Refractory carbide coatings provide good protection for metal substrates because of their great hardness and good oxidation resistance at moderately high temperatures. Tungsten carbide coatings have been prepared commercially by plasma processing in which the finely divided carbide impinges directly on the surface to be coated. Rowever, this method requires very high temperatures and is line-of-sight.

Electrodeposition from molten salts offers the advantages of lower temperatures, the ability to coat complex shapes, and the fine control that can be applied to electrical variables.

We have recently shown (1) that adherent coatings of tantalum carbide can be electrodeposited from the ternary (Li, Na, K)F eutectic (FLINAK) containing $K_{2}TaF_{7}$ as the source of tantalum and $K_{2}CO_{3}$ as the source of carbon. The method depends on the simultaneous deposition of tantalum, first worked out by Senderoff, Mellors, and Reinhart (2), and carbon. The elements react on the cathode at 750-800°; a temperature ~600° lower than that of the reaction of the elements in bulk.

Tungsten carbide was first prepared electrochemically by Weiss (3) from an alkaline borate-fluoride melt containing WO_3 as the source of tungsten and Na_2CO_3 or Li_2CO_3 as the source of carbon. Small crystals, whose composition depended on the carbonate/oxide ratio, were produced. More recently Gomes and Wong (4) reported the electrodeposition of WC from a NaCl melt containing Na_2WO_4 as the tungsten source and a graphite anode as the source of carbon. However, this method was not intended to produce a protective coating. Senderoff and Mellors (5) reported the deposition of dense, adherent tungsten metal coatings from FLINAK melts. However, their method is complicated by the requirement that the valence of tungsten be +4.5, which is achieved by the reaction of $WF_6(g)$ with metallic tungsten dispersed in the melt. The authors concluded that an irreversible step is required for the deposition, but did not otherwise elucidate the mechanism.

Because the preparation of $W^{4.5+}$ is rather cumbersome, we investigated the possibility of plating tungsten using WO_4^- as the solute; Gomes and Wong (4) had already shown the reduction occurred in NaCl. Senderoff and Mellors (2,5) had found that FLINAK was necessary to form adherent coatings, therefore we retained FLINAK as the solvent. Because F is more electronegative than O^- and is present in large excess, the effective species for electrodeposition may be a tungsten fluoride complex; e.g.

$$WO_4^{2-} + nF^- = WF_n^{6-n} + 40^{2-}$$

This procedure was successful and, combined with simultaneous carbonate reduction, has led to adherent tungsten carbide coatings.

Experimental

The procedure follows closely that employed for tantalum carbide deposition (1). Reagent $Na_2WO_4.2H_2O$ was vacuum-dried at 150° to remove water.

Quarter inch diameter tungsten rods were obtained from the Rembar Company.

Results

Current-voltage curves were determined for the addition of Na_2WO_4 in FLINAK using the cell C/FLINAK + Na_2WO_4/C . As described previously (1), the solvent was first pre-electrolyzed between carbon electrodes to remove impurities. As seen in Fig. 1, the current increases substantially, even at very low Na_2WO_4 concentrations relative to the pure solvent, showing that the solute is electro-active. Fig. 2 shows current-concentration curves at various constant voltages for the data in Fig. 1. At low voltages the current is low and nearly independent of concentration. As the voltage increases, the concentration dependence of the current becomes more pronounced and rises linearly after an initial rapid rise. Corresponding curves for carbonate reduction in FLINAK were published previously (1). We have not made any attempts to elucidate the electrode reactions. Although the mechanism is unknown, hexavalent tungsten is reduced on the cathode to the metal. The

anodic reaction is believed to be the oxidation of 0^{2-} to elementary oxygen.

When tungsten is to be plated, the inert carbon anode is re_{2}^{-} placed by a tungsten anode and the anodic process changes from 0^{2-} oxidation to tungsten oxidation. Therefore, assuming the same electrode area, for a given voltage the current will be much larger. For example, at 1.5V the current increased by a factor of ~5 when the carbon anode is replaced by tungsten. Electroplating experiments were carried out at 1.5V to maintain the current below 2A, the limit of the coulometer.

Because tungsten coatings previously had not been obtained from tungstate-containing melts, a series of experiments was run in which tungsten was plated onto nickel coupons (5x0.8cm) from FLINAK melts containing various concentrations of Na₂WO₄. The plated cathodes were cleaned ultrasonically to remove loose deposit and adherent frozen melt. The current efficiencies were determined by weighing the cleaned cathodes. Thus, they are less than electrochemical efficiencies, which apply to the total reduced material, but are more significant for a material of interest as a coating. Current efficiencies were based on W⁰⁺ + 6e = W⁰ and CO³ + 4e = C + 30⁻ (when carbide is being plated) as the only cathodic processes. Therefore, the weight of material theoretically plateable depends on the nature of the deposit. For example, for 0.01 equivalents of charge passed, the weights of W, W₂C, and WC are 0.306, 0.207, and 0.186 grams, respectively.

Current efficiencies (C.E.) for plating adherent tungsten alone generally did not exceed 20%, but higher C.E. were achieved for some carbides. Table 1 summarizes the results of several experiments relating melt composition, stoichiometry of the deposit (identified by X-ray diffraction), and C.E. Although the results are somewhat contradictory, some tentative conclusions emerge: (a) Composition -The usual composition of the coating is W_2C . Whether WC is produced depends not only on the C/W ratio, higher values favoring WC, but also on the individual concentrations. For example, with 3wt% each of Na₂WO₄ and K_2CO_3 , (C/W = 2.13) W₂C is produced; but at 7% each, WC is formed; for $C/W \le 2$, only W_2C forms. These results contrast with those of Weiss (3), who used borate melts and found that W₂C formed for $4 \le C/W \le 7$, WC formed for C/W between 12 and 14 and mixtures were obtained between 7 and 12. Evidently the reaction medium and/or other differences between the two processes also affect the composition of the deposit. Current efficiencies are generally in the range 30-50% for W_2C , but are less for WC. (b) Surface Features - Deposits were examined by scanning electron microscopy (SEM), both for the surface features and the crosssection. A typical example of the latter is shown in Fig. 3. In contrast to tantalum carbide, which shows a broad Ta-Ni interdif-

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fusion zone between the carbide coating and the nickel substrate, an interdiffusion zone between the tungsten carbide coating and the nickel substrate is not visible.

Although all the coatings examined exhibit the same gross crosssectional features, this is not true of the surface features. Figures 4 to 9 show a series of W_2C coatings at 2000X for various melt compositions between 2 and 7 wt% Na_2WO_4 and K_2CO_3 . For the more dilute melts (Figs. 4 and 5) the crystals exhibit a substructure which is clearly evident at 5000X. For melts 6 and 7 wt% Na_2WO_4 (Figs. 6,7,8) substructure is absent, although the carbonate concentration varies from 3 to 5% ($1.06 \le C/W \le 1.52$). However, a small increase in the carbonate concentration, from 5 to 7% (C/W =2.13), has a dramatic effect on both stoichiometry and structure (Fig. 9). The coating now is WC, and the coating consists of balllike structures; angular crystals are not evident. The relation of these surface features to the wear characteristics of the coatings remains to be explored.

Oxidation Tests

The oxidation resistance of the coatings was tested in still, ambient air. Coated specimens were contained in small, open alumina crucibles in a Mettler TGA apparatus, capable of measuring weight changes to \pm 0.1mg. The temperature was raised in 50° steps to determine the temperature at which weight changes became noticeable. A weight loss was taken to indicate the oxidation of carbon (without oxidation of tungsten), whereas a weight gain indicated the oxidation of tungsten as the predominant reaction.

Several representative samples were tested to see if the oxidation resistance is related to the melt composition and the deposition parameters. Six of the seven samples tested had been analyzed by X-ray diffraction to be W_2C , one was WC. For all the W_2C samples, weight changes began near 450°, and each gained weight rapidly above 600°. The final product was always an adherent coating of WO_3 . Some variations in stability occurred within this temperature range, but we cannot unambiguously attribute these reactions to differences in the electrodeposition procedure.

References

- 1. K. H. Stern and S. T. Gadomski, J. Electrochem. Soc. <u>130</u>, 300 (1983).
- S. Senderoff, G. W. Mellors, and W. J. Reinhart, J. Electrochem. Soc. <u>112</u>, 840 (1965).
- 3. G. Weiss, Ann. Chim. [12] 1, 424 (1946).
- 4. J. M. Gomes and M. M. Wong, U. S. Bur. Mines Report. Invest. 7247 (1969).
- 5. S. Senderoff and G. W. Mellors, J. Electrochem. Soc. <u>114</u>, 586



 $$\rm Fig.\ 3$$ Cross-section of tungsten carbide coating on nickel substrate



13 U 3

W X-ray map

а

Ъ



Ni X-ray map



2000X

а



Fig. 4 Surface of $\rm W_2C$ coating. 2wt% $\rm Na_2WO_4,~1\%~K_2CO_3$

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2000X



b

5000X

618



Fig. 6 Surface of W₂C coating 6% Na₂WO₄, 3% K₂CO₃, 2000X



Fig. 7 Surface of W_2C coating 7% Na_2WO_4 , 5% K_2CO_3 , 2000X



562C Fig. 8 Surface of W₂C coating 7% Na₂WO₄, 4% K₂CO₃, 2000X

Fig. 9 Surface of WC coating. $7\%~{\rm Na_2WO_4},~7\%~{\rm K_2CO_3}$



2000X



b

а

5000X

CALCIUM NITRATE TETRAHYDRATE AS AN ELECTROLYTE FOR ANODE DEPOLARIZATION BY COAL SLURRIES

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The electrochemical properties of calcium nitrate tetrahydrate were studied for use in coal electrogasification. The anode reaction was oxidation of water to oxygen at +1.1--.3V on either gold or platinum. A 1-2% slurry of coal at the anode lowered the electrolyte decomposition potential by approximately 0.65V and yielded CO₂ as product. The major electrolyte reaction on gold was reduction of nitrate to nitrite, with concomitant formation of a solid calcium hydroxide/nitrite electrode film. Small amounts of oxygen and more than the theoretically predicted qauntity of nitrite were detected, suggesting a secondary chemical reaction between oxide and nitrate to give nitrite and peroxide. The reduction reaction at platinum cleaned in nitric acid gave 50-75% of theoretical nitrite, but no detectable hydrogen or any other reduced nitrogen compounds. This suggested the reduction of a platinum oxide/adsorbed oxygen film, but the charge consumed represented hundreds of "monolayers" of oxide. The unidentified reduction at platinum gave in cyclic voltammetry a <u>cathodic</u> current peak at -1.25V in both the cathodic scan and the return <u>anodic</u> scan. The major electrolysis products were identified by their irreversible voltammetric peak potentials: OH- oxidation at +1.0-.1V (Au), +0.8-.9V (Pt); NO $_{2}$ oxidation at +0.4-.6V (Au, Pt); HNO $_{3}$ reduction at approximately OV (Au, Pt). The oxidation of HNO3 at Pt was complex, giving different peak shapes depending upon concentration and scan rate; one form exhibited a cathodic peak on the anodic return scan.

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Coughlin and Farooque (1) first demonstrated that hydrogen from the electrolysis of 4M sulphuric acid was produced at a lower voltage when coal was suspended in the stirred anolyte, and proposed that the production of oxygen in the anodic half-cell reaction:

$$2H_2O - 4e^- \longrightarrow 4H^+ + O_2$$

had changed to a direct anode-coal contact oxidation:

$$2H_2O + C - 4e^- \longrightarrow 4H^+ + CO_2$$

Subsequently, the exact mechanism of reaction and the species involved (especially iron) have been the subject of some debate (2). In an effort to both improve the efficiency and clarify the mechanisms of this coal electrogasification reaction we tested for anode depolarization in a number of different solvent systems. Having found that an anolyte coal slurry does reduce the appearance potential for electrolysis of a concentrated acid (85% phosphoric) and an ionic molten slat ($NaHSO_4$, 250° C) by 0.9 to 0.95V, we went next to molten calcium nitrate tetrahydrate.

Molten calcium nitrate tetrahydrate and similar molten hydrates are of considerable interest as solvents with properties intermediate between those of aqueous solutions and ionic melts. Conductance measurements (3), additivity of molar volumes (4), PMR studies (5), entropies of solution (6), diffusion coefficients (7,8, but see 9), accoustic velocity measurements (10) and X-ray diffraction measurements (11) all indicate that the water molecules in calcium nitrate tetrahydrate melts are strongly coordinated to the calcium ion. The result is a liquid with the properties of an ionic melt composed of bulky $(Ca(H_2O)_{+})^{+2}$ cations and nitrate anions. The low melting point of this compound (42.7°C), together with a metastable supercooled phase extending to room temperature, thus allows the direct comparison of an "ionic" solvent with dilute aqueous solutions.

Calcium nitrate tetrahydrate has been used as a supporting electrolyte in the electrochemical investigation of a number of cations (7-9, 12-17). Courgnaud and Tremillion (18) have investigated the electrochemistry of the molten hydrate itself at gold and platinum electrodes using both bulk electrolysis followed by chemical analysis and single sweep voltammetry. The anode reaction was found to give oxygen and protons, as expected for water electrolysis, but at a potential almost 0.7V more negative for Au than for Pt. The authors concluded, on the basis of their finding no detectable concentration of nitrite ion after electrolysis with a platinum cathode, that the electrolylic reduction of this melt also involved only water. Like the anode reaction, reduction appeared to occur at a more negative potential (0.3V) at gold than at platinum. These solvent electrolysis properties appeared useful for a coal electrogasification study, since only water was electrolyzed and some control over initial decomposition potentials appeared to be available simply by changing electrode materials. Our preliminary results, however, did not correspond to those reported, and we therefore reexamined in detail the electrochemical properties of calcium nitrate tetrahydrate.

Results

A well stirred 1-2% anolyte slurry of lignite, lignite char or graphite was found to reduce the appearance potential for calcium nitrate tetrahydrate electrolysis by approximaltey 0.65V. Current/ voltage profiles were run at stepped anode/cathode voltage differences by measuring current and anode potential values after three minutes at constant voltage. Figure 1 shows current/voltage profiles observed for char and lignite slurries at 115-20°C using a 66.4 cm² Pt anode and Au cathode; graphite was similar to lignite, but with lower limiting currents. Limiting currents were found in the range 0.03 to 0.3mA/cm² for char and 0.02 to 0.25mA/cm² for lignite. Both the low limiting currents observed and the higher limit for char were typical for these systems.

Chromatographic analysis of the gaseous products of char or lignite electrogasification in calcium nitrate tetrahydrate, after correction for chemical oxidation by the electrolyte, revealed no detectable hydrogen but 150% (char) to 250% (lignite) of the theoretical amount of carbon dioxide predicted for direct electrooxidation. No oxygen was detected, although nitrous and nitric oxides were observed. The carbon dioxide could have been the result of several processes besides direct electrooxidation. Nitric acid formed at the anode during electrochemical oxidation could act as a powerful chemical oxidant as was demonstrated by electrolysis of pure calcium nitrate tetrahydrate in an apparatus sealed by rubber stoppers, which yielded 30-70% of theoretical CO_2 . Chemical oxidation of partially electrooxidized coal by the solvent could also result in excess CO_2 . In the case of lignite, electrooxidation of partially oxidised material could also result in CO_2 levels higher than predicted.

The products of oxidation of pure calcium nitrate tetrahydrate $(90-95^{\circ}C, +1.3V \text{ vs. } \text{Ag/Ag}^+ \text{ ref.})$ at a platinum anode were oxygen and nitric acid, as reported (18). The nitric acid concentration in the gases above the electrolyte was substantial, and resulted in chemical attack on the gas sampling bag used in the apparatus, as well as any rubber or tygon seals or connectors used. The measured quantity of oxygen produced in such cases was somewhat variable. In a glass apparatus plus sampling bag with relatively short contact times or in runs where the theoretical amount of $Ca(OH)_2$ had been added to neutralize HNO₃, oxygen production was $100\pm5\%$ of theoretical.

The major product of reduction at a gold cathode $(90-95^{\circ}C, -1.2 \text{ to} 1.3V)$ was nitrite, as detected by both spectrophotometry (Marshall's Reagent) and Ce(IV)/Fe(II) redox titration (methods agreed within 1%). Figure 2 shows the total amount of NO₂ as a percentage of the theoretical yield relative to the total number of coulombs passed. The amount of nitrite detected in excess of 100% (8% at 68 coulombs) was well above the total estimated error. A white film was also produced on the cathode: it was relatively insoluble in water but easily dissolved in nitric acid. No significant gas bubble formation was observed on the electrode during electrolysis; indeed, the only significant gaseous cathode product was a small amount of oxygen, observed after extensive electrolysis (100-350 coulombs), amounting to 5-10% of the theoretical nitrite value. After the most extensive electrolysis, traces of hydrogen and nitrous oxide were also detected by GC.

The major product of reduction of calcium nitrate tetrahydrate at a platinum cathode (90-95°C, V-1.2 to 1.3V) was again nitrite ion, although in considerably lower yield. Figure 2 shows nitrite produced at a Pt electrode, cleaned in concentrated nitric acid before each run, as a function of total coulombs passed. Electrodes not cleaned in a systematic manner before use gave less regular nitrite/coulomb re-A white, water insoluble film was again formed on the lationships. electrode. Gas bubble formation on the electrode was sometimes observed to a slight extent. No measurable quantities of gaseous products could be detected, although traces of oxygen and nitrous oxide were suggested by GC analysis. Electrolysis under a propane atmosphere showed no significant production of nitrogen. The possibility of further reduction of nitrite ion at the electrode was considered. No significant quantities of the gaseous reduction products NO, N₂O, or N₂ were detected by GC, nor was any trace of the characteristic colour of $\rm NO_2$ or the characteristic smell of $\rm NH_3$ observed at any time. In two cases the catholyte was analyzed both by Ce(IV)/Fe(II) redox titration and spectrophotometrically for nitrite. The reducing capacity of the catholyte was found to be equivalent to the quantity of nitrite present, indicating that no other soluble oxidizable products of NO_2 reduction had been formed.

In an attempt to clarify the above results, calcium nitrate tetrahydrate was examined by means of linear sweep and cyclic voltammetry. Figure 3 shows full range (+2.0 to -2.5V) and partial range (+1.4 to -1.2V) cyclic volatammograms obtained for this electrolyte using both gold (0.062 mm^2) and platinum (0.018 mm^2) electrodes. All potentials were relative to a Ag/(0.05 molal Ag^+ in calcium nitrate tetrahydrate) reference electrode. The electrolyte oxidation potentials were found to be similar (+1.1 to 1.3V) for both Au and Pt, in contrast to the previously reported (18) difference of 0.7V. The major cathodic process was attributed, from the chemical evidence, to reduction of nitrate to nitrite with concommitant formation of an insulating film on the electrode. The apparent peak <u>A</u> in Figure 3 which occurred consistently at -1.5V with both Au and Pt electrodes at 50mV/s, was an artifact of film formation. If the reverse sweep potential was not taken above +0.7 to 0.8V, all current flow ceased. Increasing the sweep rate resulted in large cathodic shifts in the "peak" position as well as large increases in the maximum current, with the maximum shifted to the -2.5V limit at rates greater than 1V/s.

The electrode film produced during reduction of nitrate was removed by the oxidative process giving rise to anodic peak B of Figure 3 in the area of +0.8 to 1.3V. This peak was not observed where the cathodic sweep did not go beyond -1.0V. With increasing sweep rate the peak maximum shifted to more anodic values and peak current in-This position was found to correspond to the oxidation creased. potential of calcium hydroxide solution in calcium nitrate tetrahydrate, which was examined in detail. Cyclic voltammetry of this solution between +0.5 and +1.3V showed a single broad anodic peak with no trace of a corresponding cathodic peak on the return sweep. Maximum peak currents decreased rapidly on subsequent cycles. Peak voltages were similar for Au and Pt electrodes (Table 1). The single sweep peak current varied linearly with concentration for both electrodes up to approximately 0.02 molal, but fell off sharply at 0.025 molal; both gave lines with similar slopes, with a zero intercept for Au and a small positive current intercept for Pt. A linear relationship between peak current and the square root of scan rate was found for scan rates from 10 to 300 mV/s for both metals, with a similar slope and small negative current intercept for each.

Table 1

PEAK POTENTIAL VALUES OF ELECTROACTIVE SOLUTES

$$Ca(NO_3)_2 \cdot 4H_2O_1, 70^{\circ}C$$

solute	0.005 molal Au Pt		0.025 molal Au Pt		
Ca(OH) ₂	+1.03	+0.84	+0.99	+0.88	
NaNO ₂	+0.42	+0.55	+0.44	+0.47	
HNO ₃	+0.17	+0.03	+0.31	+0.28*	

I Variable Concentration, 50 mV/sec

II Variable Scan Rate, 0.010 molal

	25 mV/sec		300 mV,	/sec	
solute	Au	Pt	Au	Pt	
Ca(OH) ₂	+1.01	+0.83	+1.08	+0.86	
NaNO ₂	+0.44	+0.45	+0.45	+0.55	
HNO ₃	+0.23	+0.23*	-0.3	+0.05	

* leading peak

Voltammetry cycles between +1.3 and -1.3V gave rise to an additional anodic peak at approximately +0.5V on a gold electrode (peak D, Figure 3). This was identified as the oxidation peak of nitrite ion by studies of dilute solutions of sodium nitrite in calcium nitrate tetrahydrate. Cyclic voltammograms of such solutions showed a broad peak near +0.5V (Table 1) with both Au and Pt electrodes; peak currents decreased rapidly on subsequent cycles. Both metals also gave a small shoulder about 0.2V less anodic, which disappeared on subsequent cycles. The gold electrode gave a small additional anodic peak near +0.75V. Single sweep voltammetry anodic peak currents were shown to vary linearly with concentration for both metals (similar slopes, intercepts near 0) up to about 0.015 molal $NaNO_2$; the slope curved down sharply for Au and more gradually for Pt above this concentration. The peak current/(sweep rate)¹/₂ relationship was linear from 10 to 300 mV/s, with a small positive intercept and a slope slightly greater for Au than Pt. This relationship was also roughly linear for the small +0.75V peak on gold.

Cyclic voltammetry of NaNO₂ solutions with either Au or Pt gave, on the cathodic sweep, a broad cathodic peak at +0.1 to 0.3V, also seen in the voltammograms of pure calcium nitrate tetrahydrate (peak <u>C</u>, Figure 3), and identified as characteristic of nitric acid (below). An additional sharp cathodic peak was also seen with a gold electrode in both systems (peak <u>Z</u>, Figure 3), and was investigated further. Cyclic sweeps in 0.01 molal NaNO₂ at 100 mV/s were run from -0.2V to positive potentials beginning at +0.6V and incremented by +0.1V. The sharp cathodic peak was just detectable (at +0.66V) on the return from a sweep to +0.8V. The peak grew and shifted to +0.56V over the next 3 cycles (to +1.1V), after which it stayed approximately constant. A similar experiment run with pure calcium nitrate tetrahydrate, however, showed no trace of this peak until anodic sweeps to +1.3 to 1.4V were run, i.e. until some nitric acid had been generated by solvent electrolysis. In addition, cycles run as far as +1.3V in circumstances where an oxidizable species (NO₂, OH⁻, film) was present but nitric acid could not persist (eg. sat. $Ca(OH)_2$) did not produce a +0.56V peak on the cathodic return, but rather led to a new cathodic peak at -0.2V. This indicated that the formation of the electroactive species responsible for the +0.56V peak required both a potential greater than +0.7V and the presence of nitric acid.

The electrochemistry of nitric acid in calcium nitrate tetrahydrate proved to be very complex, giving considerably different voltammograms with gold and platinum microelectrodes. With gold, a sweep from +1.0 to -0.5V gave two cathodic peaks (Figure 4, Table 1): a large, broad peak at about +0.2V and a sharp peak, corresponding to peak \underline{Z} above, at about +0.6V. The former peak current varied linearly with added HNO₃ concentrations up to 0.025 molal at a sweep rate of 50mV/s (Figure 5). The sharp peak showed an approximately constant current at all HNO₃ concentrations. The peak current/(sweep rate)^{1/2} relationship for the broad peak due to 0.010 molal HNO3 was composed of two linear portions with a distinct break between 100 and 150mV/s, also observable in the peak potential values (Figure 6). The anodic sweep of the cycle showed a broad peak at about +0.5V (Figure 4), the position of nitrite reduction. An anodic shoulder and a minor peak at 0.8V, observed in the case of NO_2^- were also seen here. The drop in cathodic peak current on repeated cycling was relatively small for the broad HNO_3 reduction peak, while the return NO_2 oxidation peak increased in size. A relatively stable reduction/oxidation cycle could be achieved by cycling between +1.0 and 0.0V.

The shape of the voltammetric curves due to nitric acid on a platinum electrode was dependent upon both the nitric acid concentration and the sweep rate. At low concentrations or high sweep rates the cathodic sweep gave a single peak near 0.0V (Table 1), of a simple symmetrical shape with a trailing diffusion current much smaller than that from a gold electrode. The return anodic sweep gave a broad peak at +0.6V, characteristic of nitrite oxidation. At low sweep rates or high concentrations the voltammograms had the form shown in Figure 4. On the cathodic sweep, a relatively sharp peak appeared to be superimposed upon the leading edge of a broadened peak or "plateau" region around OV which terminated over a range of 150mV in the area of -0.2V. The <u>anodic</u> return sweep, starting from 0 current, produced a strong <u>cathodic</u> current, again with the form of a sharp peak superimposed on This was followed by the leading edge of a broad peak around +0,2V, a typical anodic nitrite peak at +0.6V. The relationship observed between cathodic peak currents and HNO3 concentration at a 50mV/s sweep rate is shown in Figure 5. The transition between simple peaks and the type shown in Figure 4 occurred between 0.005 and 0.010 molal. Figure 6 shows the dependance of cathodic peak currents on (sweep rate) $\frac{1}{2}$ for 0.010 molal HNO₃. Voltammograms of the type shown in Figure 4 occurred at sweep rates of 50mV/s or less, simple voltammograms were observed at 200mV/s or greater, and transitional shapes were observed at intermediate sweep rates. This transition was a function of both sweep rate and concentration: the transitional area for 0.019 molal HNO₃ was between 100 and 300mV/s, while for 0.1 molal acid it had just started at 1V/s. A further complication was observed in a 50mV/s cyclic sweep of 0.01 molal nitric acid between +1 and -0.8V. In this case a small new cathodic peak appeared on the cathodic sweep (-0.7V), and an additional anodic peak appeared on the anodic sweep (-0.6V). The appearance of these peaks was accompanied by deterioration in the +0.2V cathodic peak (in the anodic sweep), which completely disappeared if the cathodic sweep was taken beyond -1.1V. A similar set of small peaks at a slightly more anodic potential was also detectable in the pure solvent voltammograms (peaks R and S, Figure 3).

Aside from nitric acid reduction, the most marked difference between calcium nitrate tetrahydrate voltammograms using Au and Pt microelectrodes was the appearance of a large cathodic peak at -1.25V (peak Y, Figure 3) only with platinum. The peak, which partly overlapped the nitrate reduction "peak", was presumed to represent the process which did not lead to nitrite production during coulometric analysis using a Pt cathode at -1.2V to -1.3V. Cyclic voltammograms were run from various positive potentials to -1.35V. Those run from +0.7V or less deteriorated rapidly to 0 current flow. However, cycles from +1.25V to -1.35V gave a stable system which showed the -1.25V peak on the cathodic sweep. On the <u>anodic</u> sweep, a <u>cathodic</u> current peak appeared at approximately the same potential (Figure 7). The only other current observed was an anodic peak at +1.0V, as expected for hydroxide film removal. Table 2 shows the results obtained from cyclic voltammetry at various sweep rates; as rate increases the cathodic peak current stays almost constant while the anodic sweep cathodic current increases until it is the greater of the two, then levels off. Peak potentials are almost constant throughout. In order to determine which reaction was responsible for film formation, 500mV/s cyclic voltammograms were run from 0.0V to negative potentials starting at -1.20V and incremented by -0.05V. Runs to -1.20 and -1.25V showed no significant change in the maximum (edge) current after 10 cycles. Runs to -1.30, -1.35, and -1.40V showed a drop in maximum current of 10, 20 and 40% respectively after 10 cycles. Thus, film formation appeared much more closely related to the nitrate reduction "peak" than to peak Y.

The effect of added water on the voltammetry of calcium nitrate tetrahydrate was studied. Full +2.0 to -2.5V cycles at 50mV/s with a gold electrode and added water (1 to 10 molal) showed no additional peaks. The nitrate reduction "peak" height increased with water concentration, as did the film/hydroxide oxidation current peak. A general increase in current flow beyond -1.5V was also observed. The platinum electrode behaved similarly, but the unique peak Y appeared to decrease slighly in size and shift to a slightly more anodic value.

Table 2

Peak Current and Potential Values, $Ca(NO_3)_2 \cdot 4H_2O$, 70°C, Pt Electrode +1.25 to -1.35V, Variable Scan Rate

Scan Rate (mV/sec)	Cath. Vp(V)	Scan I*	Vp(V)	Anodic Sc I*	an Vp(V)	I*
50	-1.21	-0.94	-1.17	-0.31	+0.9	0.19
100	-1.22	-1.25	-1.20	-0.86	+1.0	0.31
250	-1.22	-1.31	-1.31	-1.42	+1.0	0.47
500	-1.22	-1.31	-1.20	-1.53	+1.0	0.58
1000	-1.21	-1.31	-1.20	-1.53	+1.0	0.69

 $* mA/mm^2$

Examination of the peak shapes suggested that the apparent loss of peak height was due to a decreasing contribution from the edge of the nitrate reduction current rather than an actual decrease in cathodic peak current. With both electrodes, the current flow did not entirely cease on the initial part of the return anodic sweep at high water concentrations. This suggested that the increased peak heights were due to better dissolution of electrode film with increasing water concentration. Peak current values obtained from 50mV/s cyclic voltammetry between +1.4V and -1.4V are shown in Table 3 as a function of added water concentration. The cathodic peak potential becomes slightly more positive with increasing water content, while the <u>anodic</u> sweep <u>cathodic</u> current increases. These peak current changes may again be related to electrode film dissolution by water.

Attempts to detect a number of other species in calcium nitrate tetrahydrate solution by voltammetry were not successful. Bubbling of oxygen, hydrogen, or nitrous oxide for up to 1/2 hour gave no detectable peaks in this solvent or in solvent saturated in Ca(OH)₂, although changes in the nitrate reduction area beyond -1.5V were noted in the latter two cases. The lack of reactivity of oxygen has been noticed previously (8,18), and attributed to the low solubility of the gas in this melt.

Table 3

Peak Current and Potential Values, H₂O/Ca(NO₃)₂·4H₂O, 70°C, Pt Electrode +1.4 to -1.4V, 50 mV/sec

[H ₂ 0] (molal)	Cath. So Vp(V)	can I*	And Vp(V)	odic Scar I*	Vp(V)	I*
0	-1.27	-3.05	-1.22	-1.35	+1.12	0.75
1	-1.24	-2.80	-1.21	-1.35	+1.05	0.95
2.5	-1.23	-2.55	-1.20	-1.40	+1.00	0.65
5	-1.20	-2,25	-1.19	-1.45	+0.95	1.05
7.5	-1.19	-2.15	-1.17	-1.70	+0.90	0.85
10	-1.19	-2.35	-1.19	-2.35	+0.86	1.15

 $* mA/mm^2$

Discussion

The solvent oxidation reaction in calcium nitrate tetrahydrate appears to be a straightforward oxidation of water. We have not been able to reproduce the 0.7V difference in oxidation potential previously observed (18) between gold and platinum electrodes in this electrolyte. Both voltammetry and the potentials observed during bulk electrolysis indicate similar oxidation potentials at both electrode materials. If the previous workers used the gold electrode to find the cathode limit first, it is possible that the current observed during the anodic sweep was due to oxidation of a calcium hydroxide/nitrite film on the electrode. The value observed here for the oxidation potential at a platinum electrode is similar to that reported by these workers, after correction for the difference in reference electrodes.

The major solvent reaction at a gold cathode is clearly reduction of nitrate to nitrite ion. The excess of nitrite observed appears to be real, and when coupled with the observation of oxygen as a cathode product suggests the results observed in the reduction of alkali nitrate melts (19). In these systems, oxide dianions produced in the electrochemical reduction of nitrate react chemically with nitrate ion to give additional nitrites and peroxide ions. The existance of oxide ions in a hydrate melt appears unlikely, but in this system an insoluble basic film as shown by cyclic voltammetry forms rapidly on the cathode. Similar films occur at the cathode during the reduction of $Ca(NO_3)_2/KNO_3$ melts (20). Local depletion of water could occur near the electrode surface, allowing oxide ions to exist long enough to react with nitrate. The concentration of free water in these systems is low, and the rate of diffusion of bulky $(Ca(H_2O)_4)^{+2}$ into the film should be relatively slow. Peroxide ions produced by the oxide/nitrate reaction would diffuse out and produce oxygen after reaction with water. This evidence for the production of oxide dianion suggests that water is not involved in the initial electrochemical reduction reaction.

The previously reported 0.3V difference in solvent reduction potential between Au and Pt appears to be due to the identification of the slope of peak \underline{Y} (Figure 3) as due to solvent reduction; a peak in this position was in fact observed in voltammetry of the 2.6H₂O hydrate melt (18). The fact that the reaction represented by peak \underline{Y} does not give nitrite as a reduction product explains why the authors concluded that water reduction was the major solvent reaction in this system.

The reaction represented by peak Y has not been identified with confidence. The apparent absence of both hydrogen and nitrogen-bearing reduction products suggests that reduction of a platinum oxide film is occurring. The observed reaction, however, represents a very large quantity of material. If one assumes that the roughly linear increase in nitrite production (Figure 2) represents a linear decrease in peak Y material, the $NO_{2}/coulomb$ data can be used to estimate that, with \overline{a} 19 cm² platinum electrode, about 12.5 coulombs or 0.65 coulombs/cm² are required for the complete reduction of this material. The surface area of bright platinum has been estimated to be 1.5 to 2.5 times the theoretical value by hydrogen charging experiments. These values imply that the total charge required to reduce one monolayer of PtO will be 400 to 650 C/cm² (21-23). It has been demonstrated that more than one monolayer may be deposited on a Pt electrode but, although the exact nature of this oxide/oxygen film is controversial, there is general agreement that it amounts to no more than 2-5 additional "monolayers", whether deposited by anodization (21-24) or chemically using HNO_3 (25-27). This gives an estimated charge required for complete film removal of 1-3 mC/cm², or approximately 300 time less than the estimated charge consumed here. Although it has been shown that the effective area of Pt-black/Pt electrodes can be over 100 times greater than shiny Pt (21), there is not visual evidence for surface changes of that magnitude in this case. The large charge capacity of the reaction is confirmed by the large peak current observed for this reaction by voltammetry. The estimated peak area in Figure 3 represents about 120μ C, which on the microelectrode surface of 0.018mm² converts to a value of $0.7C/cm^2$. It thus appears either that Pt exhibits a much

greater capacity for oxygen/oxide adsorption/coating in this system than in other (mostly acidic) electrolytes tested or that some, as yet unidentified, product of nitrite reduction has been formed.

The uncertainty in identification of the reaction represented by peak Y is complemented by the unusual behavior of this peak during cyclic voltammetry. The observation of cathodic peaks during the anodic sweep of the cycle has been reported in a few other cases. Johnson and Sawyer (28) observed this phenomenon during the study of N₂O reduction in alkaline aqueous solution. The cathodic sweep was found to give a cathodic peak at a Pt (but not Au) electrode in the presence of N₂O. Reversing the sweep direction, after this peak had been passed, again gave a cathodic peak at the same position. The authors proposed that N₂O had to be adsorbed upon a clean Pt surface before it could be reduced. Such adsorption only occurred at potentials below a value slightly more negative than that required for reduction. At more negative potentials the N₂O molecules were desorbed from the electrode and reduction ceased until, on the reverse sweep, the potential became low enough to once again allow adsorption.

Narayan et al. (13-15), using a hanging mercury drop electrode in calcium nitrate tetrahydrate melt, have observed cathodic peaks in the anodic sweep of cyclic voltammograms of Cd(II) in the presence of bromide ion or thiourea, Pb(II) in the presence of bromide, and T1(I). These peaks were attributed to convective diffusion in the mercury drop due to a non-uniform reduction of an adsorbed film. Margaretha and Tissot (29) also observed an anodic sweep cathodic peak at a HMDE during cyclic voltammetry of 1-halo alkenones in the presence of tetraalkylammonium fluoroborates in acetonitrile or DMF. These were attributed to formation of a mercury insoluble amalgam at the electrode surface which blocked further reduction until the film was oxidized on the reverse sweep. A related phenomenon was reported by Bockris et al. (30) at a Pt rotating disk electrode. In sulphuric acid, which had been chemically but not electrochemically purified, current measurements due to reduction of oxygen resulted in a peak current value as the potential was raised, with current dropping to almost 0 on further increase in potential. As the potential was lowered, this reduction peak reappeared at the same value. The decrease in current at high potential disappeared when electrochemically purified acid was used, but the effect was shown to reappear on addition of minute quantities of toluene. The phenomenon was therefore attributed to adsorption of organic impurities.

In this system, as in the preceeding, the appearace of a cathodic peak on the anodic sweep is probably associated with an electrode absorption/desorption system, but none of the previously observed examples are completely analagous. Explanations based upon the properties of mercury are obviously not applicable in this case. The mechanism proposed for N_2O (28) is a reasonable possibility, but we were unable to identify any neutral electroactive molecules which could participate in this reaction. N_2O and O_2 showed no effect upon this peak. Water did cause both a change in peak current and a small positive shift in peak potential, but in the absence of any detectable water reduction product this must be attributed to a solvent effect. An important difference in the $Ip/(scan rate)^{\frac{1}{2}}$ relationship was also observed: with the N_2O reduction peak these values were found to be directly proportional, while in this work such a relation was not found. The explanation involving trace organic impurities may be relevant to this system: reagent grade calcium nitrate tetrahydrate shipped in plastic bottles was used without further purification and may well have contained trace organics.

The overall cyclic voltammogram of calcium nitrate tetrahydrate indicates no reversible electrochemical reactions for any of the solvent oxidation or reduction products. Of the three major products, soluble hydroxide, presumably in the form $(CaOH(H_2O)_3)^+$, behaves in the simplest manner on both gold and platinum electrodes. Linear relationships with near zero intercepts are seen, for both metals, between peak current values and both the concentration up to 15-20 millimolal and the square root of scan rate up to 300 mV/s. Peak potentials show a small increase with increasing scan rate. The peak potential on Pt is in reasonable agreement with a single scan value derived previously (18).

The oxidation of nitrite also appears reasonably straightforward. Variations of peak current with concentration are again linear up to 15-20 mmolal, as is the relationship with (scan rate)^{1/2} up to 300mV/s. The detection of proportional quantities of HNO₃ on the reverse sweep indicates that the overall reaction must be:

 $NO_2^- + H_2O - 2e^- \longrightarrow NO_3^- + 2H^+$

The "shoulders" on the oxidation peaks at values about 0.2V more anodic may represent the first of two single electron transfers with slightly different energies. The inflection point of the shoulder on the nitrite/Au reduction peak appears to remain at about 1/2 Ip with changes in either concentration or sweep rate. This does not appear to be true for the less distinct shoulder on Pt, which appears to grow more rapidly than 1/2 Ip. This was also noticed in the single sweep voltammetry work of Courgnaud and Tremillion (18), who found the diffusion current representing the shoulder to be approximately proportional to concentration while the current to the second diffusion plateau was roughly constant.

A small secondary peak on the nitrate diffusion current seen at +0.75V only on a gold electrode appears to be associated with the growth of a cathodic peak at +0.6V rather than nitrite reduction. The

+0.6V peak, also unique to gold, is apparently a gold oxide film reduction peak. It is observed only in the presence of nitric acid and when the potential is more positive than +0.7V, but the peak current is independant of nitric acid concentration. The peak is narrow (Ep-Ep/2 = 30mV) and symmetrical; there is no detectable diffusion current due to this peak. In the absence of nitric acid but in the presence of oxidizable substances this peak is not observed; rather a peak with similar characteristics appears at -0.2V. This suggests at least two different forms of oxide film on gold, which may be formed in two steps:

 $\begin{array}{rcl} Au(0xI) &+& X0^{-} &-& ne^{-} &\longrightarrow & Au(0xII) &+& X^{(n-1)+} && Ep <+0.5\\ Au(0xII) &+& HNO_{3} &-& ne^{-} &\longrightarrow & Au(0xIII) &+& H^{+} &+& (NO_{2})^{(n-1)+} && Ep =+0.7\\ Nitric acid may also be able to directly oxidize Au(0xI) to Au(0xIII).\\ Au(0xII) is reduced on the cathodic sweep at -0.2V; Au(0xIII) at +0.7V. \end{array}$

The reduction mechanism of nitric acid appears complex, with substantial differences between gold and platinum electrodes. The reduction peak shape on gold is simple (Figure 4), and the relationship between peak height and concentration is linear at 50mV/s to at least 25 mmolal (Figure 5). The Ip/(scan rate)^{$\frac{1}{2}$} relationship, however, shows a sharp break to a lower slope at approximately 100mV/s (Figure 6). Changes in slope of this kind are characteristic of a change from reversible (fast electrode kinetics) to irreversible (slow electrode kinetics) systems, as is the simultaneous change from constant peak potential to decreasing peak potential observed here. In simple cases of this kind, however, there is a substantial, non-linear, "quasi-reversible" zone not seen here. Additionally, the low slope and high slope linear portions of the relationship both extrapolate to the origin in the simple system (31), whereas in this case the low slope line extrapolates to a large positive current. Behaviour of this type implies a more complex reduction mechanism. Switches from high to low slope roughly similar to that observed are predicted in systems where reversible or quasi-reversible electrode kinetics are followed by irreversible chemical reaction. The present system will be still more complex since reduction here will produce two molecules, one of which will be basic anion which should react irreversibly with an additional molecule of the starting material, HNO₃.

The situation at the platinum electrode appears even more complex. Two entirely different peak shapes are observed, depending upon both HNO₃ concentration and scan rate. The low sweep rate/high concentration form (Figure 4) features, on the cathodic sweep, a leading peak which trails into a level plateau region terminating in a drop to near zero current over only 150mV. This is accompanied on the reverse <u>anodic</u> sweep by a <u>cathodic</u> current peak, also of complex shape. Other instances of reverse current peaks have already been described with reference to peak Y. In this case, the observation that continuation of the sweep beyond -0.6V gives rise to a new peak with concommitant loss of the return cathodic current suggests that an adsorbed insulating film is responsible for the current drop at -0.2V in the anodic sweep. Presumably the <u>anodic peak cathodic</u> current results from desorption of the film allowing further reduction, while the -0.6V peak represents reductive destruction of the film and renewed reduction of HNO₃. The correlation of this peak system with HNO₃ concentration suggests that the adsorbed material is a product of HNO₃ reduction (or chemical reaction). The shape of the cathodic peak/plateau is of a type predicted for either a reversible chemical reaction followed by irreversible catalytic chemical reaction. Neither of these simple situations is likely to describe the system fully.

At high sweep rates or low concentrations the peak shapes simplify to a single cathodic peak on the cathodic sweep with no detectable cathodic peak on the anodic return sweep. The simple cathodic peak has, however, an exceptionally low trailing diffusion current relative to that observed with a gold electrode, while the Ip/(scan rate)¹/₂ relationship (Figure 6), although apparently linear, has a large negative current intercept. Both observations suggest a continuing effect due to adsorbed material. The reason for the change in peak shape with scan rate, which is not of the type predicted for simple systems, is unclear. The disappearence of the cathodic peak on the anodic sweep shows that the role of adsorption has changed; the rate of formation of adsorbable material, the total quantity of adsorbable material, and the rate of desorption at potentials less than -0.2V may all be involved. The possibility of a complex equilibrium network involving NO₃, NO₂, HNO₃, HNO₂, and H₂O also requires consideration in the reductions at both Pt and Au electrodes.

REFERENCES

- R.W. Coughlin and M. Farooque, Nature, 1979, <u>279</u>: 301; M. Farooque and R.W. Coughlin, Fuel, 1979, <u>78</u>: 705; R.W. Coughlin and M. Farooque, Ind. Eng. Chem. Pr. Rev., 1980, <u>19</u>: 211.
 G. Okada, Y. Guruswamy and J. O'M. Bockris, J. Electrochem. Soc.,
- (2) G. Okada, Y. Guruswamy and J. O'M. Bockris, J. Electrochem. Soc., 1981, 128: 2097; P.M. Dooghe, D.E. Stillwell and S-M. Park, Abstract 457, Electrochem. Soc., Montreal, 1982; K.E. Johnson et al, Abstract 456, Electrochem. Soc., Montreal, 1982.
- (3) C.A. Angell, J. Électrochem. Soc., 1965, <u>112</u>: 1224; C.A. Angell, J. Chem. Phys., 1966, <u>70</u>: 3988.
- (4) J. Braunstein, L. Orr and W. MacDonald, J. Chem. Eng. Data, 1967, 12: 415.

- C.T. Moynihan and A. Fratiello, J. Am. Chem. Soc., 1967, 89: 5546. (5)
- B. Burrows and S. Noersjamsi, J. Phys. Chem., 1972, 76: 2759.
- (6) (7) J. Braunstein et al, J. Electroanal. Chem., 1968, 15: 337.
- C.T. Moynihan and C.A. Angell, J. Phys. Chem., 1970, 74: 736. D.G. Lovering, J. Electroanal. Chem., 1974, 50: 91. E. Yeager et al, J. Phys. Chem., 1982, 86: 4980. (8) (9)
- (10)
- R. Caminiti et al, Z. Naturforsch., 1981, 36A: 831. (11)
- (12)D.G. Lovering, Col. Czec. Chem. Comm., 1972, 37: 3697; ibid 1973, 38: 1719.
- (13)C. Nanjundiah and R. Narayan, Electrochim. Acta, 1981, 26: 203; ibid 26: 367.
- (14)R. Narayan and K.T. Valsaraj, Electrochim. Acta, 1982, 27: 153.
- (15) R. Narayan and C. Nanjundiah, J. Electroanal. Chem., 1982, 136: 159.
- (16)N.P. Bansal and J.A. Plambeck, J. Electrochem. Soc., 1977, 124: 1036.
- N.P. Bansal and J.A. Plambeck, Electrochim. Acta, 1978, 23: 1053. (17)
- (18) R.P. Courgnaud and B. Tremillion, Bull. Soc. Chim. Fr., 1965: 758.
- (19) P.G. Zambonin, J. Electroanal. Chem., 1970, 24: 365; K.E. Johnson
- and P. Zacharias, J. Electrochem. Soc., 1977, 124: 448. V.D. Prisyazhnyi, D.A. Tkalenko and N.A. Chmilenko, Soviet (20)
- Electrochemistry (Elektrokhimiya), 1980, <u>16</u>: 115. D. Gilroy and B.E. Conway, Can. J. Chem., <u>1968</u>, <u>46</u>: 875. R. Thacker and J.P. Hoare, J. Electroanal. Chem., <u>1971</u>, <u>30</u>: 1. (21)
- (22)
- (23) A.J. Appleby, J. Electroanal. Chem., 1970, 24: 97.
- T. Biegler and R. Woods, J. Electroanal. Chem., 1969, 20: 73. (24)
- (25)
- J.P. Hoare, J. Electrochem. Soc., 1963, <u>110</u>: 1019. J.P. Hoare, R. Thacker and C.R. Wise, J. Electroanal. Chem., 1971, (26) <u>30</u>: 15. J.P. Hoare, J. Electrochem. Soc., 1979, <u>126</u>: 1502.
- (27)
- (28)
- K.E. Johnson and D.T. Sawyer, J. Electroanal. Chem., 1974, 49: 95.P. Margaretha and P. Tissot, J. Electroanal. Chem., 1979, 99: 127. (29)
- (30)A. Damjanovic, M.A. Genshaw and J. O'M. Bockris, J. Electrochem. Soc., 1967, <u>114</u>: 446.
- D.D. MacDonald, "Transient Techniques in Electrochemistry", Plenum (31) Press, New York, 1977, ch. 6.



Figure 1 Current/Voltage relationship for 1-2% coal slurries/Ca(NO₃)2^{•4}H₂O Pt anode, Au cathode, 115-20[°]C.



Figure 2 Nitrite as a % of theoretical yield relative to total charge passed through Ca(NO₃)₂·4H₂O



Figure 3 Cyclic voltammograms with Pt and Au microelectrodes of $Ca(NO_3)2.4H_{20}$ at $70^{\circ}C$


Cathodic peak current relative to the square root of scan rate for 0.01 molal $HN03/Ga(N03)2 \cdot 4H_2O,700C$



Figure 4 Cyclic voltammograms with Pt and Au Cyclic voltammogram with platinum electrodes of HN03/Ca(N03)2·4H20 at microelectrode of Ca(N03)2·4H20 at 70°C, 50mV/s 70°C, 250mV/s

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EQUILIBRIUM MEASUREMENTS FOR THE ABSORPTION OF H₂S, COS AND HC1 BY ALKALI METAL CARBONATES

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ABSTRACT

Battelle Pacific Northwest Laboratories (PNL) has developed through the bench scale a process to remove H₂S and COS from hot fuel gas with a solution of Li, K, Na and Ca carbonates supported on a solid substrate. In order to extend this process to operate in integrated coal gasification/molten carbonate fuel cell power plants, equilibrium data are needed for various cation compositions in the presence of high CO₂ and H₂O back pressures. A pressure-capable laboratory system has been recently constructed and is being used to study the carbonate/sulfide, carbonate/sulfate and carbonate/chloride equilibria.

INTRODUCTION

Gasification of coal produces a hot gas laden with H_2S and HC1. It is desirable to remove these contaminants at high temperatures and pressure before utilization of the gas in a molten carbonate fuel cell. Removal of H_2S from hot coal gas with solid supported molten salt has been demonstrated (1). This paper describes measurements of gas-liquid equilibria relevant to meeting the contaminate removal, temperature and pressure conditions for anode feed gas. Under operating conditions, the molten salt comprises the Li, Na, K, Ca/CO₃, OH, S, SO₄, Cl system. Although measurements in several subsystems have been reported (2-6) and some correlations made with the conformal ionic solution theory (7), additional measurements are required for design and evaluation of the hot gas clean-up system.

PREVIOUS WORK AT BATTELLE, PACIFIC NORTHWEST LABORATORIES

The reversible reaction of H_2S with molten carbonates has been under study at PNL since 1982. Letting M represent Li₂, Na₂, K₂ or Ca, the reaction is:

$$MCO_3(\ell) + H_2S(g) \rightleftharpoons MS(\ell) + CO_2(g) + H_2O(g).$$

The process was first developed based on continuous, countercurrent gas liquid contacting (9). Absorption of H_2S and particulates, de-entrainment and regeneration of the carbonate were demonstrated in a process development unit (PDU) operating on gas from a fixed-bed gasifier. A venturi scrubber provided the first sulfur absorption stage and also circulated the molten salt between bubble-cap absorption and stripping columns. In the latter, steam and CO_2 were used to recover H_2S . Circulation of the hot, corrosive molten salt led to severe equipment problems, and operation was never sustained for more than a few hours at a time.

The Solid-Supported Molten Salt (SSMS) Concept was developed as a practical means for handling the corrosive molten carbonates (1). Several ceramics were investigated as potential supports. Lithium aluminate was chosen for chemical stability and for ease of fabrication of strong, porous pellets. Although the pellets could be fluidized, use in a cyclically-operated fixed-bed avoided possible agglomeration problems and still allowed the advantages of a gas-liquid equilibrium system to be exploited. Laboratory and bench-scale testing demonstrated up to 99.5% sulfur removal from a feed gas containing 1% H₂S and produced regeneration gases containing up to 50% H₂S on a dry basis. Operation was relatively trouble-free with bench-scale absorption cycles of up to 7 hours duration.

APPLICATION TO MOLTEN CARBONATE FUEL CELL POWER PLANTS

Demonstrated performance of the Solid-Supported Molten Salt Process is adequate for clean-up of low pressure gasifier product to meet stack emission sulfur specifications. Three areas require additional attention for application to high pressure gasifiers whose product must meet fuel cell feed requirements. Sulfur loading in the presence of high steam and CO₂ back pressures, high efficiency sulfur removal, and the removal and regeneration of chlorides.

Sulfur Loading

Absorption of H₂S according to Equation 1 is favored by low pressures of steam and CO₂. It is desirable to operate molten carbonate fuel cells at high pressures to reduce power plant size and cost. The gasifier product gas must contain at least enough steam and CO₂ at a void carbon deposition at the projected 650° C/7.5-15 atm operating conditions.

Figure 1 is a plot of equilibrium data obtained by Stegen (1) and Moore (3) for free liquid and solid-supported molten carbonates respectively. The broken line represents the equilibrium expression:

$$K_{1} = \frac{[S^{=}] P_{CO_{2}} P_{H_{2}O}}{[CO_{3}^{=}] P_{H_{2}S}} = 1.8$$

where mole fractions are used in place of activities of the anions.

For a gasifier product containing 8% CO₂, 12% H₂O and 0.5% H₂S, the equilbrium sulfide/carbonate ratio would be 0.94 at atmospheric pressure, but would reduce to 0.064 at 15 atm total pressure. If the hot-gas clean-up step must be operated at the 650° C fuel cell

temperature, a less favorable equilibrium would be expected. Based on pure component data, Reaction 1 should be endothermic by about 28 Kcal/mole. At 650° C, K₁ should drop to 0.22 giving a sulfide/carbonate ratio of 0.008 for 15 atm total pressure.

The initial goal of the current experimental program is to determine whether the sulfur capacity of the molten carbonate can be increased by changes in cation composition. The lithium-rich composition used by Moore and Stegen was chosen for its low freezing point and was not optimized for sulfur capacity. Standard thermodynamic data (10) can be used to calculate K₁ for each of the pure components in the solid phase (Table I). All of the calculated values are higher than K₁ from the measurements of Figure 1, but calcium and potassium would seem to be the preferred cations. For sodium and potassium, K₁ can be calculated for the pure component sub-cooled liquids (Table I). In the cases of lithium and calcium, however, the required liquid phase data are not available. Predictions cannot be made with confidence from the solid phase data for calcium because its carbonate and sulfide melt at temperatures well above the temperature of interest.

TABLE I.	Equilibrium Constants* for Reaction of
	Pure Carbonates with H ₂ S

Solid Phase or (Sub-cooled Liquid) K, Atmospheres, Reaction 1

800 0 K	Li ₂ 0.038	Na ₂ 0.038 (0.093)	K ₂ 0.838 (0.986)	Ca 8.43
900 ⁰ K	0.429	0.344 (0.594)	5.22 (5.83)	52.5
1100 ⁰ К	12.29	7.39 (7.34)	63.4 (62.5)	708.0

* Calculated from tabulations of Barin and Knacke (10)

Sulfur Removal Efficiency

Gasifier product typically contains 3000 to 5000 ppm H₂S and 500 to 1000 ppm COS. The MCFC requires H₂S/COS concentrations to be less than 1 ppm. For a fixed-bed absorber that is well regenerated, clean breakthrough behavior requires that the equilibrium curve be convex toward the axis of the absorbed phase (11). Figure 1 shows that this condition is met by the molten carbonate system over a wide range of compositions. In so far as Reaction 1 applies, a single bed capable of high sulfur loading should, if well regenerated, be able to meet any effluent H₂S specification.

Optimization of sulfur removal efficiency has not been a primary goal in previous work at PNL. However, Stegen (1) did achieve prebreakthrough sulfur levels below his 10 ppm detection limits for several cycles in laboratory scale absorption tests. Bench-scale tests removed sulfur down to 50 ppm. Problems with high, pre-break-through sulfur levels were traced to oxidation of sulfide in the salt during regeneration. Addition of CO and H₂ during regeneration gave improved results. The best laboratory runs used 10% H₂ addition while only 4.5% H₂ was added during bench-scale regeneration. This reduced H₂ addition may explain the failure to achieve lower effluent sulfur levels in the latter tests.

If the oxidation product is sulfate and the regeneration gas CO_2/H_2O ratio is close to one, the reaction can be written:

$$MS + 2CO_2 + 2H_2O \approx MSO_4 + 2CO + 2H_2$$
. 3

Sulfate formed during regeneration would be reduced to sulfide in the subsequent absorption cycle contaminating the effluent gas. Table II lists equilibrium constants for the pure components. For the range of constants in the table between 0.4 and 9% H₂ + CO would be required in the regeneration gas to keep the sulfide/sulfate ratio above 5. The actual requirement is critical to process design. The sulfate/ carbonate equilibrium in mixtures of molten Li, Na and K carbonates has been studied using conformal ionic solution theory (7). Measurements are required to determine the equilibrium constant for Reaction 3 in mixtures containing calcium.

TABLE II. Equilibrium Constants* for Oxidation of Sulfides to Sulfates

Solid Phase of (Sub-cooled Liquid) K, Reaction 3

800°K	Li ₂ 5.47E-9	Na2 4.40E-7 (1.97E-7)	K ₂ 1.64E-6 (4.31E-7)	Ca 1.90E-11
900 ^o K	3.31E-8	1.36E-6 (8.33E-7)	4.71E-6 (1.72E-6)	1.19E-10
1100 ⁰ К	5.40E-7	8.48E-6 (8.03E-6)	2.58E-5 (1.49E-5)	2.03E-9

* Calculated from tabulations of Barin and Knacke (10)

HC1 Removal

Gasifier product is projected to contain 50 to 200 ppm HCl which must be reduced to <1 ppm before feeding to a MCFC. Removal of HCl

with molten carbonates has not been tested at PNL. Table III lists pure component equilibrium constants for the reaction:

$$2HC1 + MCO_3 = MC1_2 + CO_2 + H_2O.$$
 4

Absorption of HCl is apparently much more favorable than the absorption of H₂S. For all components and temperatures listed in the table, 200 ppm HCl would be removed more rapidly than 5000 ppm H₂S from a gas under 15 atm total pressure. As a result, chloride would accumulate near the entrance of a fixed bed during absorption. Its concentration in the salt may be limited only by its vapor pressure. If increased steam and CO2 pressures or decreased temperatures are used for regeneration, comparison of the equilibrium expressions for Reactions 4 and l indicates sulfide would be more rapidly stripped than chloride. Regeneration conditions would be chosen to produce a sulfur-rich gas for recovery and chloride would tend to accumulate during multiple cycles. It may be possible to add one long chloride regeneration cycle to eliminate such accumulation after several absorption-sulfur regeneration cycles. Although absorption and regeneration kinetics would also be involved, the feasibility of such a scheme would depend upon the relative equilibria for H₂S and HCl absorption.

TABLE III. Equilibrium Constants* for Reaction of HCl with Pure Carbonates

Solid Phase or (Sub-cooled Liquid) K, Reaction 4

800 ⁰ К	Li ₂ 2.48E+6 (5.20E+6)	Na ₂ 8.80E+10 (3.74E+10)	K ₂ 1.77E+13 (9.62E+12)	Ca 7.90E+4
900 ⁰ К	9.94E+5 (1.93E+6)	7.08E+9 (4.65E+9)	8.68E+11 (7.51E+11)	3.84E+4
1100 ⁰ К	2.39E+5 (4.15E+5)	1.70E+8 (2.10E+8)	9.96E+9 (1.64E+10)	1.31E+4

* Calculated from tabulations of Barin and Knacke (10)

EXPERIMENTAL

A bubble contactor provides a convenient method to study a variety of gas-liquid equilibria in molten salts. Gases are metered through a pool of salt and the effluent gas is analyzed. Molten carbonates can be loaded with a sulfur or chlorine-rich gas, then stripped with a gas of appropriate composition. The equilibrium concentrations of H_2S/COS and HCl can be measured and confirmed by adding them in excess to the stripping gas and noting any increase in the outlet. The effect of CO₂ and H₂O on the primary reactions, 1 and 4, and of CO and H₂ on the oxidation Reaction 3 can all be studied by variation of the stripping gas, careful analysis of the effluent gas and material balance.

Equilibrium measurements are being made with a system which will later be converted to study breakthrough and regeneration behavior with solid-supported molten salt over three decades of contaminant concentration and under total pressures up to 15 atm. Measurements can therefore be made over a wide range of H_2S , HC1, CO_2 , H_2O , CO and H_2 pressures.

Figure 2 depicts the laboratory system in use for equilibrium measurements. The molten carbonates are contained in an alumina thimble with a loose fitting lid. The thimble is contained in a pressure vessel which allows operation up to 15 atm. The only alumina that contains differential pressure is small diameter tubing extending through the top flange. The space surrounding the thimble is purged with nitrogen which flows into the off-gas system and is accounted for in the material balance. The Inconel 800-H vessel body can be heated to 800°C while the stainless steel flanges remain below 150°C. Gases from cylinders pass through rotameters and a heated tube where water is added. They are joined by H2S or HC1 and conducted to the bottom of the thimble by an alumina tube. Bulk additions of H₂S and HCl are metered through a rotameter and checked by weight. mass flow meter allows additions to the feed gas in the 3000 to 5000 ppm range.

Determination of H₂S and HCl from 1 to over 1000 ppm in a wet, pressurized gas stream presents some unique problems. The H₂S and HCl are scrubbed from the reactor effluent gas under pressure in circulating, caustic-sodium carbonate solution. Tubing from the alumina reactor outlet is heat traced and teflon lined. The rate of accumulation of chloride and sulfide in the solution is determined by periodic sampling and analysis with Orion Model 94 specific ion electrodes. The ability to vary scrubber solution volume as well as sample timing extends the range of concentration that can be measured. The scrubbers also provide absolute integration of sulfur and chlorine values leaving the salt so that changes in salt composition can be accounted for during experiments without sampling. After scrubbing and pressure letdown the effluent gas is analysed by gas chromatography. After correcting for purge nitrogen, the CO/N_2 and H_2/N_2 ratios can be checked for the extent of the shift reaction and of Reaction 3.

INITIAL RESULTS AND DISCUSSION

Initial experiments conducted in our pressurized laboratory system have resulted in poor sulfur balance among total H_2S loading, effluent analysis and analysis of the quenched salt. This problem

has not been completely resolved, but may be due to overloading of the scrubbers while loading the salt with an H_2S -rich gas. Data obtained from two experiments using the quenched salt analysis to calculate sulfur contents are reported in Figure 3. These data are being confirmed by additional testing.

The equilibrium constant for Reaction 1 is plotted against reciprocal temperature in Figure 3. Data for $Li_2/Na_2/K_2/Ca$ ratios of 1.9/0/1.0/0.7 from this work are compared with data by Moore (3) for ratios of 1.7/1.3/1.0/0 and 1.7/1.3/1.0/0.7 and with calculated values from Table I for the pure components. The lower values for the mixed alkali carbonates indicate that activity coefficients for the sulfides are higher than those for the carbonates. Negative deviations from Raolt's Law (low activity coefficients) are well established for the carbonates.

The slopes of the lines in Figure 3 all reflect heats of reaction between 25 and 35 Kcal/mole except Moore's Ca-containing system with an apparent 16 Kcal/mole. Data for that system show considerable scatter and could reflect a contribution from Reaction 3 which would raise the apparent K at lower temperatures.

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REFERENCES

- Stegen, G. E. 1982. <u>Development of a Solid Absorption Process</u> for <u>Removal of Sulfur from Fuel Gas.</u> DOE/ET/11028-9, prepared for the U.S. Department of Energy under Contract DE-AC21-79ET11028 by Battelle, Pacific Northwest Laboratory.
- (2) Forland, T. 1955. "An Investigation of the Activity of Calcium Carbonate in Mixtures of Fused Salts." J. Phys. Chem. 59:152-156.
- (3) Moore, R. H., G. F. Schiefelbein and G. E. Stegen 1976. Molten Salt Scrubbing Process for Removal of Particles and Sulfur Compounds from Low Btu Fuel Gases. BNWL-SA-6030, Battelle, Pacific Northwest Laboratory, Richland, Washington.
- (4) Fuerstenau, M. C., C. M. Shen and B. R. Palmer 1981. "Liquidus Temperatures in the CaCO₃-Ca(OH)₂-CaO and CaCO₃-CaSO₄-CaS Ternary Systems. 1." Ind. Eng. Chem. Process Des. Dev. 20(3):441-445.

- (5) Ong, E. T. and T. D. Claar 1982. "Electrolyte Vaporization Losses from Molten Carbonate Fuel Cells." Paper presented at the Electrochemical Society Symposium on Molten Carbonate Fuel Cell Technology, May 9-14, 1982, Montreal.
- (6) Smith, S. W. and S. M. Kapelner 1983. J. Electrochemical Society 130(2):405-407.
- (7) Pelton, A. D., C. W. Bale and P. L. Lin 1981. <u>Calculation of Thermodynamic Equilibria in the Carbonate Fuel Cell.</u> DOE/ET/ 15416-2. Ecole Polytechnique, Montreal, Quebec.
- (8) Moore, R. H., C. H. Allen, G. F. Schiefelbein and R. J. Maness 1974. "A Process for Cleaning and Removal of Sulfur Compounds from Low Btu Gases". Interim Report October 1972-August 1974, GPO Cat. No. I:63. 10:100/Int. 1.
- (9) Moore, R. H. et al. 1979. Process for Cleaning and Removal of Sulfur Compounds from Low Btu Gas. PNL-2851 PT 1, Pacific Northwest Laboratory, Richland, Washington.
- (10) Barin, I. and O. Knacke 1973. Thermochemical Properties of Inorganic Substances. Springer-Verlag, Berlin.
- (11) King, C. J. 1971. <u>Separation Processes</u>, pp. 317-327. McGraw-Hill, New York.







DISCUSSION

G. Peny (AWRE, Aldermaston, Reading, England)

In using Li₂0·Al₂0₃ as a support material for molten carbonate do you not find exchange of Li₂0 taking place with the melt, i.e., Li₂0·(Al₂0₃)_n + MCO₃ \rightarrow M₂0·(Al₂O₃)_n + Li₂CO₃?

S. Lyke, Reply:

According to thermodynamic calculations reported by Stegen (1), the reaction in question has a positive free energy change on the order of 10 Kcal for M = Na or Ca. Potassium is not expected to be significantly different. Since Li_2CO_3 is a component of the salt, the cited reaction is not expected to occur. Physical stability of the $Li_2O^*(Al_2O_3)_n$ ceramic was demonstrated through months of contact with the mixed alkali carbonates and multiple thermal cycles.

ACIDITY AND THERMOCHEMICAL STABILITY OF MOLTEN SODIUM NITRATE AND NITRITE MIXTURES

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ABSTRACT

The influence of acidity on the thermochemical stability of molten sodium nitrate-nitrite mixtures used as heat transfer fluids (as in the case of the French electrosolar power system called Thémis) has been demonstrated by considering the potential-p0²⁻ diagram relative to redox systems corresponding to these mixtures, and established from thermochemical data. The importance of fixing the pO^{-1} value with a buffer has been clarified. The couple H₂O(g)/OH⁻ whose acid-base constant was previously determined appears as the most efficient for this purpose. The potential-p0⁴ diagram could be set up experimentally by studying the disproportionation of nitrite ion into nitrate and nitrogen monoxide and by determining the standard potential of the electrochemical system NO3/NO by means of potentiometric measurements with a platinum electrode and with an yttria-stabilized zirconia membrane electrode indicator of pO^{2-} . This diagram has allowed us to specify, as a function of temperature, the boundary values of pO^{-} which should not be gone beyond in order to avoid the decomposition of the mixtures as a result of the nitrite disproportionation.

INTRODUCTION

Molten alkali nitrate-nitrite mixtures are known for their high heat capacities and their low melting points, which have led to their use as heat transfer fluids at temperatures not greater than 450°C. The use of the mixture called HITEC (KNO₃ 53 -NaNO₂ 40 - NaNO₃ 7 w.[®]) in the French electrosolar power system Themis built by Electricité de France, makes necessary that this liquid can circulate in a thermal loop where the extreme working temperatures are 250 and 500°C. In view of this use, we have undergone to study the chemical factors influencing the thermal stability of molten NaNO₃-NaNO₂ mixtures.

The thermochemical decomposition of nitrates

(1,2) and nitrites (3-5) has been the subject of many studies, but authors do not agree about the reactions which take place. It seems nevertheless well established that decomposition is accompanied by the release of nitrogen, nitrogen oxides and oxygen, with the production of alkaline oxide. The complexity of these reactions has incited us to undertake a preliminary study based on the existing thermochemical data (6). Because the reactions put into play the redox systems of nitrogen on the one hand, and oxide ion on the other hand, the results have been expressed in the form of a potential-pO² diagram $(pO^2 = -\log m(O^2))$ measures the acidity of the medium (7)). This sort of presentation has already been used for alkali nitrates and for alkali nitrites by Conte and Casadio (8), Marchiado and Arvia (9) and by Haan and Van Der Porten (10), but not for their mixtures.

The calculated diagram has subsequently been specified by experimental determinations and the results obtained have finally permitted the definition of the conditions which would be favourable to the thermochemical stability of the heat-transfer fluid.

We present here a part of our investigation concerning the effect of acidity, in studying especially the nitratenitrite-nitrogen monoxide systems.

CONCENTRATION UNITS AND SYMBOLS USED

The alkali nitrate-nitrite mixtures have been shown to behave ideally (11). So the activities of their components can be expressed by their mole fractions $N(NO_2)$ and $N(NO_2)$. The concentrations **m** of the dissolved (and consequently solvated) species, other than the "solvent" ones, are given in the molality scale. The partial pressures of gases are in atm.

The various compositions of the NaNO $_3$ -NaNO $_3$ mixtures that we have considered, have been indicated in the figures by the following symbols.

Mark			•	0	•
N(N0 ₃)	0.99	0.85	0.50	0.15	0.01
N(N0 ₂)	0.01	0.15	0.50	0.85	0.99

EXPERIMENTAL SECTION

Technical.

• Products, preparation of melts and apparatus. After drying at 150°C, sodium nitrate and nitrite (MERCK) were mixed in the desired proportions. Dehydration of the mixtures was carried out by a progressive raising of the temperature and by maintaining for four hours at work temperature while bubbling dry nitrogen. The other products used were sodium carbonate dried at 1000°C, sodium hydroxide without any previous treatment (pure products for analysis PROLABO), and nitrogen monoxide (99% pure) supplied by COOP-LABO.

For each experiment, 100 g of the nitrate-nitrite mixture thus prepared were introduced into a cylindrical platinum crucible. Platinum was choosen in order to avoid the effect of silica as an acid (12-14). The platinum crucible was itself contained in a Pyrex glass cell. The temperature was maintained at the desired value (420,470 or 520°C) at \pm 1°C by means of an oven thermoregulated by a DIGITOP(CHAUVIN-ARNOUX) coupled to a Teledyne (TEKELEC-AIRTRONIC) relay.

The pipes for the different fluids and the tubes of the thermocouples were in alumina AI 23 (from DESMARQUEST). Partial pressures of water vapor were imposed above the melt by saturators at fixed temperature.

The e.m.f. were recorded with the help of a voltmeter TACUSSEL ARIES 20000 and a SEFRAM recorder (Servofram type).

Reference electrode.

The reference electrode used was made up of a silver wire (C.M.P.) dipped into a 0.057 mol kg⁻¹ AgNO₃ solution in (Na-K)NO₂ eutectic contained in a Pyrex glass tube.

All potentials are given in V vs. this reference electrode (whatever the $NaNO_3$ - $NaNO_2$ mixture used).

• Platinum working electrode.

The indicator electrode used was made from 1mm diam-platinum rod supplied by JOHNSON-MATTHEY.

 pO^{2-} measurements.

Description of the indicator electrode used.

In order to measure pO^{2-} in alkali nitrates, it has been shown (15) that an electrode with an oxide ion selective membrane is preferable to an oxygen electrode. A calcia-stabilized zirconia membrane electrode with a solid inner filling used for the first time by Eichler et al (16) and by Tremillon et al (17) in molten alkali chlorides, works quite well at temperatures above 600°C, but its potentiometric response becomes slow (equilibrium potential reached with difficulty) at lower temperatures. Flinn and Stern (15) for molten alkali nitrates, and Picard, Séon and Trémillon (18-20) for molten alkali chlorides, have therefore preferred to employ a mambrane of yttria-stabilized zirconia, which is twice more conductive, and a liquid inner filling. Such a device does not present the same problems as mentioned above. The galvanic chain set up to measure pO²⁻ is schematized below :

(the yttria-stabilized zirconia is supplied by DESMARQUEST : ZFYE tube).

tical expression :

$$E = E^{\circ} + \frac{2.3RT}{2F} pO^{2-}$$

In order to verify the potentiometric response of the yttria-stabilized zirconia membrane electrode (YZME) and to make its calibration, we have used sodium hydroxide. If we add to the melt a quantity m_o of sodium hydroxide (per kg of molten mixture), the respective molalities of free O^{2-} and remaining OH^{-} are linked by the equilibrium :

$$2 \text{ OH}^{-} \neq \text{H}_2 \text{O(g)} + \text{O}^{2-}$$
 (1)

The e.m.f. of this cell has the following theore-

When the partial pressure of water is made sufficiently low, the dissociation of OH_{-} can be considered as practically total, and the concentration of O_{-}^{-} ions is given by :

$$m(O^{2^{-}}) = 0.5 m_{0}(OH^{-})$$

We have shown that a partial pressure of H_2O less to 10^{-3} atm is convenient for this (21).

The introduction of oxide ions by dissociation of OH⁻ was preferred to the direct addition of sodium oxide because this product is generally impure (presence of peroxide and superoxide).

Acidity buffers and acidity function.

The YZME allows us to study various buffers by means of acid-base titrations, as it has been described previously (21-22). We give only here the buffers studied with the ranges of acidity that they cover on pO^{-1} scales (Fig. 1).

In order to analyze the effect of acidity on the thermochemical stability of molten nitrate-nitrite mixtures, we have choosen to consider, and to substitute for pO^{2-} , the temperature-independent function log $P(H_2O)/m(OH^-)^2$ which corresponds to the quantities (water pressure and hydroxide concentration) which are experimentally imposable whatever the temperature may be. This

procedure is analogous to that employed in molten chlorides (23).

Thanks to the values of constant K, of equilibrium (1) which have been determined (table 1) and which do not vary practically with the composition of the mixtures at a given temperature (21, 22), it is possible to obtain the correspondance between this acidity function and pO⁻ (Fig. 1).

Disproportionation of nitrite ions.

It has been <code>observed_that</code> increasing acidity produces the disproportionation of NO₂ in to NO₃ and nitrogen monoxide, according to the equilibrium :

$$3 NO_2^- \neq NO_3^- + 2 NO(g) + O^{2-}$$
 (2)

whose constant K₂ is defined by :

$$K_2 = N(NO_3).P(NO)^2.m(O^{2-}).N(NO_2)^{-3}$$
 (3)

This constant has been determined by simply measuring with the YSZME the pO^{2-} imposed by bubbling nitrogen monoxide (1 atm) into NaNO₃-NaNO₂ mixtures of given compositions. The results obtained at three different temperatures, verify a straight line variation of pO^{-} with the ratio $N(NO_{3})N(NO_{2})^{3}$ as predicted by equation (3). The variation of pK₂ with the temperature (Fig. 2) has been determined by regression analysis (see table 1). We can notice on Fig. 2 a slight dispersion of the measurements carried out in mixtures different from the 0.5 - 0.5 mixture for which a very good adjustment has been obtained.

NO₂/NO₂ electrochemical system.

 $\label{eq:themality} {\ensuremath{\mathsf{The melts studied contained the two components}} \\ {\ensuremath{\mathsf{of the redox couple}}\xspace : }$

$$NO_{2} + 2e^{-} = NO_{2} + O^{2-}$$

So, the redox potential E of a given melt (i.e. at fixed NO_3 and NO_2 mole fractions) has to follow the Nernst relations :

$$E = E_{3}^{\circ} + (\lambda/2) \log [N(NO_{3}^{-})/N(NO_{2}^{-})] + (\lambda/2).pO^{2-}$$
(4)
($\lambda = \frac{2.3RT}{E}$)

and consequently, only varies with the activity of oxide ion. Then, measurements of the potential of a platinum electrode deeping in molten NaNO₃-NaNO₂ mixtures must allow us to determine the standard potential value of the NO₃/NO₂ redox couple.

But, while making these determinations we have to take care not to let pO^2 increase beyond the value corresponding to the disproportionation of nitrite ion according to equilibrium (2). This limit value of pO^2 depends on the nitrogen monoxide partial pressure, the maximum value of pO^2 being reached for P(NO) = 1 atm. This limit is represented in Fig. 3 for the three temperatures considered ; on this figure we have also plotted the variations of potential versus $p0^{2^{-}}$ observed with five mixtures of sodium nitrate and sodium nitrite.

We observe in all cases that the variations of potential check very well the Nernst relation (4). It is thus justified to determine the potential of the NO₃/NO₂ system at $pO^{-} = 0$ by extrapolation. Then by plotting as a function of the ratio N(NO₃)/(NO₂), this potential at $pO^{-} = 0$, a straight line agreeing with relation (4) is obtained and permits to us to determine the standard potential of the NO₃/NO₂ electrochemical system. The results obtained according to this procedure at the three temperatures have led to the expression of the variation of the NO₃/NO₂ standard potential as a function of temperature given in table 2.

The standard potentials E_{μ}° and E_{5}° of the NO₂/NO(g) and NO₃/NO(g) electrochemical systems :

$$NO_{2} + e^{-} = NO(g) + O^{2}$$

and :

$$NO_{2}^{-} + 3e^{-} = NO(g) + 20^{2-}$$

defined by the respective Nernst relations :

$$E = E_{\mu}^{\circ} + \lambda \log \left[N(NO_{2}^{-}) / P(NO) \right] + \lambda pO^{2-}$$

and :

 $E = E_5^{\circ} + (\lambda/3) \log[N(NO_3)/P(NO)] + (2\lambda/3)pO^{2-1}$

can be determined by combining the value of K₂(constant of the NO⁻_2 disproportionation equilibrium) with the value of E^o₃ (standard potential of the NO⁻₃/NO⁻₂ system).

We have in fact :

$$E_4^\circ = E_3^\circ - (\lambda/2) pK_2^\circ$$

 $E_4^\circ = (2E_3^\circ + E_4^\circ)/3$

and :

The values of E_4° and E_5° are also given in table 2.

DISCUSSION

Potential-acidity diagram.

Fig. 4 summarizes our results under the form of a potential- $p0^{2-}$ diagram. Only the curves corresponding to the equimolar sodium nitrate - sodium nitrite mixture, in the cases where the nitrogen monoxide pressure is equal to 0.1 and 1 atm, are represented.

In this diagram, the value of pO^{2-} corresponding to the disproportionation of nitrite is given by the abscissa of the intersection of the straight lines representating the systems NO_3/NO_2 ,

 $NO_3/NO(g)$ and $NO_2/NO(g)$. This intersection is designated, in the following, as the "triple point". For example, in the case of the equimolar mixture, the triple point is represented by letter A for P(NO) = 0.1 atm, and by letter B for P(NO) = 1 atm.

So, we can assert that a molten NaNO₃-NaNO₂ mixture keeps its composition only if the pO^2 value remains less than the value of the triple point.

Composition-acidity diagram.

Fig. 5 gives the variation of composition of the NaNO₃-NaNO₂ mixtures (by the logarithm of $N(NO_2)$) versus pO^2 at T = 743 K. This diagram clearly shows the influence of the partial pressure of nitrogen monoxide on the range of acidity inside which a given mixture is stable. So, we can remark that it is impossible to reach media more acidic than $pO^2 = 6$ (point B) for the equimolar mixture and P(NO) = 1 atm, without an increase of the nitrate ratio by disproportionation of nitrite.

Acidity-temperature diagram.

The influence of temperature on the stability of nitrite in mixtures of various pO² has been specified. Fig. 6 corresponds to the case of the equimolar sodium nitrite-sodium nitrate mixture. This figure represents the variation of the value of the acidity function $\log [P(H_0)/m(OH_)^2]$ defined above (values of pO² are also given at T = 743 K for example) corresponding to the triple point, and various nitrogen monoxide partial pressures. So, at a given temperature, the decomposition of the mixture by disproportionation of nitrite (réaction (2)) can be avoided by fixing $\log [P(H_0)/m(OH_)^2]$ at values less than the ones corresponding to these curves. If for security reasons we want to keep the partial pressure of nitrogen_monoxide less than 0.01 atm, $\log [P(H_0)/m(OH_)^2]$ has to be maintained, at 743 K, at a value less than -0.7 (point C). For a melt containing 1 weight % NaOH (m(OH_) ≈ 0.25 mol.kg⁻¹), the partial pressure of water must be maintained lower than 10^{-2} atm.

CONCLUSION

The influences of pO^{2^-} and temperature on the decomposition of molten sodium nitrite-sodium nitrate mixtures (disproportionation of nitrite ions) have been studied. In particular we have given the relation between the mixtures composition, pO^{2^-} and the partial pressures of nitrogen monoxide and water.

At the present time, this research is being completed by studying the stability of the mixtures in basic media, in which peroxide and superoxide ions can appear as it has been shown in particular by Zambonin for low temperature melts (24).

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REFERENCES

- 1. J. Alexander Jr and S.G. Hindin, Ind. Engin. Chem., <u>39</u>,1046 (1947).
- 2. R.F. Bartholomew, J. Phys. Chem., 70, 3442 (1966).
- 3. J. Cases-Casanova, Bull. Soc. Chim. Fr., 429 and 435 (1959).
- 4. A. Peneloux, C.R. Acad. Sc., 237, 1082 (1953).
- 5. D.H. Kerridge, Inorg. Chim. Acta, 7, 665 (1973).
- I. Barin, O. Knacke and O. Kubaschewski, "Thermochemical Properties of Inorganic Substances", Springer Verlag, Berlin-Heidelberg - New York, (1973); I. Barin from the data bank "Thermodata".
- 7. B. Trémillon, Pure and Applied Chem., 25, 592 (1971).
- 8. A. Conte and S. Casadio, Ric. Sci., 36, 488 (1966).
- 9. S.G. Marchiano and A.J. Arvia, Electrochim. Acta, <u>17</u>,25 and 861 (1972).
- 10. A.D. Haan and H. Van Der Poorten, Bull. Soc. Chim. Fr., <u>11</u>, 2894 (1973).
- 11. E. Freeman, J. Phys. Chem., 60, 1487 (1956).
- 12. P.G. Zambonin, J. Electroanal. Chem., 33, 243 (1971).
- 13. J.D. Burke and D.H. Kerridge, Electrochim. Acta, 19,251(1974).
- 14. G. Picard, T. Flament, J.M. Bruneau and B. Trémillon, to be published.
- 15. R.B. Flinn and K.H. Stern, J. Electroanal. Chem., 63, 191(1975).
- B. Eichler, D. Naumann and H. Ullmann, Z. Phys. Chem., <u>236</u>, 372 (1967).
- R. Combes, J. Vedel and B. Trémillon, Electrochim. Acta, <u>20</u>, 191 (1975).
- G. Picard, F. Séon, and B. Trémillon, J. Electroanal. Chem., <u>102</u>, 65 (1979).
- G. Picard, F. Séon, B. Trémillon and Y. Bertaud, Electrochim. Acta, 25, 1453 (1980).
- G. Picard, F. Séon and B. Trémillon, J. Electrochem. Soc., 129, 1450 (1982); J. Electroanal. Chem., 138, 315 (1982).

- 21. G. Picard, T. Flament and B. Trémillon, to be published.
- B. Trémillon and G. Picard, "Proc. 1st Internat. Symposium on Molten Salt Chemistry and Technology", Kyoto (1983), p. 93; G. Picard, T. Flament and B. Trémillon, ibid, p. 85..
- 23. B. Trémillon and G. Picard, Anal. Chim. Acta, 82, 273 (1976).
- 24. P.G. Zambonin and J. Jordan, J. Amer. Chem. Soc., <u>91</u>, 2225 (1969).

Table 1 : Constants K_i of chemical equilibria.

Equilibria	Mass action law	$pK_i = A +$	B.1000/T
	expressions	A	В
(1) 2 0H ⁻ = $H_2 O(g) + 0^{2-}$	$K_1 = P(H_2^{0}) \cdot m(0^{2}) \cdot m(0H^{-})^{-2}$	- 4.80	5.48
(2) $3 \text{ NO}_2 = \text{NO}_3 + 2\text{NO}(g) + 0^2$	$K_2 = P(NO)^2 \cdot m(0^2) \cdot N(NO_3) \cdot N(NO_2^2)^{-3}$	- 15.8	15.75

Table 2 : Redox equilibria and standard potentials E_{j}^{o} (λ = 2.3RT/F)

-				
.10 ⁻³ T	B	0.50	2.08	1.03
$E_{i}^{\circ} = A+B$	A	- 1.317	- 2.887	- 1.840
₩	Equilibrium potencials	$E = E_{3}^{\circ} + \frac{\lambda}{2} \log \frac{N(NO_{3}^{-})}{N(NO_{2}^{-})} + \frac{\lambda}{2} \cdot pO^{2-}$	$E = E_4^\circ + \lambda \log \frac{N(NO_2)}{P(NO)} + \lambda \cdot p0^{2-}$	$E = E_5^\circ + \frac{\lambda}{3} \log \frac{N(NO_3)}{P(NO)} + \frac{2\lambda}{3} \cdot p0^{2}$
Electrochemical	systems	(3) $NO_3^- + 2e^- = NO_2^- + 0^{2-}$	$(4) \ \text{NO}_2^{-} + e^{-} = \text{NO}(g) + 0^{2-}$	(5) $NO_{3}^{-} + 3e^{-} = NO(g) + 2 O_{3}^{-}$



Figure 1 : Acidity scales in molten NaNO₃-NaNO₂ mixtures.



Figure 2 : Variation of constant K₂ of the disproportionation of nitrite ions as a function of temperature.



Figure 3 : Equilibrium potentials of the NO₃/NO₂ electrochemical system in various sodium nitrate-sodium nitrite mixtures.



Figure 4 : Potential-pO²⁻ diagram at 743 K.



Figure 5 : Composition-acidity diagram at 743 K.



Figure 6 : Acidity-temperature diagram.

ELECTRODE REACTIONS INVOLVING LEAD OR CADMIUM IONS IN MOLTEN NITRATES

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ABSTRACT

Cyclic voltametric studies show that the addition of either Pb⁺⁺ or Cd⁺⁺ ions to molten nitrates produces a new cathodic wave, yet no reversible anodic wave is observed. Previous workers have always attributed this experimental result to the reduction of the metal ion to the free metal followed by the rapid reaction of the deposited metal with the molten nitrate. Our studies suggest that reduction to the metal never occurs in molten nitrates for Pb⁺⁺ and Cd⁺⁺ ions. Instead, the nitrate ion in Pb(NO₃)⁺ or Cd(NO₃)⁺ complexes is the actual substance reduced, i.e., Cd(NO₃)⁺ + 2e⁻ \rightarrow CdO4 + NO₂. Electrons, not the metal ions, transfer the charge across the double layer. This reaction is shifted to more positive potentials than the normal NO₃ reduction wave due to the strong electric field of the metal ion in the complex.

INTRODUCTION

Numerous electrochemical studies have shown that the addition of lead or cadmium ions to various molten nitrate mixtures produces a new cathodic wave (1-6). The experimental current in various voltametric studies is found to be proportional to the concentration of the added metal ion (2-6). These observations have led previous workers to conclude that the cathodic reaction is the reduction of the metal ion to the free metal. There is no concrete evidence for a new phase of lead or cadmium metal ever forming on the electrode surface during the cathodic reaction in molten nitrates. When the current flow or potential sweep is reversed, the expected reversible anodic wave is never observed. This has been attributed to the reaction sequence

$$M^{++} + 2e^{-} \rightarrow M \tag{1}$$

$$M + NO_3 \rightarrow MO + NO_2$$
(2)

postulating that the reduction to the metal is followed by the rapid oxidation of the deposited metal phase by the molten nitrate (3,4,6).

Our studies indicate that reduction to the free metal never occurs for lead or cadmium ions in molten nitrates. Instead, the $\rm NO_3$ ion in

 $Pb(NO_3)^+$ or $Cd(NO_3)^+$ complexes is the actual substance reduced; i.e.,

$$M(NO_3)^+ + 2e^- \rightarrow MO + NO_2^-$$
(3)

In sharp contrast to Eq. 1, charge transfer across the double layer is accomplished via electrons rather than metal ions.

EXPERIMENTAL

The electrochemical cell was constructed from a section of glass tubing (pyrex or quartz, 3.2 cm diameter and 48 cm length) with a design similar to that described in a previous study (7). The platinum working electrode was in the form of a wire sealed in glass and cut to a length to give a geometrical area of 0.2 cm^2 (0.7 cm length and 0.08 cm diameter). The counter electrode consisted of either a platinum wire coil at the bottom of the cell or a platinum wire spiral separated from the main cell compartment by a section of fritted glass tubing. All potentials were measured against the AgNO₃(0.1 m)/Ag reference electrode described elsewhere (7). Electrochemical studies were made with the cell placed in a fluidized sand bath (Tecam) where the temperature was monitored with a chromel-alumel thermocouple digital thermometer (Fluke, 2165A).

The regent grade nitrate salts used in the cell were dried under vacuum at 130° C for several days. The bubbling of dried helium gas through the molten salt in the cell at 350° C for at least 1 hour was effective in removing any residual water as evidenced by the disappearance of the water wave (8,9). Generally, either 30.0 g of LiNO₃ or 33.0 g of KNO₃ were used in the cell. In experiments requiring mass transport by diffusion, both the sand bath and the helium flow were turned off to give a quiescent solution. The hot sand surrounding the cell acted as a thermal insulator, thus the temperature measured in the cell remained constant within $\pm 1^{\circ}$ C for time periods up to 10 minutes.

Experimental measurements involved the use of a potentiostat/ galvanostat (PAR 173) equipped with a current follower plug-in (PAR 176). In potential scan studies, a programmer was also used (PAR 175). Results were monitored with a X-Y recorder (Hewlett-Packard 7047A) or with a digital oscilloscope (Nicolet Model 206). The reproducibility of the potential scan experiments was improved by a standard conditioning of the working electrode between successive potential sweeps that involved an anodic treatment evolving NO_2 and O_2 followed by a waiting time of 30 seconds at the initial potential before beginning another sweep. For experiments involving exhaustive electrolysis, a large platinum electrode (A = 10 cm²) of rectangular shape was used in the molten nitrate solution that was rapidly stirred by the flow of helium gas to maximize mass transport.

RESULTS AND DISCUSSION

Cyclic voltametric studies of 0.10 mole % Pb(NO₃)₂ in molten LiNO3 at 350°C are shown in Figure 1. The addition of Pb++ ions produces a new cathodic wave beginning at -0.1 V with a peak potential near -0.3 V. The only new anodic peak is at a much more positive potential (0.4 V) and can be related to the oxidation of nitrite ions that are produced in the cathodic wave. Experiments at several other scan rates shown in Figure 2 yield similar peaks. These results are in striking contrast to the studies of 0.10 mole % AgNO3 in molten LiNO3 shown in Figure 3. The reduction of Ag+ ions to the free metal in molten nitrates is well documented (4,10,11); furthermore, the silver deposits can be visually observed with the aid of a microscope. The reversibility of the Ag⁺/Ag reactions is illustrated by the overlap in potentials for the cathodic and anodic waves and by the performance of the Ag+/Ag reference electrode in molten nitrates. The characteristic sharp drop in current observed following the anodic peak is due to the rapid depletion of the deposited silver. None of these features are observed for the electrochemical reactions involving Pb++ ions in molten nitrates.

Results of a potentiostatic study of the cathodic wave produced by the addition of 0.10 mole % $Pb(NO_3)_2$ to molten LiNO₃ are shown in Figure 4. The platinum electrode remained bright throughout this study with no apparent changes in the effective surface area. This suggests that there is no deposition of lead metal or lead oxide. The Tafel slope (b = -0.27 V) and transfer coefficient (α = 0.45) obtained from this study are very similar to those obtained previously for the electrochemical reduction of molten LiNO₃, i.e., b = -0.22 V and α = 0.57 (8). The second wave that begins at -0.8 V in Figure 4 is due to the direct reduction of molten LiNO₃.

These electrochemical studies of $Pb(NO_3)_2$ in molten $LiNO_3$ suggest that the actual cathodic reaction is the reduction of nitrate ions complexed with Pb++ ions as proposed in Eq. 3. Since lead oxide is more soluble than Li_2O in molten $LiNO_3$ (12), the final reaction products are Li_2O and NO_2 ions. This reduction reaction transfers electrons across the double layer rather than Pb++ ions; therefore, deposition of the metal never occurs. By letting Pb(NO_3)⁺ represent the reactive complex, the proposed reaction mechanism involves the steps

$$(Pb " 0 - NO_2)^+ + e^- \rightarrow Pb0 + (NO_2)_{ads}$$
 (slow) (4)

$$(NO_2)_{ads} + e^{-} \rightarrow NO_2^{-}$$
 (fast) (5)

$$Pb0 + LiN0_3 + Li^+ \rightarrow (Pb " 0 - N0_2)^+ + Li_20 \downarrow (fast)$$
 (6)

that yield the net reaction

$$\operatorname{Lino}_{3} + \operatorname{Li}^{+} + 2e^{-} \rightarrow \operatorname{Li}_{2}0^{\downarrow} + \operatorname{NO}_{2}^{-}$$
(7)

The added Pb⁺⁺ ions, therefore, act as a catalyst for the reduction of molten LiNO₃. Previous studies have shown that there is a considerable energy barrier associated with the reduction of molten nitrates (13). The positive electric field of the metal ion complexed with NO_3 aids both the electron transfer and the rupture of the O-N bond in the slow step.

Cyclic voltametric studies of 0.10 mole % Pb(NO₃)₂ in molten KNO₃ at 385°C are shown in Figure 5. The addition of Pb⁺⁺ ions produces a new cathodic wave beginning at -0.3 V with a peak potential near -0.45 V. Since PbO is insoluble in molten KNO₃ (12), the reaction mechanism involves only Eqs. 4 and 5 to give the net reaction

$$Pb(NO_3)^{\dagger} + 2e^{-} \rightarrow PbO\downarrow + NO_2^{-}$$
(8)

In contrast to $LiNO_3$ results, the added Pb⁺⁺ ions are consumed in molten KNO_3 by their conversion to insoluble PbO that forms a yellow film on the electrode surface. Three new anodic peaks are visible in Figure 5, but these are considerably more positive in potentials than the reduction peak and can be related to the oxidation of insoluble lead oxides as well as to the oxidation of the nitrite ions formed. Possible anodic reactions involving lead oxides include

$$4Pb0 \rightarrow Pb_{3}0_{4} + Pb^{++} + 2e^{-}$$
(9)

$$Pb_{2}0_{4} \rightarrow 3Pb^{++} + 20_{2}\uparrow + 6e^{-}$$
(10)

As suggested by these reactions, anodic treatment of the platinum electrode was an effective method of removing the PbO film.

If any metal were deposited during the cathodic reaction of $Pb(NO_3)_2$, it seems reasonable to expect that it may be detected at fast scan rates before it has time to completely react with the molten nitrate. It is also possible that some of the deposited lead could be stabilized by alloying with the platinum electrode and then be detectable in the anodic sweep. Furthermore, any deposited metal should be more stable in molten KNO₃ than in molten LiNO₃ due to the less acidic character (Lux-Flood) of K⁺ ions. Studies of Pb(NO₃)₂ reactions in molten KNO3 at fast scan rates up to 1000 V/s presented in Figure 6 failed to reveal any new anodic peaks. The corrosion rate for lead in molten KNO₃ would have to be of the order of $10^6 \ \mu g \ hr^{-1} \ cm^{-2}$ to completely react with KNO_3 within the 0.5 ms required to sweep 0.5 V at 1000 V/s. In contrast, the corrosion rate of silver is only 0.04 μ g hr^{-1} cm⁻² in molten NaNO₃ - KNO₃ at 324°C (14). Figure 6 shows that the net current remains cathodic during the reverse anodic sweep until the potential exceeds -0.5 V. As the cathodic reaction decreases during the anodic sweep, the net current becomes anodic due to the large capacity current at fast scan rates that merges in with the oxidation of lead oxides, but no reversible peaks are found as with AgNO3 reactions (Figure 3). The fast anodic scans for $Pb(NO_3)_2$ in molten LiNO₃

in Figure 7 show only the capacity current and a single anodic peak due to nitrite oxidation.

Reactions involving Cd⁺⁺ ions in molten nitrates are similar to those for Pb⁺⁺ ions except that CdO is insoluble in both $LiNO_3$ and KNO_3 . The net reduction reaction, therefore, is

$$Cd(NO_3)^{\dagger} + 2e^{-} \rightarrow CdO_{\downarrow} + NO_2^{-}$$
(11)

in both fused salts. Cyclic voltammograms at various potential sweep rates are shown in Figures 8 and 9 for 0.10 mole % Cd(NO₃)₂ in molten LiNO₃. The addition of Cd⁺⁺ ions produces a new cathodic wave, but there is no reversible anodic wave. The only anodic wave observed begins at a much more positive potential (0.4 V) and is likely due to the oxidation of both CdO and NO₂ merged into one wave. Fast scans again failed to produce any evidence for the deposition of any new metallic phase. The scan at 100 V/s (Figure 9) clearly shows that only the capacity current is observed during the anodic sweep up to a potential of 0.4 V.

Exhaustive electrolysis studies at low current densities in rapidly stirred solutions are presented in Figure 10 for $Cd(NO_3)_2$ and Pb(NO₃)₂ additions to molten KNO₃. The 2e⁻ yield per added metal ion is in agreement with Eqs. 8 and 11 yielding the insoluble metal oxide. In molten LiNO₃, reduction of $Cd(NO_3)_2$ to insoluble CdO again yields $2e^{-}/Cd^{++}$ however, the reduction wave due to the addition of Pb(NO₃)₂ continues indefinitely since Pb⁺⁺ ions act as a catalyst for the reduction of LiNO₃ as represented by Eqs. 4 through 7. The fact that both Eqs. 1 and 3 involve $2e^{-}/M^{++}$ has contributed to the incorrect assumption that the electrode reaction in molten nitrates is the reduction of the metal ion.

Studies of $Pb(NO_3)_2$ additions to molten $LiNO_3-KNO_3$ at $150^{\circ}C$ are shown in Figure 11. A new cathodic peak is produced, yet there is no corresponding reversible anodic peak. This lowering of the experimental temperature by 200°C or more should have greatly reduced the corrosion rate of any deposited lead metal, yet there is no evidence for such a reaction. Thus, even at relatively low temperatures in molten nitrates, the cathodic reaction involves the reduction of nitrate ions in $Pb(NO_3)^*$ complexes.

The cyclic voltammogram for 0.10 mole % Pb(NO₃)₂ in aqueous KOH (60 wt %) at 160°C is shown in Figure 12. This study shows the typical pattern for the reversible reduction of metal ions to the free metal during the cathodic sweep and the stripping of the deposited metal from the electrode surface during the anodic sweep similar to

results for Ag⁺ ions in molten nitrates (Figure 3). The Pb(NO_3)⁺ complexes probably do not exist in aqueous systems due to preferential solvation of the metal ions by water molecules (15). For electrode reactions such as

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$$Pb(H_20)_x^{++} + 2e^- = Pb + x H_20$$
 (12)

desolvation steps are usually rate-determining for the reduction reactions (16). This reversible reaction readily establishes a stable potential at a platinum surface and was used as the reference electrode. The cyclic voltammogram in Figure 12 shows that the deposited lead is quite stable against corrosion at 160° C in aqueous KOH.

Previous studies have suggested that the free energy of activation for the reduction of the $\rm NO_3^-$ ion is lowered by the cation in the complex such that

$$\Delta G^{0 \neq} = \Delta G_{0}^{0 \neq} - ZqF/4\pi\varepsilon_{0}\varepsilon r$$
(13)

where Zq is the charge on the cation, r is the cation radius, and $\Delta G \{\}^{\neq}$ is the free energy of activation in the absence of cation effects (13). Table I presents values for Zq/r in coulomb/meter for various cations. As predicted by its low Zq/r value, Ag+ is readily reduced to the free metal in molten nitrates (10, 11). It is interesting to note that the Ag+/Ag couple is also one of the few metal ion/metal reference electrodes that give stable potentials in molten nitrates. The experimental overvoltage for the reduction of nitrate melts is strongly dependent on the cation radii and increases in the order LiNO₃ < NNO₃ (8). For many transition metal ions such as Ni⁺⁺ and Fe⁺⁺⁺, the potential field of the cation is sufficiently large that the nitrate complex decomposes in molten nitrates

$$(M \cdots 0 - NO_2)^{\top} + NO_3^{-} \rightarrow MO + 2NO_2^{+} + 1/2 O_2^{+}$$
 (14)

to form the oxide even without the aid of any electron transfer at the electrode.

The charge-to-size ratios in Table I suggest that other metal ions may aid the reduction of nitrate ions as observed for Pb⁺⁺ and Cd⁺⁺ ions. Figure 13 shows that the addition of 0.50 mole % Ca(NO₃)₂ produces a new reduction peak at -0.75 V. This cathodic reaction is obviously not the reduction of Ca⁺⁺ ions to the metal since opencircuit potentials of -2.8 V versus Ag⁺/Ag have been measured for the calcium anode in molten KNO₃ (17). By analogy with the results for Pb⁺⁺ and Cd⁺⁺ ions, the cathodic reaction can be represented by

$$Ca(NO_3)^+ + 2e^- \rightarrow CaO_4 + NO_2^-$$
(15)

The large anodic peak at -0.1 V is likely due to the oxidation of the insoluble CaO $\,$

$$Ca0 \rightarrow Ca^{++} + 1/2 \ 0_2^{+} + 2e^{-}$$
 (16)

As expected from these reactions, areas under the cathodic and anodic peaks are approximately equal.

Additions of 0.50 mole % $LiNO_3$ to molten KNO_3 produces a new cathodic wave at -1.35 V as shown in Figure 14. Due to the preponderant amount of K⁺ ion in the melt, the formation of the $LiK(NO_3)^+$ complex is more likely than the $Li_2(NO_3)$ complex, hence the cathodic wave can be represented by the reaction

$$\operatorname{LiK}(\operatorname{NO}_3)^{\dagger} + \operatorname{Li}^{\dagger} + 2e^{-} \rightarrow \operatorname{Li}_20 \downarrow + \operatorname{K}^{\dagger} + \operatorname{NO}_2^{-}$$
(17)

The reduction of this complex occurs at potentials intermediate to those for the reduction of pure $LiNO_3$ and pure KNO_3 . The new anodic peak at -0.7 V can be attributed to the reaction

$$\text{Li}_{2}0 \rightarrow 2 \text{ Li}^{\dagger} + 1/2 0_{2}^{\dagger} + 2e^{-}$$
 (18)

Electrode reactions involving the deposition and oxidation of metallic lithium are implausible at these experimental potentials.

The peak cathodic currents produced by the addition of Pb^{++} , Cd^{++} , Ca^{++} , and Li^+ ions are all directly proportional to the amount of metal ion added. This implies that the dominant equilibria in molten nitrates are

$$M(NO_3)_2 \xrightarrow{\longrightarrow} M(NO_3)^+ + NO_3^-$$
(19)

$$LiNO_3 + KNO_3 + KNO_3^+ + NO_3^-$$
(20)

and that essentially all of the added nitrate salt is in the ionized form. Simple calculations show that for $K_{eq} > 10$, more than 99% of the

added nitrate salt will be in the ionized form for concentrations up to 10 mole %. Further dissociation of $M(NO_3)^+$ to form M++ appears to be negligible in molten nitrates. The cathodic peak current for 0.50 mole % Ca(NO_3)_2 is about twice that observed for 0.50 mole % LiNO_3 in molten KNO_3 (Figures 13 and 14). This is reasonable since Eq. 17 involves only le⁻ per added Li⁺ ion as opposed to 2e⁻ per added Ca⁺⁺ ion in Eq. 15.

Thermodynamics provides further evidence that the experimental reduction waves observed for Pb⁺⁺, Cd⁺⁺, Ca⁺⁺, and Li⁺ additions to molten nitrates do not involve reduction of these ions to the metal. The experimental potentials for reduction to the metal as measured versus the Ag⁺(0.1 m)/Ag reference electrode should be within 0.2 V, considering errors and activity corrections, of the standard thermodynamic potentials calculated for the cell

$$n Ag + M(NO_3)_n \rightarrow M + n AgNO_3$$
(21)

at 350°C. Table II presents the calculated thermodynamic potentials (E^0) for comparison with the experimental potentials (E) at which the reduction wave commences. The experimental potentials for these reduction waves are considerably positive to the calculated E^0 in every case except for Ag+ ions. Thermodynamically, reduction of Pb++, Cd++, Ca++, and Li⁺ ions to the metal is not possible in molten nitrates at the observed potentials. The reduction of solvent anions that are complexed with polarizing metal ions may also occur in other oxidizing fused salt systems such as molten sulfates (18).

CONCLUSIONS

Experimental results obtained for the cathodic reactions of Pb++ and Cd⁺⁺ ions in molten nitrates can be clarified by the reaction in Eq. 3 involving the reduction of complexed nitrate ions. The confusing results of other workers can be explained by this simple reaction. Reports on the cathodic deposition of alkaline-earth ions at unusual potentials (19, 20) is more likely the reduction of $Ca(NO_3)^+$, $Sr(NO_3)^+$, or $Ba(NO_3)^+$ complexes as given by Eq. 3. The observed potentials for the reduction shift towards more electropositive values in the sequence Ba++ < Sr++ < Ca++ due to the kinetic effects of Zq/r (Table I) as predicted by Eq. 13. Experimental diffusion coefficients should be reported for the nitrate complex rather than for the metal ion when the latter is not actually reduced to the metal. Previous reports on the electrochemical reduction of various metal ions in molten nitrates (1-6, 19-23) need to be re-examined in terms of Eq. 3.

REFERENCES

- 1. J. E. B. Randles and W. White, Z. Electrochem. Ber. Bunsenges. Physik. Chem., 59, 666 (1955).
- 2. M. Francini and S. Martini, Z. Naturforsch., 23 a, 795 (1968).
- S. Casadio, A. Conte, and F. Salvemini, Electrochem. Acta, 16, 3. 1533 (1971).
- W. K. Behl and H. C. Gaur, J. Electroanal. Chem., <u>32</u>, 293 (1971).
 M. Saito and T. Miura, <u>Bull Chem. Soc. Japan</u>, <u>50</u>, <u>1347</u> (1977). 4.
- 5.
- V. Jiamsakul, Ph.D. Dissertation, University of Southampton, 6. (July 1978).
- 7. M. H. Miles, D. A. Fine, and A. N. Fletcher, J. Electrochem. Soc., 125, 1209 (1978).
- 8. M. H. Miles and A. N. Fletcher, J. Electrochem. Soc., 127, 1761 (1980).
- 9. D. G. Lovering and R. M. Oblath in "Ionic Liquids." pp. 165-176, D. Inman and D. G. Lovering, Eds., Plenum Press, New York (1981).

- 10. D. L. Manning, <u>Talanta</u>, <u>10</u>, 255 (1963).
- G. J. Hills, D. J. Schiffrin, and J. Thompson, <u>Electrochim. Acta</u>, 19, 657 (1974).
- M. Salaha, J. Gilbert, and P. Claes, <u>J. Chim. Phys. Phys.-Chim.</u> <u>Biol.</u>, <u>79</u>, 63 (1982).
- A. N. Fletcher, M. H. Miles, and M. L. Chan, <u>J. Electrochem. Soc.</u>, <u>126</u>, 1496 (1979).
- 14. A. Conte and M. D. Ingram, <u>Electrochim. Acta</u>, <u>13</u>, 1551 (1968).
- 15. J. Padova, <u>J. Phys. Chem.</u>, <u>72</u>, 796 (1968).
- M. H. Miles and H. Gerischer, <u>J. Electrochem. Soc.</u>, <u>118</u>, 837 (1971).
- 17. M. H. Miles, <u>J. Appl. Electrochem.</u>, <u>11</u>, 325 (1981).
- 18. T. K. Hoa and B. J. Welch, <u>J. Appl. Electrochem.</u>, <u>3</u>, 45 (1973).
- 19. S. Sternberg and T. Visan, <u>Rev. Roumaine. Chim.</u>, <u>24</u>, 219 (1979).
- 20. S. Sternberg and T. Visan, Electrochim. Acta, 26, 75 (1981).
- D. G. Lovering and R. M. Oblath, J. Electrochem. Soc., 127, 1997 (1980).
- J. A. Plambeck in "Enclyclopedia of Electrochemistry of the Elements," Vol. 10, pp. 165-232, A. J. Bard, Ed., Dekker, Inc., New York (1976).
- 23. G. Mamantov, J. M. Strong, and F. R. Clayton, Jr., <u>Anal. Chem.</u>, 40, 488 (1968).

Cation	$r = 10^{10}$ (m)	$7a/r = 10^{9}(c/r)$
		24/1 x 10 (0/ш)
к+	1.33	1.20
Ag ⁺	1.26	1.27
Na ⁺	0.95	1.69
Li ⁺	0.68	2.36
Ba ⁺⁺	1.35	2.37
Pb ⁺⁺	1.20	2.67
Sr ⁺⁺	1.13	2.84
Ca ⁺⁺	0.99	3.24
Cd ⁺⁺	0.97	3.30
Ni ⁺⁺	0.72	4.45
Fe	0.64	7.51

TABLE I. Comparison of Charge-to-Size Ratios for Various Metal Ions.

TABLE II. Thermodynamic (E⁰) and Experimental (E) Potentials for the cell reaction: $n \text{ Ag } + M(\text{NO}_3)n \rightarrow M + n \text{ AgNO}_3.$

-		
Metal Ion	E ⁰ (v)	E (v) ^a
Ag ⁺	0.00	-0.1
Pb ⁺⁺	-1.05 ^b	-0.1
ca ⁺⁺	-1.08 ^b	-0.1
Ca ⁺⁺	-3.43	-0.6
Li ⁺	-3.43	-1.2

 a Experimental potential at which reduction wave commences in molten KNO₃.

^bBased on ΔH^0 .



Fig. 1. Cyclic voltammetric study of 0.10 mole % $Pb(NO_3)_2$ in molten LiNO₃ at 350°C. Dashed line shows background current.



Fig. 2. Cyclic voltammetric studies of 0.10 mole % $Pb(NO_3)_2$ in molten LiNO₃ at scan rates of 0.2, 1.0 and 5.0 V/s.



Fig. 3. Cyclic voltammetric studies of 0.10 mole % AgNO₃ in molten LiNO₃ at 350°C for scan rates of 1, 5, and 20 V/s.



Fig. 4. Potentiostatic study of the cathodic reaction of 0.10 mole % Pb(NO_3)₂ in molten LiNO₃ at 350°C.



Fig. 5. Cyclic voltammograms at 0.1 V/s and 0.5 V/s for 0.10 mole % Pb(NO₃)₂ in molten KNO₃ at 385°C.



Fig. 6. Fast potential scan studies of 0.10 mole % Pb(NO₃)₂ in molten KNO₃ at 385°C.



Fig. 7. Fast potential scan studies of 0.10 mole % Pb(NO₃)₂ in molten LiNO₃ at 350°C.



Fig. 8. Cyclic voltammograms for 0.10 mole % Cd(NO_3)_2 in molten LiNO_3 at 350°C.


Fig. 9. Fast potential scan studies of 0.10 mole % Cd(NO_3)_2 in molten LiNO_3 at 350°C.







Fig. 11. Studies of $Pb(NO_3)_2$ additions to molten $LiNO_3-KNO_3$ at 150°C.



Fig. 12. Cyclic voltammogram for 0.10 mole % Pb(NO₃)₂ in aqueous KOH at 160°C.



Fig. 13. Cyclic voltammetric study of 0.50 mole % Ca(NO₃)₂ in molten KNO₃ at 385°C. Dashed line shows background current.



Fig. 14. Cyclic voltammetric study of 0.50 mole % LiNO₃ in molten KNO₃ at 385°C. Dashed line shows background current for the cathodic sweep.

ELECTROLYSIS REACTIONS IN INORGANIC ACETATE MELTS

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Analysis of the electrolysis products of the molten eutectic mixture of sodium and potassium acetates in the temperature range $230 - 330^{\circ}C$ showed that the only gaseous cathode product was methane. Carbon dioxide and acetone were the major anode products. Cyclic linear potential sweeps over the range 0.5V anodic to 0.8V cathodic with respect to a micro-platinum reference electrode indicated that the system was only quasi-reversible. The siting and appearance of the adsorption and desorption peaks on the potentiodynamic curves confirmed the hypothesis from Faradaic efficiency considerations that the anodic decarboxylation of the acetate ion was a mixed potential process resulting in the formation of a carbonium ion which was discharged at the cathode producing methane gas. When hydrogen gas was fed to a porous nickel working electrode the redox reaction for hydrogen was observed occasionally though usually only the gas adsorption and desorption processes were noted.

INTRODUCTION

For many years the Kolbe electrosynthesis reaction has been studied in aqueous solution and there are extensive reviews on this subject (1-5). The reaction is believed to proceed by a decarboxy-lation process at the anode (6-7):-

сн ₃ соо-	· →	сн ₃ соо. + е	(1)
сн ₃ соо.	→	со ₂ + сн ₃ .	(2)
2Сн ₃ .	÷	с ₂ н ₆	(3)

In alkaline solutions the methyl radical formed on decarboxylation will preferentially react with a hydroxyl radical to give an alcohol (8):-

$$H_0 \rightarrow H^+ + OH^* + e$$
 (4)

 $CH_{2}^{*} + OH^{*} \rightarrow CH_{2}OH$ (5)

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Recently there has been much interest in electrosynthesis, and reactions in solvents other than water in which the radicals formed couple with solvent molecules, dimerise or abstract hydrogen (5). Solvents can range from organic acids (9), to acetonitrile (10) and dimethyl formamide (11) whilst similar processes involving the oxidation of oxalic acid (12), fluorocarboxylic acids (13,14), formic acid, formaldehyde and methanol (15,16) have been investigated. Few electrochemical investigations have been carried out in molten carboxylate salts. Marassi and coworkers (17,18) have reported the behaviour of water and acetic acid in molten alkali acetates whilst Tissot has investigated electrochemical oxidation reactions in molten alkali trifluoroacetates (19,20). The results reported in this paper follow investigations into the thermal stability of alkali acetates (21,22,23) and the use of these melts as the electrolyte in a medium temperature fuel cell.

EXPERIMENTAL

The chemicals used were anhydrous reagent grade CH₃COONa (99.0%) and CH₃COOK (98.0%) supplied by Hopkins and Williams. Previous work (21,22,23) had shown that careful drying and exclusion of oxygen from the melt were essential. The salts were initially dried at 140°C in a vacuum furnace (7 N/m²) for 24 hours. The eutectic mixture (53.7 mol % CH₃COO K) (24) was then prepared in a dry box under an atmosphere of N₂ (O₂ < 10 ppm) and the mixture further dried under vacuum for several hours before melting (mp 230°C) in the electrolysis cell.

A simple U-shaped Pyrex electrolysis cell (CELL I) was used with 10 mm diameter, 0.38 mm thick, bright platinum electrodes fused into supporting glass sheaths and 30 mm apart. The anode and cathode compartments were separated by a sintered glass disc (porosity 3) and connected individually to two isolated gas traps and manometers. Electrolyses were carried out at 245 (\pm 2) ^oC. In the presence of slight traces of water, i.e. in air, the threshold voltage required to produce an appreciable current (1 ma) was lower (1.5 volt) than for the thoroughly dry melt under vacuum or an atmosphere of dry N_2 (2.2volt) The power supply was a stabilized D.C. unit O-15 V and O-160 ma; polarisation voltages and currents were measured using a digital voltmeter and milliameter. The electrolyses were at 2.5 \pm 0.2 volt for 1 to 2 hours and the products at the electrodes were collected in gas traps cooled by liquid nitrogen. After allowing the gas collected to warm up to room temperature the volume and the gas pressure were noted and the gas pressure made up to atmospheric with N_2 .

Analysis was by means of gas chromatography using both katharometer and flame ionisation detectors. The chromatographs Phase Separation LC2 and Perkin Elmer F30 were calibrated quantitatively using standard gas samples; product identification was by retention time coincidence. In the potentiodynamic studies a platinum wire (0.05 mm diameter) reference electrode was introduced into the electrolysis cell in close proximity to the working electrode (Cell II, figure (1)). The cell was adaptable to enable the behaviour of various electrodes in the melt to be studied. The outputs from the potentiostat (Chemical Electronics TR40/JA) and linear sweep generator were fed to a Hewlett Packard model 7035B X-Y recorder, so that the current potential curves could be recorded directly. Particular care was taken to ensure that the bright platinum, nickel and reference electrodes were clean before use in the melt. The electrodes were boiled in nitric acid for several minutes, rinsed in distilled water, oven dried and stored in a desiccator before mounting in the cell.

In order to study the effect of an oxidisable gas feed to the fuel electrode in a fuel cell a three electrode cell was constructed such that gas could be fed to one side of a working porous nickel electrode (Cell III, figure (2)). The porous nickel electrode had to be arranged so that although wetted by the melt it was not flooded. The porous nickel disc (porosity 50%), 10 mm diameter and 1 mm thick, was pressure welded to a nickel current lead and supported on a sintered glass disc (porosity 2) sealed into a Pyrex tube. To overcome internal cell resistance a 1 mm diameter hole was drilled through the sintered disc immediately above the platinum wire tip reference electrode. Good three-phase contact was then maintained by careful control of the feed gas and nitrogen pressures; the secondary electrode was of bright platinum.

As the main object of the research was to investigate the behaviour and improve the performance of a molten acetate fuel cell using porous nickel electrodes a platinum wire micro electrode was inserted in the melt paste close to the fuel electrode in a fuel cell. The micro electrode was only separated from the working electrode by a glass fibre paper insulating disc. The system was then connected to the potentiostat and linear sweep generator. Hydrogen gas was fed to the fuel electrode and nitrogen, to balance the gas pressure, to the counter electrode. It should be noted that the voltage sign convention is opposite to that in common use.

RESULTS AND DISCUSSION

The current voltage curves for electrolysis of wet and dry alkali acetate eutectic melt using Cell I at 245°C were obtained. In the wet melt a point of inflection on the current voltage curve was evident at 2.7 volt comparable to the reduction waves for water at 1.8 volt obtained by Marassi against a silver/silver nitrate electrode (17,18).

Electrolyses at voltages between 2.3 and 2.7 volts in the dry melt corresponding to anodic current densities of 4 to 14 ma/cm² gave the same relative proportions of products. At 2.3 volt and current density of 4.5 ma/cm^2 the apparent anodic Faradaic efficiency was 92%. The platinum electrodes and melt remained clean even after 2 hours electrolysis indicating that there was little polymerisation at low current densities. At 2.7 volt and current density of 13.4 ma/cm^2 a blue polymer film appeared on the anode and there was a considerable tarry deposit in the melt after only 1 hour of electrolysis (25,26). The Faradaic efficiency was now only 60%.

Table 1 Apparent Faradaic Electrolysis Yields Current Anode Cathode Anodic Voltage Time Density Yield Yield Faradaic moles $x 10^{+4}$ moles $x 10^{+4}$ ma/cm^2 Volts (secs) Yield % 4.5 1.54 92 2.3 7200 5.4 13.4 2.7 6.1 1.54 3600 60

The proportions of product gases obtained in these direct electrolysis results are shown in table (2). The results are from several electrolysis runs and the proportions of major gases found at the anode and cathode showed an average deviation of ± 1 % despite wide variations in current densities. This accords with Tissot's observations on the electrolysis of CF₃COOK - CF₃COO Na eutectic melt at 116°C when the proportions of products were essentially independent of the anodic current density (19). Water was also detected in trace amounts but not CO, ethane or ethylene.

Table 2	Electrolys	is Products	from GLC	Analysis

Gases	Total Products	Anode Products	Cathode Products
	Mol %	Mol %	Mol %
Methane	26.8	6.3	20.5
Isobutene	0.5	0.1	0.4
Acetone	15.2	14.5	0.7
Carbon Dioxide	57.5	57.5	trace

Previous work (23) on the thermal decomposition of the alkali acetate eutectic melt had shown that there was no significant thermal decomposition at 250° C (hence the products should only be due to the electrolysis reaction). Three to four times more electrolysis product gases were formed at the anode than at the cathode so that overall the ratios of the main decomposition products were approximately methane : acetone : carbon dioxide 1.75 : 1 : 3.8.

Step-wise potential sweeps using the potentiostat and Cell (II), increasing the potential at a rate of 15 mv every 30 seconds, showed that the decomposition potentials were approximately + 0.8 V cathodic and - 0.5 V anodic with respect to the platinum micro-electrode. With

nickel electrodes the cathodic decomposition potentials were also + 0.8 V but slightly less at - 0.35 V (bright nickel) and - 0.4 V (porous nickel) for anodic decomposition. In the potentiostatic experiments the proportion of methane to other products found at the anode was rather less than in the direct electrolysis experiments and there was also a slight increase in tarry products and in production of water. Isobutene was not identified possibly because the sample quantities collected were small. Current densities varied from 15 ma/cm^2 to 90 ma/cm² at the electrodes. There was little difference in the proportions of products collected if nickel rather than platinum was used for the electrodes.

Table 3 Potentiostatic Electrolysis Products

Ele	ctrode	<u>CH</u> 4	<u>co</u> 2	Acetone	<u>H</u> 20
Pt	anode	1	26	11	3.6
Ni	anode	1	24	11	0.15
Pt	cathode	1	nil	nil	0.02
Ni	cathode	1	nil	nil	0.10

a) Ratio of Products

Gases	Total Products	Anode Products	Cathode Produc	ts
	mol %	mol %	mol %	
Methane	21.65	2.15	19.5	
Acetone	24.0	24.0	. nil	
Carbon dioxide	e 52.0	52.0	nil	
Water	2.35	2.15	0.2	

b) Average Mole % of Products at Anode and Cathode

Ethane was never identified as an electrolysis or thermal decomposition product in contrast to the Kolbe synthesis in aqueous solution (1-7) and in non-aqueous solutions (9-11). Even in molten alkali trifluoro-acetates the main products were the dimer (C_2F_6) and CO_2 (19,20), as in the electrolysis of $CF_3COO Na$ in acetonitrile (10).

The limiting anodic reaction appears to be the oxidation of the acetate ion to a methyl radical and CO_2

$$CH_3COO^- \rightarrow CH_3' + CO_2 + e$$
 (6)

However, the main anodic reaction products are acetone and CO₂ with only a little methane and no ethane, hence the above reaction probably takes place in stages beginning initially with the adsorption of the acetate ion, followed by desorption of the acetate radical:-

$$CH_{3}COO^{-} \rightarrow CH_{3}COO^{-} + e \rightarrow CH_{3}COO^{-}$$
 (7)
Ads Ads
acetate
radìcal

Vasil'ev et al (27,28,29) from pulse potentiostatic techniques find that the slow step is the discharge of the adsorbed acetate ion. In their scheme the charged acetate ion is adsorbed rapidly before the slow discharge of an acetate radical followed by methyl radical formation by decarboxylation:-

$$CH_3COO^{-} \rightarrow CH_3COO^{-} \rightarrow CH_3COO^{-} + e \rightarrow CH_3^{-} + CO_2^{-} + e$$
 (8)
fast Ads slow

This is in contradiction to the mechanism proposed by Lord Wynne Jones and co-workers (6,7) where the adsorbed radical CH_3COO° reacts at the electrode surface with acetate ion

$$CH_3COO_{Ads} + CH_3COO^- \rightarrow C_2H_6 + 2CO_2 + e$$
 (9)

In our experiments it was not possible to differentiate between the schemes, but if the methyl radical were produced in significant quantities on adjacent sites at the anode one would expect immediate dimerisation to C_2H_6 ethane, but this does not occur. If, however, the acetate radical was first discharged into the solvent melt before decarboxylating the formation of ethane would be unlikely.

At the higher current densities in the direct electrolysis experiment there is a slight increase in the proportion of methane in the products and a marked increase in tarry polymer products coupled with a decrease in Faradaic yields of anodic products to 60%. At the low current density some 80% of the anode product is CO_2 so that the Faradaic efficiency for decarboxylation and production of CO_2 is 70% which is consistent with the supposition that the primary electrochemical reaction is the one electron discharge of the carboxylate radical which disproportionates rapidly in the melt to give a methyl radical and CO_2 :

$$CH_3COO^{\bullet} \rightarrow CH_3^{\bullet} + CO_2$$
 (10)

The chemical reactions which follow are probably:-

a) Hydrogen abstraction from solvent acetate ions producing methane

$$CH_{3} + CH_{3}C_{0}^{\neq 0} + CH_{4} + CH_{2}C_{0}^{\neq 0}$$
(11)

b) Formation of acetone

$$CH_3 + CH_3 C < 0 \rightarrow CH_3 > C = 0 + 0^-$$
 (12)

Oxygen could not be detected but it is very probable that the melt contained trace quantities of oxide or hydroxide ions as eventually water was detected at both anode and cathode. The above two reactions compete and (12) is probably favoured at higher temperatures as shown by the thermal decomposition results (23).

Only relatively small quantities of methane were recorded at the anode, 2-6% of the total, whilst the total gaseous product collected at the cathode (20%) was almost exclusively methane. The mechanism of the cathodic reaction is rather uncertain. Discharge of Na⁺ and K⁺ is possible. The decomposition potentials of molten NaOH and KOH are 2.3 and 2.35 volts respectively (30), however, the potentiostatic experiments showed rapid electrochemical decomposition at cathodic potentials of only 0.7 to 0.8 volt.

Scheme (1)

If alkali metal deposition occurs the metal atom might react with the acetate solvent to form methyl radicals followed by hydrogen abstraction.

$$Na^+ + e - Na^-$$
 (13)

$$CH_{3}C\overset{0}{\underset{0^{-}}{\checkmark}} + Na^{\cdot} \rightarrow CH_{3}^{\cdot} + NaCO_{2}^{-}$$
(14)
very unstable

The cathodic efficiency for production of methane was 25%. No tarry products were formed at the cathode nor was there any CO_2 which could be the final product of the highly unstable $NaCO_2^{-1}$.

Scheme (2)

An alternative scheme is via the production of carbanions (31)

$$CH_{3}C \swarrow_{0^{-}}^{0} + e \rightarrow CH_{3}C \swarrow_{0^{-}}^{0^{-}} \rightarrow CH_{3} + CO_{2}^{2^{-}}$$
(15)

Scheme (3)

A third possibility is the formation of a metal alkyl $CH_3 - Na^+$ at the anode which is discharged at the cathode giving a methyl radical.

Scheme (4)

If, however, the anodic process is a mixed potential process involving both single electron transfer to give the carboxylate radical followed by transfer of a second electron to the carboxylate radical which is still adsorbed on the electrode, then a carbonium ion CH_3^+ could be formed at the anode

 $CH_{3}COO^{-}_{Ads} \rightarrow CH_{3}COO^{+} + e \rightarrow CH_{3}COO^{+} + e \rightarrow CH_{3}^{+} + CO_{2}$ (16)

The CH_3^+ carbonium ion transfers to the cathode where it is discharged as the methyl radical which abstracts hydrogen from the solvent giving methane,

$$CH_3^+ + e \rightarrow CH_3^- + CH_3COO^- \rightarrow CH_4 + CH_2COO^-$$
 (17)
solvent

If the theoretical quantities of products which should be formed at the anode are calculated for a <u>single electron transfer</u> process and compared with the actual quantities of products obtained at the anode it is found that the Faradaic anodic efficiency for current density of 4.5 ma/cm^2 based on the amount of CO₂ produced is 70%. Whereas Faradaic anodic efficiency based on total moles of methane and acetone produced at the anode is only 20%. There is, however, a large amount of methane (95% of gaseous product) at the cathode, but as mentioned earlier the actual quantity produced is only equivalent to a cathodic efficiency of 25% for a single electron process such as schemes (1) or (2).

Scheme (3) involving the reaction of the methyl radical at the anode with Na⁺ ion and then transfer to cathode for single electron transfer discharge would mean that the organic ion discharge efficiency at the anode would still only be 45%. However, if as in scheme (4), the discharge of the carboxylate ion were immediately followed at slightly higher potentials by removal of a second electron to form a carbonium CH_3^+ ion the two electron process would use twice the amount of electrical energy so that the efficiency of the electrode reaction entailing formation of a carbonium ion is doubled to 50%. Thus the overall anodic efficiency based on total production of organic molecules $(CH_4, (CH_3)_2CO)$ at both electrodes is 70% which is consistent with the anodic Faradaic efficiency for production of CO_2 . Scheme (4) therefore seems the most likely from electrical energy efficiency considerations.

The potentiodynamic work was an attempt to trace the possible electrode reactions in the melt as outlined above. Working slightly within the decomposition potentials previously determined with reference to a point Pt electrode, both cathodic and anodic potential sweeps were carried out in the molten acetate melts at various temperatures and sweep rates using the different electrode materials. Typical potentiodynamic curves are shown in figures 3 - 6. In most cases two adsorption current peaks and two desorption current peaks were observed in addition to the anodic and cathodic decomposition currents.

Electrode	Region II Adsorption (Peak IIc)	Region III Adsorption (Peak IIIc)	Region IV Desorption (Peak IVa)	Region III Desorption (Peak IIIa)	Region II Desorption (Peak IIa)
	(volts)	(volts)	(volts)	(volts)	(volts)
Pt black	+ 0.15	+ 0.59	Nil	+ 0.42	Nil
Pt bright	- 0.08	+ 0.35	+ 0.65	+ 0.21	Nil
Ni bright	- 0.07	0.4 to 0.5	Nil	+ 0.25	- 0.09
Ni porous	- 0.15	+ 0.64	+ 0.62	+ 0.39	- 0.11
Fuel Cell	+ 0.06	+ 0.45	Nil	+ 0.20	- 0.13

Table 4 Potentiodynamic Adsorption & Desorption Peaks

The melt temperature was 245°C except for Pt black electrodes when a temperature of 305°C was used. The peak adsorption currents varied linearly with the square root of the sweep rate in accordance with the general equation for a redox reaction at a planar electrode i $\propto \sqrt{V}$, indicating that the reactions are diffusion controlled (32).

On the reactive platinum black electrode at 305° C two adsorption peaks at + 0.15 (Region II) and + 0.59 volts (Region III) against the microplatinum reference electrode were observed. The desorption peak was at + 0.42 volt (Region III). On the less reactive bright platinum electrode peaks observed were at - 0.08 volt (Region II) and + 0.35 volt (Region III) with the corresponding desorption peak at + 0.21 volt (Region III). There was also an earlier desorption peak at + 0.65 volt (Region IV) in this case, probably due to desorption of methane as predicted by the electrolysis experiments. For the nickel electrodes there is an adsorption plateau at + 0.4 to 0.5V (bright nickel) and at + 0.68V (porous nickel) followed by a desorption peak in Region III at + 0.25 volt (bright nickel) and + 0.43 volt (Porous nickel). There was also an earlier desorption peak at + 0.6V (Region IV) in the case of porous nickel due to desorption of methane.

Cairns (3) reports that methane is adsorbed on platinum black at a potential of 0.3 volt at 100° C and the electro-oxidation of methane has been extensively studied (3,4,33,34). Reduction of adsorbed methane gives not only methane but ethylene and ethane at the cathode (35). However, it is unlikely that the adsorption process at the cathode is due to adsorption of methane; it is more likely to be due to adsorption of methyl radical at the anodic or slightly cathodic potentials in Region II or to adsorption of the methane carbonium ion CH₃⁺ at the main adsorption peak in Region III followed by reduction of the methyl radical at the cathodic of the methyl radical at the methane cathodic of the methyl radical at the state of 0.8V.

Desorption of the reduced species CH_4 was not always observed but where it does occur it is at + 0.65V (Bright Pt) and + 0.6V (Porous Ni). The peak current corresponding to desorption of CH_3^+ was about a third of peak adsorption current, consistent with the observation that a good deal of CH_A was obtained at the cathode.

$$CH_3^+ + e \rightarrow CH_3^-$$
 (18)

is given by $\Delta E_p = \frac{2.3 \text{ RT}}{\text{F}}$ so that $\Delta E_p = 0.114 \text{V}$ at 305°C, or

 $\Delta E_{p} = 0.104 \text{V} \text{ at } 250^{\circ} \text{C}$.

Table 5 Sweep Rates and ΔE_p for Carbonium ion discharge

Electrode

Ρt	Black	Sweep Rate mV/sec	33	21	10.5	4.2	2.1
		$\Delta E_{p}(v)$	0.28	0.15	0.13	irr.	irr.
Pt	Bright	Sweep Rate mV/sec	-	21	-		
		$\Delta E_{p}(V)$		0.14			
Ni	Bright	Sweep Rate mV/sec	-	21	-		
		$\Delta E_{p}(v)$		0.15			
Por	ous Ni	Sweep Rate mV/sec	25	21	16	4.2	2.1
		$\Delta E_{p}(V)$	0.20	0.17	0.16	irr.	irr.

The above results, even for single electron transfer indicate that the reaction is only quasi-reversible. At very low sweep rates the anodic peak was absent indicating that under some conditions the reaction is completely irreversible. More probably, however, the absence of the anodic peak is due to the rapid irreversible reduction of the adsorbed carbonium radical to CH₄. This is corroborated by the fact that the peak separation also tended to increase with sweep rate being at a minimum at about 10 to 20 mV/sec., indicating that the electron transfer was slow and that the chemical reaction was faster than the electrochemical one as evidenced by the disappearance of the anodic peak at very slow sweep rates (36,37).

Sweep rate data is not very comprehensive for the bright platinum and nickel electrodes as the main interest was in the porous nickel electrode. Here it was evident that the process was somewhat more irreversible than at the platinum black electrode though the adsorption and desorption currents observed were about 100 times greater corresponding to the large surface area of the porous nickel. A pronounced peak presumed to be desorption of the hydrogen-reduced species CH_A was observed at + 0.6 Volt.

Similar peak locations were found in the fuel cell experiments. A typical example is shown in figure 7 which also shows the adsorption and desorption peaks for H₂ gas at - 0.08V and -0.4V respectively, i.e. a ΔE_p of 0.32V. The adsorption and desorption peaks for H₂ in molten acetate melt in the potentiostat electrolysis cell III are + 0.32V and - 0.13V with ΔE_p = + 0.45V at a scan rate of 33 mV/sec.

Considerable difficulties were experienced in the gas feed cell (figure 2) and careful balancing of the gas pressures was required in order to maintain three phase contact and avoid flooding the porous nickel electrode. The reference electrode was also separated from the working electrode by the sintered glass disc with the result that the potentiodynamic curves were somewhat featureless. It is estimated that the potential displacement was 0.3V positive due to the IR drop. The potential span was kept well within the decomposition limits. Figure 8 illustrates the appearance of the curves when hydrogen gas is adsorbed at the porous electrode. The anodic and cathodic peaks are ascribed to adsorption and desorption of hydrogen at the electrode rather than to the formation of hydrogen ions as similar adsorption peaks were observed when nitrogen was the gas feed to the electrode. Much more detailed results were obtained when hydrogen was fed to the working electrode in a fuel cell. Separation distances here are negligible though the cathodic adsorption peak is not very evident. ${\tt N}_2$ was the feed to the counter electrode in both cases. When the effect of varying H_2 gas pressure in the fuel cell was investigated it was found that the peak H (cathodic adsorption of hydrogen) is only observed for low gas pressures ($<5000~Nm^{-2})$ indicating that at the higher pressures the electrode is fully saturated with adsorbed hydrogen gas. Hydrogen peak separation in the fuel cell is 0.34 v at 21 mV/s though with a lower hydrogen concentration $\Delta E_{\rm p}$ at 26 mV/s was only 0.08 volt which agrees with the value calculated by Saveant (38).

In the potentiostatic cell with gas feed $\Delta E_{\rm p}$ appeared to decrease with decreasing scan rate.

Table 6	Scan Rate	and Shift	of Hydrogen	Peaks in	Potentiostatic	Cell
Scan	Rate (mV/s)	50	33.3	16.	7 10	
нс	(volts)	+ 0.42	+ 0.32	+ 0.	22 + 0.23	
Ha	(volts)	- 0.10	- 0.13	+ 0.	.02 + 0.08	
Δe _r	(volts)	0.52	0.45	0.	20 0.15	

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Anodic and cathodic currents were approximately the same which is consistent with the theory that these peaks are due to adsorption and desorption of hydrogen and are not due to the formation of H⁺ ions. Similar peaks were found if N₂ was the gas feed.

Marassi (17,18) has investigated the behaviour of water and acetic acid on Bright Pt electrodes in acetate eutectic melt at 250° C. The melts were wet and the voltages for adsorption and desorption were approximately + 0.12V and + 0.03V respectively with respect to a Ag/Ag⁺ electrode as secondary reference electrode. The peak separation for the water reaction

$$H_2O + e \leftarrow \frac{1}{2}H_2 + OH^-$$
 (19)

was 0.085V at a scan rate of 100 mv/sec. The hydrogen peaks for water formation are not so well developed as for acetic acid formation where the adsorption and desorption peaks are - 0.40V and - 0.53V with a peak separation of 0.13V for the reaction

 $H_2 + CH_3COO^- - 2CH_3COOH + 2e$ (20)

comparable with the calculated values of 0.0795V and 0.0789V respectively (38).

Nickel is much less electrochemically active than platinum hence it is to be expected that it is difficult to observe the electron transfer reaction on porous nickel in the potentiostatic cell. The high internal resistance of this cell meant that the potentiodynamic curve was rather featureless apart from the adsorption and desorption of the gases. It is possible however that in the fuel cell with its much lower internal resistance the hydrogen peaks sometimes observed are due to the electron transfer redox reaction for hydrogen.

CONCLUSIONS

Analysis of the cathodic and anodic gaseous electrolytic decomposition products of the sodium and potassium acetate eutectic melt indicated that the process was not a simple decarboxylation reaction. The calculated Faradaic efficiency at low current densities for decarboxylation was 70% for a single electron transfer. The appearance of methane at the cathode indicated that the electrochemical step was a multi-electron transfer leading to formation of a carbonium ion at the anode followed by decarboxylation. Ethane production was not observed so that it is unlikely that the methyl radical is present at adjacent sites on the anode hence it is postulated that the two electron transfer at the anode involves first of all charge transfer from the adsorbed acetate ion forming an acetyl radical which remains adsorbed on the electrode (Eqn. 16). The second electron transfer process is from this acetyl radical and not from a methyl radical and it is the discharge of the acetyl radical ion (CH_2COO^+) which results in the formation of the carbonium ion (2,5).

All the potentiodynamic traces showed evidence of adsorption and desorption of a cationic species at potentials very much lower than those expected for discharge of a metal cation. These peaks in region III of the traces would fit in very well with the presence of a carbonium ion in the melt. The peak potential separation for the oxidation reduction couple of the carbonium ion tended to a minimum value at moderate sweep rates indicating that the electron transfer reaction was slower than the subsequent chemical hydrogenation. At very slow sweep rates the anodic desorption peak disappeared completely showing that the methyl radical formed on discharge had been completely hydrogenated.

The current peaks observed when hydrogen gas was fed to a working porous nickel electrode are attributed to adsorption and desorption of the gas. These peaks are at more negative potentials than those observed by Marassi (18) for the oxidation of hydrogen to water at platinum electrodes, hence it is thought unlikely that the peaks we observed are due to the formation of a hydrogen ion.

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REFERENCES

- 1. A. K. Vijh and B. E. Conway, Chem. Rev. 67, 623 (1967)
- L. Eberson in "Chemistry of Carboxylic Acids and Esters". ed. S. Patai, p. 53, Interscience, New York 1969.
- E. J. Cairns, "Anodic oxidation of hydrocarbons and the hydrocarbon fuel cell", p. 337, Advances in Electrochemistry and Electrochemical Engineering. ed. J. O'M. Bockris, Vol. 8, 1971.
- M. W. Breiter, Adsorption of organic species on platinum metal electrodes, ibid, p. 161, Vol. 10, 1974.
- M. Fleischmann and D. Pletcher, 'Electrode reactions of organic molecules', ch. 8, p. 347 in 'Reactions of Molecules at Electrodes', ed. N. S. Hush, Wiley-Interscience, London 1971.
- T. Dickinson and W. F. K. Wynne-Jones, Trans. Faraday Soc., 58, 382, 388, 400 (1962).
- M. Fleischmann, J. R. Mansfield, W. F. K. Wynn-Jones, J. Electroanal. Chem. 10, 511, 522 (1965).

- G. Atherton, M. Fleischmann and F. Goodridge, Trans. Faraday Soc., 63, 1468 (1967).
- 9. S. D. Ross, M. Finkelstein, R. C. Peterson, J.A.C.S., <u>89</u>, 4088 (1967).
- 10. J. P. Waefler and P. Tissot, Electrochim. Acta, 23, 899 (1978).
- 11. G. Bélanger, C. Lamarre, A. K. Vijh, J. Electrochem. Soc., <u>119</u>, 679 (1972); ibid, 122, 46 (1975).
- 12. S. A. Sargisyan, Yu. B. Vasil'ev, Sov. Electrochem, <u>17</u>, 1236 (1981); ibid, 18, 848, 854 (1982).
- V. A. Grinberg, L. S. Kapevskii, Yu. B. Vasil'ev, ibid, <u>15</u>, 737 (1979).
- 14. B. E. Conway and A. K. Vijh, J. Phys. Chem. 71, 3637 (1967).
- S. S. Kuliev, V. N. Andreev, N. V. Ostrova, V. S. Bagotskii and Yu. B. Vasil'ev, Sov. Electrochem., 18, 700 (1982).
- 16. R. R. Adzic, W. E. O'Grady and S. Srinavasan, J. Electrochem. Soc., 128, 1913 (1981).
- R. Marassi, V. Bartocci, F. Pucciarelli, Talanta, <u>19</u>, 303 (1972) and J. Electroanal. Chem. <u>47</u>, 509 (1973).
- R. Marassi, V. Bartocci, M. Gusteri, P. Cescon, J. Ap. Electrochem., 9, 81 (1979).
- R. Dallenbach, O. John, P. Tissot, J. Ap. Electrochem., 9, 643 (1979).
- 20. O. John, P. Tissot, ibid, 10, 593, (1980).
- F. J. Hazlewood, E. Rhodes, A. R. Ubbelohde, Trans. Faraday Soc. 62, 3101 (1966).
- J. J. Duruz, H. J. Michels and A. R. Ubbelohde, Proc. Roy. Soc. Lond. A. 322, 281 (1971).
- D. W. M. Williams, Ph.D. Thesis, University of Wales 1973. Stability and electrochemical properties of some molten salt electrolytes for use in fuel cells).
- 24. N. M. Sokolov, Zhur. Obschei Khim, 24, 1150 (1954).
- 25. F. Bruno, J. E. Dubois, Electrochim. Acta, 17, 1161 (1972).

- A. Wieckowski, J. Sobkowski, P. Zelenay and K. Franazczuk, Electrochim. Acta, 26, 1111 (1981).
- G. L. Arkharova, G. A. Bogdanovskii, Yu. B. Vasil'ev, Sov. Electrochem., 14, 1313 (1978).
- V. I. Dushnikov, L. S. Kanevskii, Yu. B. Vasil'ev, ibid, 15, 1243 (1979).
- V. L. Lushnikov, O. A. Khazova, V. A. Gromyko and Yu. B. Vasil'ev, ibid, 17, 144 (1981).
- G. J. Janz, Molten Salts Handbook, Academic Press, New York, 1967.
- 31. M. E. Peover, p. 276 'Reactions of Molecules at Electrodes' ed. N. S. Hush, Wiley-Interscience, London 1971.
- D. R. Browning, Electrometric Methods, McGraw-Hill, London, 1969.
- 33. B. B. Damaskin, O. A. Petrii, V.V. Batrakov, "Adsorption of organic compounds on electrodes", chaps. 8 & 10, Plenum Press, New York, 1971.
- 34. E. J. Cairns & A. M. Breitenstein, J. Electrochem. Soc. <u>114</u>, 764 (1967).
 - E. J. Cairns, A. M. Breitenstein & A. J. Scarpellino, ibid, 115, 569 (1968).
- 35. L. W. Niedrach, J. Electrochem. Soc., 111, 1309 (1964).
 - L. W. Niedrach, S. Gilman & I. Weinstock, ibid, <u>112</u>, 1161 (1965).
- 36. R. S. Nicholson, Anal. Chem. 37, 1351 (1965).
- 37. R. S. Nicholson & I. Shain, ibid, 37, 190 (1965).
- 38. J. M. Saveant & V. Vianello, Electrochim. Acta., <u>12</u>, 1545 (1967).



Figure l





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PREDICTION OF THE SELECTIVE CHLORINATION OF OXIDES BY GASEOUS MIXTURES IN MOLTEN LICI-KCI EUTECTIC

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ABSTRACT

Ores constituted by mixtures of oxides are among the principal mineral sources of metals. These ores can be treated in molten salts, in order to be transformed in compounds allowing the obtaining of the corresponding metals in an easy way. In particular, it is possible to use gaseous mixtures for the chlorination of oxides in suspension in molten chlorides.

The use of mixtures like HCl + H₂O, HCl + H₂ + H₂O, HCl + CO + H₂, Cl₂ + O₂, Cl₂ + CO or COCl₂ and also Cl₂ + C(s), has been explained in terms of oxidation-reduction and acidity. As an example, molten LiCl-KCl eutectic at various temperatures is considered and selective chlorinations of mixtures of oxides are predicted from potential-pO⁻ diagrams.

INTRODUCTION

The development of metal electrowinning in molten salts has caused an increase in the interest of using these media for the treatment of raw materials (salts or ores), in order to prepare salts for feeding electrolytic cells.

Chlorides are among the most used molten salts; however, oxides are often insoluble in them and, as a consequence, must be transformed into the corresponding soluble chlorides. An interesting way in this aim could consist in selectively chlorinating mixtures of oxides in suspension in molten chlorides.

The purpose of this paper is to show how it is possible to take up this problem, from a thermodynamic point of view.

CHLORINATION REACTIONS AND CHLORINATING REACTANTS

Chlorination reactions.

Chlorination of a metallic oxide corresponds to a reaction of exchange of O⁻ by Cl⁻ ions. Thus, for example, the chlorination reaction of an oxide like MO can be written :

MO (+ 2C1⁻) \neq MC1₂ (+0²⁻)

In order to realize it, it is necessary to provide a donor of Cl⁻ions and of an acceptor of O^{2-} , or of a compound which would be both a donor of Cl⁻ and an acceptor of O^{2-} . In a chloride melt, the introduction of an oxide gives rise to the equilibrium :

 $MO + 2 (M^+, Cl^-) \neq MCl_2 + M_2O$ (solid) (melt) (solvated)(solvated)

which can be written in a simpler manner :

$$MO(s) \rightleftharpoons M^{2+} + O^{2-}$$

This equilibrium corresponds to the partial dissolution of MO(s) characterized by the solubility product :

$$K_{s}(MO) = [M^{2+}][O^{2-}]$$

In order that chlorination may occur this dissolution equilibrium must be shifted towards the formation of metallic ions. In general, the action of the melt is not sufficient (except in the rare cases of soluble oxides for which chlorination is only due to the effects of solvation). We must therefore use a compound called chlorinating agent (or reactant) whose role is to shift the oxide dissolution equilibrium.

Among the most efficient chlorinating mixtures, the oldest to be used is carbon with either chlorine (6) or hydrogen chloride (7). It was proven at the beginning of this century (8) that no oxide can hold out against this method of chlorination. However, it is usable only for the preparation of volatile chlorides for which one does not fear a contamination by the excess of carbon necessary to obtain a complete transformation. In order to overcome this limitation, carbon monoxide (9) and even hydrocarbons (10) have been used instead of carbon. This process is still in use now (11,12).

A widespread method for the preparation of anhydrous chlorides from oxides makes use of volatile carbon-, sulfuror nitrogen-containing compounds. One of the oldest chlorinations calls for the use of carbon tetrachloride (13). Methyl chloride and chloroform have also been envisaged (14), as well as phosgene (15). Sulfur dichloride and sulfur monochloride with chlorine or not (16,17), as well as thionyl chloride (18), have also been used ; above 400°C thionyl chloride is dissociated and the chlorination reaction is similar to the one obtained with a $S_2CI_2 + CI_2$ mixture. Among the nitrogen compounds, ammonium chloride is one of the most efficient (19); nitrosyl chloride has also been considered sometimes (20).

Ways of action of a chlorinating reactant.

A chlorinating reactant (labelled in the following by CR) can act either as an acid, i.e. an acceptor of O^{2-} (1-4), or as an oxidant, or as both.

A chlorinating reactant which only works as an acid has to be stronger than M^{2+} ; then, chlorination is reduced to the simple reaction of exchange of oxide ion :

$$MO(s) + acid \neq M^{2+} + base$$
CR

Hydrogen chloride reacts in this way, giving water vapor (as the base).

A chlorinating reactant can also act by oxidizing $\rm O^{2^-}$ into oxygen according to the following reaction :

$$MO(s) + O_{X} \neq M^{2+} + \frac{1}{2}O_{2}(g) + R$$

which is the sum of the oxide dissolution equilibrium and of the two redox systems :

and :

$$0^{2-} - 2e^{-} = \frac{1}{2} O_2(g)$$

Chlorine reacts in this way. Side reactions such as oxidation of the metallic cation to an upper oxidation state can also take place at the same time.

When one deals with very stable oxides, no sufficiently strong acceptor or oxidant of O² does exist and one must have recourse to compounds or mixtures whose action calls into play both acidity and oxidation-reduction at the same time. This latter method of chlorination brings about multiple chemical reactions which often allow one to obtain the selectivity desired.

Thus, from a thermodynamic point of view, two sorts of data permit one to obtain the knowledge of the reactions for chlorinating metallic oxides in molten chlorides : on the one hand, the solubility products of the oxides, and more generally the dissociation constants of the oxide complexes of metallic cations, and on the other hand, the acid-base constants and redox potentials of the chlorinating reactants under consideration.

Solubility products of oxides as well as acidbase constants of oxide complexes of metallic cations have been the aim of numerous determinations (5). On the contrary, the equilibrium constants of the chlorinating reactants had not yet been determined. Obtaining of the chlorination equilibrium constants.

In this study, we have only considered the main chlorinating mixtures whose reactions on oxide ion are given in table 1. Only equilibrium constant K_1 corresponding to the acidic strength of hydrogen chloride has been experimentally determined at various temperatures (21-23). The log K_1 vs T function which results from these experimental values has permitted us to deduce the variation, as a function of temperature, of the equilibrium constants relative to the other chlorinating gases (equilibria (2) to (10), table 1).

The method used consists in comparing the chlorinating strengths of the different gaseous mixtures to that of hydrogen chloride. As an example, constant K_3 of equilibrium (3) :

 $Cl_2(g) + O^{2-} \ddagger \frac{1}{2} O_2(g) + 2Cl^{-}$

has been calculated from constant k_3 of the Deacon equilibrium :

$$Cl_{2}(g) + H_{2}O(g) \neq 2HCl(g) + \frac{1}{2}O_{2}(g)$$

obtained from thermochemical data from the litterature (25). We thus obtain :

$$\log K_3 = \log k_3 + \log K_1$$

Analogous calculations for the other chlorinating gaseous mixtures have led to the variations given in table 1.

Comparison of strengths of the chlorinating gaseous mixtures.

Preliminary classification.

The logarithm of the constant of each equilibrium can be expressed as :

$$\log K = pO^{2-} + \Sigma \log P$$
,

an expression in which $\Sigma \log P$ is the algebraic sum of the logarithm of the partial pressures of the gases intervening in the reaction. The strength of a chlorinating mixture is related to the pO²⁻ value which it can impose. A classification is thus possible by comparing the logarithms of the constants of equilibria (1) to (10).

Figure 1, which represents the variations of these constants as a function of temperature, brings to the fore three groups of mixtures of increasing strengths : (i) Equilibria (1), (2) and β) correspond to the weakest chlorinating mixtures; (ii) equilibria (9) and (10) (containing sulfur and chlorine) correspond to mixtures of intermediate strengths; (iii) equilibria (4) to (8) correspond to the most powerful chlorinating mixtures.

In the following we shall only consider the most currently employed chlorinating mixtures, belonging to the first and third groups.

Potential-p0²⁻ domains of action of some chlorinating gaseous mixtures.

We have seen that the chemical action of these mixtures implies in general the intervention of acid-base and oxidation-reduction properties, so that it can be represented in the potential- pO^{2-} diagram as it will be shown through the following example.

A Cl₂ + O₂ mixture imposes a pO^{2-} value given

by :

 $pO^{2-} = \log K_3 + \log P(Cl_2) - \frac{1}{2} \log P(O_2)$

In the potential- $p0^{2^-}$ diagram (fig. 2), this value is the abscissa of the point of intersection of the straight lines representative of the two electrochemical systems Cl₂(g)/Cl and O₂(g)/O²⁻. It characterizes the chlorinating strength of the mixture: the higher this value is, the greater the chlorinating strength. Moreover, the mixture imposes a potential value (which characterizes its oxidizing strength) given by :

$$E = \frac{2.3RT}{2F} \log P(CI_2)$$

These potential and pO^{2-} values depend on the partial pressures of the different gases. In fig. 2, points corresponding to two compositions [mixture M₁ : Cl₂(0.1 atm) + O₂(10⁻² atm) + inert gas ; mixture M₂ : Cl₂ (0.5 atm) + O₂(0.5 atm)] have been represented.

By making the partial pressures vary, between definite limits, a domain of potential and pO^{2-} can be covered by means of one type of mixture. In fig. 2, we have chosen arbitrarily the upper limit of 1 atm for the total pressure and the lower limit of 10^{-3} atm for each component.

For each of the gaseous mixtures we have considered, such domains have been calculated by using data from tables 1 and 2; they are represented in fig. 3a and 3b, for the temperatures of 723 K and 1023 K.

HCl + H_2O mixtures fix the pO²⁻ but not the potential, which can be imposed by the addition of hydrogen. HCl + + CO + H_2 mixtures have an oxidizing power close to the HCl + H_2O + H_2 mixtures, but a greater chlorinating strength. Chlorine (whether or not in the presence of oxygen) alone possesses a weak chlorinating strength, whereas, in the presence of carbon, it leads to the greatest chlorinating action (like phosgene).

PRINCIPLE OF CONCEIVING A SELECTIVE METHOD OF CHLORINATION

As an example we shall consider the chlorination of a mixture of iron, titanium, aluminium and silicon oxides in molten LiCl-KCl at 743 K. Such a case can correspond to practical applica-

tions concerning the treatment of aluminum and titanium ores.

The reactions of aluminum and iron chlorides with O^{2-} ion have been studied experimentally. The solubility products and other acid-base constants in molten LiCl-KCl have been determined by titrations followed by means of an yttria-stabilized zirconia membrane electrode indicator of pO^{2-} (15,26-29). Similar constants for titanium and silicon have been deduced from literature data (25,30). The potential- pO^{2-} diagrams so obtained are given in fig. 4.

The simple superimposition of each of these diagrams with the one representing the reactivity domains of the chlorinating gaseous mixtures demonstrate which mixtures are capable of chlorinating one particular oxide, and consequently show a method appropriate to selectively chlorinate the mixture of oxides.

From the iron diagram, for example, it can be noticed that all the iron oxides can be easily chlorinated by all the chlorinating mixtures, with the one restriction that chlorine-oxygen mixtures must have a sufficiently weak oxygen partial pressure. Moreover the reducing mixtures HCl + $H_2O + H_2$ and HCl + $CO + H_2$ lead to chlorination of ferric oxide into ferrous chloride and not into (volatile) ferric chloride as with the other mixtures.

Titanium dioxide is a more stable oxide than Fe_2O_3 , so that the HCl + H₂O mixture (with H₂ or not) and the Cl₂ + O₂ mixture will be inefficient on it. Only the HCl + CO + H₂ mixture (at an appropriate composition) and the Cl₂ + CO mixture (or COCl₂) are able to extract the volatile tetrachloride TiCl_n.

Concerning aluminum and considering only α -alumina, its chlorination can take place through the action of chlorine in presence of carbon or of carbon monoxide, or through the action of phosgene.

Finally silica, which is the most stable oxide, can only be chlorinated by using the $Cl_2 + CO$ mixture, or phosgene.

To sum up, a selective chlorination process of the oxide mixture can be the following. Ferric oxide can be chlorinated at first by HCl, then TiO_2 by a HCl + CO + H₂ mixture at a suitable composition (i.e. not corresponding to the highest chlorinating power in order to avoid chlorination of alumina). Finally aluminum trichloride and silicon tetrachloride can be obtained with chlorine and carbon monoxide mixtures (aluminum and silicon chlorides are then separable by a fractional condensation).

CONCLUSION

By consideration of potential-pO²⁻ diagrams it appears possible to predict the thermodynamic conditions which have to be satisfied in order to realize the selective chlorination of mixtures of various oxides in suspension in molten chlorides, by means of gaseous chemical agents. Obviously this estimated approach has to be completed by experimental kinetical studies (31,32).

Such a method can also be applied to investigate the possibility of separation by selective precipitation. In fact, the way of reasoning, here described, demonstrates the interest of the potential- pO^{-} diagrams as a very useful tool to conceive, in a more general manner, any chemical process of metallurgical treatment of ores in molten salts.

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REFERENCES

- 1. H. Lux, Z. Elektrochem., 45, 303 (1939).
- 2. H. Flood and T. Forland, Acta. Chem. Scand., 1, 592 (1947).
- 3. B. Trémillon, Pure and Appl. Chem., 25, 395 (1971).
- 4. B. Trémillon, "Chemistry in Non-Aqueous Solvents", D. Reidel Publ. Co. Boston, (1974).
- B. Trémillon and G. Picard, "Proc. 1st Internat. Symposium on Molten Salt Chemistry and Technology", KYOTO, (1983), p. 93.
- 6. H.C. Oersted, Over. D. Vid. Selk. Forts., 251 (1824).
- 7. O. Peterson, Z. Anorg. Chem., 4, 1 (1893).
- 8. F. Bourion, Ann. Chim. Phys., 20, 547 (1910).
- 9. P. Didier, C.R. Acad. Sc., 101, 882 (1885).
- 10. A. Faure, C.R. Acad. Sc., 107, 339 (1888).
- 11. Ger. Offen. 1 237 995 (1967) ; Ger. Offen. 2 244 041 (1973) ; Neth. Appl. 75 11 084 (1976) ; Ger. Offen. 2 651 072 (1977).
- 12. H.P. Alder, H.P. Mueller et W. Richarz, Light Met.(New York), <u>1</u>, 219 (1977).
- 13. E. Demarçay, C.R. Acad. Sc., 104, 111 (1887).
- 14. C. Renz, Deutsch. Chem., 39, 246 (1906).
- 15. E. Chauvenet, C.R. Acad. Sc., 152, 87 (1911).

- 16. F. Bourion, Ann. Chim. Phys., 21, 49 (1910).
- 17. C. Matignon et F. Bourion, C.R. Acad. Sc., 138, 760 (1904).
- 18. Z. Darzens et F. Bourion, C.R. Acad. Sc., 153, 270 (1911).
- 19. B.S. Hopkins, J.B. Reed et L.F. Audrieth, J. Am. Chem. Soc., <u>57</u>, 1159 (1935).
- 20. Neth. Appl. 75 11 084 (1976).
- 21. F. Séon, Thesis, Paris, France (1981).
- 22. R. Lisy and R. Combes, J. Electroanal. Chem., 83, 287 (1977).
- 23. G. Picard, F. Séon and B. Trémillon, J. Electroanal. Chem., <u>102</u>, 65 (1979).
- 24. B. Trémillon and G. Picard, Anal. Chim. Acta, 82, 273 (1976).
- Barin, O. Knacke and O. Kubaschevski, "Thermochemical properties of inorganic substances", Springer Verlag, Berlin-Heidelberg - New-York, (1973).
- 26. G. Picard, F. Séon, B. Trémillon and Y. Bertaud, Electrochim. Acta, 25, 1453 (1980).
- 27. G. Picard, F. Séon and B. Trémillon, J. Electrochem. Soc., <u>129</u>, 1450 (1982).
- F. Séon, G. Picard and B. Trémillon, J. Electroanal. Chem., <u>138</u>, 315 (1982).
- G. Picard, F. Séon and B. Trémillon, Proc. 1st Internat. Symposium on Molten Salt Chemistry and Technology, Kyoto (Japan), April 1983, p. 49.
- 30. J.A. Plambeck, "Encyclopedia of Electrochemistry of the Elements", Fused Salt Systems, Vol. X , A.J. Bard ed., Marcel Dekker, New York (1976).
- 31. F. Séon, G. Picard and B. Trémillon, Electrochim. Acta, <u>28</u>, 209 (1983).
- 32. F. Séon, G. Picard and B. Trémillon, to be published.

Table 1 - Values of constants K of some chlorination equilibria in molten LiCl-KCl eutectic (concentrations in mol kg⁻¹, pressures in atm, T in Kelvins).

CHLORINATION EQUILIBRIA			log K = A	+ B.10 ³ .T ⁻¹	
				A	В
(1)	$2HCI(g) + 0^{2-}$	ŧ	H ₂ O(g) + 2Cl ⁻	-3.477	9.980
(2)	2HCI(g) + CO(g) + 0 ²⁻	ŧ	CO,(g) + H,(g)+2C1	-5.264	11.88
(3)	Cl ₂ (g) + 0 ²⁻	#	$\frac{1}{2}O_{2}(g) + 2C1^{-1}$	-2.651.10-2	6.912
(4)	$Cl_{2}(g) + CO(g) + 0^{2-}$	≠	$CO_{1}(g) + 2C1^{-1}$	-4.583	21.62
(5)	$COCI_{2}(g) + 0^{2-}$	≠	$CO_{2}(g) + 2CI^{-}$	2.465	16.01
(6)	$Cl_2(g) + \frac{1}{2}C(s) + 0^{2-1}$	ż	$\frac{1}{2} CO_2(g) + 2CI^-$	2.086.10 ⁻²	17.14
(7)	$Cl_2(g) + C(s) + 0^{2-1}$	ŧ	CO(g) + 2C1	4.603	12.68
(8)	$\frac{1}{2}$ CCl ₄ (g) + 0 ²⁻	≠	$\frac{1}{2}$ CO ₂ (g) + 2C1 ⁻	3.503	14.77
(9)	$SOCI_2(g) + 0^{2^-}$	Ż	SO ₂ (g) + 2CI	2.776	11.49
(10)	$\frac{1}{4} S_2 C_2(g) + \frac{3}{4} C_2(g) +$	0 ²⁻	$\pm \frac{1}{2} \tilde{SO}_2(g) + 2CI^{-1}$	-0.3999	14.48
1					

Table 2 - Equilibrium potential expressions and standard potential values(in V vs standard chlorine electrode), as a function of temperature T (in K), for some electrochemical systems in molten LiCl-KC1 eutectic (concentrations in mol kg⁻¹ and pressures in atm).

CIECTIOCHEMICAI SYSTEMS	Equilibrium potentials	Standard potentials E° = A+B, 10 ⁻⁶ T		
		^	8	
$\begin{array}{rcl} H_{1}(g) &- 2e^{-1} + 2C1^{-1} = 2HCI(g) \\ H_{1}(g) &- 3e^{-1} + 0^{21} = H_{1}O(g) \\ 0^{21} &- 2e^{-1} &= 0.5 O_{2}(g) \\ C(s) &- Ms^{-1} + 20^{21} = CO_{2}(g) \\ C(s) &- 2e^{-1} + 0^{21} = CO_{3}(g) \\ C(s) &- 2e^{-1} + 0^{21} = CO_{3}(g) \end{array}$	$ \begin{split} & E = E^{o} + 2.3 \ RT, F^{-1} \ log \ P(HC1) - 2.3 \ RT, 0.5, F^{-1} \ log \ P(H_2) \\ & E = E^{o} + 2.3 \ RT, 0.5, F^{-1} \ log \ P(H_20) / P(H_2) + 2.3 \ RT, 0.5, F^{-1}, p0^{2^{-}} \\ & E = E^{o} + 2.3 \ RT, 0.25, F^{-1} \ log \ P(O_2) + 2.3 \ RT, 0.5, F^{-1} \ p0^{2^{-}} \\ & E = E^{o} + 2.3 \ RT, 0.25, F^{-1} \ log \ P(C0) + 2.3 \ RT, 0.5, F^{-1} \ p0^{2^{-}} \\ & E = E^{o} + 2.3 \ RT, 0.5, F^{-1} \ log \ P(C0) + 2.3 \ RT, 0.5, F^{-1} \ p0^{2^{-}} \\ & E = E^{o} + 2.3 \ RT, 0.5, F^{-1} \ log \ P(C0) / P(C0) + 2.3 \ RT, 0.5, F^{-1} \ p0^{2^{-}} \end{split} $	-0.971 ₆ -1.968 -0.689 ₂ -1.709 -1.268 -2.156	-67,27 281.9 2.693 -2.695 -459.0 457.0	



Fig. 1. - Constants of chlorination equilibria corresponding to various gaseous mixtures in molten LiCl-KCl (see table 1).

 $\begin{array}{rrrrr} 1 & : & HC1 & + & H_20 & ; & 2 & : & HC1+C0+H_2 & ; & 3:C1_2^{+}0_2 & ; \\ 4 & : & C1_2^{+}C0 & ; & 5 & : & C0C1_2 & ; & 6-7 & : & C1_2^{-} + & C & (s) & ; \\ 8 & : & CC1_4 & ; & 9 & : & S0C1_2 & ; & 10 & : & S_2C1_2^{-} + & C1_2 \\ \end{array}$



Fig. 2. - Potential-p0 $^{2-}$ domain of Cl₂ + 0₂ mixtures in molten LiCl-KCl at 743 K.





IV : HC1 + H₂0

704







STANDARD REFERENCE ELECTRODE FOR MOLTEN SALTS

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ABSTRACT

The definition of the Ag(I)/Ag reference electrode as a standard reference electrode for fused salt media is discussed. The required definitions are three: the definition of the fused salt solvent system in terms of nominal composition, nominal temperature, and nominal composition; the definition of a solute concentration in terms of mole ratios; and the definition of the standard state of Ag(I) as that which prevails in sufficiently (ideally, infinitely) dilute solutions. The experimental construction of such an electrode is discussed.

Introduction

Molten salts constitute a diverse class of solvent systems in which various reference electrodes have been proposed and used. These reference electrodes have been of diverse types, but in virtually all cases the potential of the Ag(I)/Ag(0) couple has been carefully measured against the reference electrode used. It is proposed that the standard reference electrode in molten salts be based upon the Ag(I)/Ag(0) couple. In order to do so the conditions of measurement and of the standard itself must be unambiguously specified both in terms of the molten salt solvent system and in terms of the state of components of the reference electrode couple.

Definition of a Solvent System

A solvent system, whether for fused salt media or not, is defined as a uniform single-phase liquid chemical system whose nominal temperature, nominal pressure, and nominal composition can be unambiguously expressed in SI units. The nominal temperature is best expressed in kelvins (K), the nominal pressure in pascals (Pa), and the nominal composition in terms of amount of substance for which the unit is the mole. Specification of several fused salt solvent systems has been done in detail elsewhere (1).

The nominal composition of a fused salt solvent system is its most fundamental defining parameter. The solvent system can be defined as consisting of a single compound, such as NaCl or NaAlCl₄, but it is more often convenient to specify a fixed mole ratio of two or more compounds, such as equimolar NaCl-KCl or NaOH-KOH, because the melting point of the mixture is well below that of either of the pure compounds and the range of temperatures accessible to measurement is significantly increased. Alternative specifications include mass ratio, which requires knowledge of the molecular weights of the constituent salts, or the eutectic composition, in which case the mole ratio of the eutectic composition must be It is fortunate that preparation of a accurately known. molten salt solvent system by measurement of component volumes is sufficiently inconvenient as to be unknown and so specification of composition as a volume ratio is not used; the complication that the volume of a mixture is not equal to the sum of the separate volumes of its components is thereby avoided.

The nominal temperature of a solvent system is defined empirically, but generally a consensus exists (1); in any event, measurements are usually made over a range of temperatures above and below the nominal temperature. The nominal temperature is selected as a convenient temperature above, usually well above, the melting point of the defined composition and below the temperature at which undesirable reactions of the solvent (decomposition, vaporization) or of the container materials (softening of glass, corrosion) become significant within the few hours normally required for completion of a series of experiments in a molten salt system.

The nominal pressure is almost invariably taken as one standard atmosphere (101.324 kPa) of an inert gas, i.e., a total pressure of exactly one atmosphere made up of the vapor pressure of the molten salt (very low) plus a pressure of an inert gas. For certain molten salts, such as carbonates, the gas cannot be inert and must be specified in order to prevent solvent decomposition; the total pressure remains one atmosphere.

The compilations of Janz and co-workers on density (2) and eutectic composition (3) are extremely valuable in

definition and characterization of molten salt solvent systems. Specific preparation procedures are compiled by Plambeck (1).

Definition of a Solute

A solute in a solvent system is any component present other than those of the nominal composition. The amount of solute is specified in terms of its concentration, which must be interpretable as a ratio between amount of solute (in mol) and amount of solvent system (in mol). This ratio is itself the concentration on the mole fraction scale, which is the most fundamental measure of concentration but is also the concentration scale on which unity is the farthest removed from actual experimental conditions of measurement in dilute solutions. The use of the molality scale (mol solute/kg solvent system) and molarity scale (mol solute/dm 3 solution) is common in molten salt studies since unit concentration on these scales is experimentally accessible. Conversion of molality data to mole fraction requires only knowledge of molecular weights, but conversion of molarity data requires knowledge of the solvent system density (2) as well. The density of the solvent system can be taken as equal to the density of the solution, as is the almost universal practice, only for dilute solutions without introduction of serious error. The molarity scale is therefore suitable only for measurements in dilute solutions. In practice, measurements below a mole fraction of 0.01 will have a neglegible error from this source.

Definition of Standard States for Reference Couples

Any electrochemical couple which can produce a reversible electromotive force consists of at least two species which differ in charge. In molten salt solvent systems, either one or both of these species are solutes and for the simplest couples such as Fe(III)/Fe(II) or Ag(I)/Ag(0) these solutes are ions. The standard states of all species involved in an electrochemical couple are the states which define the conditions under which the actual potential of the couple is taken as its standard potential against a reference electrode or, in the case of a reference electrode, the conditions under which its actual potential is taken to be exactly zero so that the entire measured potential difference is ascribed to the
electrode whose potential is being measured against that of the reference electrode.

The standard state is necessarily taken as that of the nominal temperature, pressure, and composition of the molten salt solvent system. For a pure element or compound such as silver metal no more is required; if the nominal temperature is above 961°C the standard state is liquid silver and below that it is the solid metal. Likewise, for a material which is a constituent of the solvent system itself or is linked to a constituent by an equilibrium, no more is required because the activity of such a species is fixed by the composition of the solvent system. Couples for which both or all of the species involved are thus of fixed activity are often used as reference electrodes in molten salts. Examples include the Cl₂(g, 1 atm), C/Cl⁻ couple in equimolar NaCl-KCl (4) and the Al(III)/Al(0) couple in melts containing AlCl₃ as a constituent. Such reference couples are convenient, or even possible, in a comparatively small number of melts and differ considerably from one melt composition to Although the standard states are indeed well another. defined and the potentials are often well poised, such couples cannot form the basis of a universal or widelyapplicable standard reference electrode for molten salt solvents.

As a consequence, the standard state of a solute such as Ag(I) must be taken as the state of Ag(I) in which the Ag(I) has a neglegible effect upon the composition of the molten salt solvent system, which is to say in a sufficiently dilute solution that the behavior with concentration is, within experimental error, that of the infinitely dilute solution. For the purposes of the measurement of potentials, this is equivalent to the requirement that Henry's law, and thus the Nernst equation in concentration form, be obeyed.

Experimentally, in nearly all melts the potential of the Ag(I)/Ag couple varies with the logarithm of Ag(I) concentration at Ag(I) concentrations of at least 10^{-5} to 10^{-2} mol/dm³. At lower concentrations of Ag(I), the potential deviates from this Nernstian response in a manner which is often nonreproducible and depends upon the melt, its preparation, and its history. At higher concentrations the potential deviates in a reproducible and systematic manner. The deviation at very low Ag(I) concentrations is probably due to the presence of other couples as impurities; their significance increases as the concentration of Ag(I) decreases because the exchange current, though comparatively high for the Ag(I)/Ag(0) couple, decreases with concentration until it is too low to control the potential. The deviation at high concentration is expected because, as concentration increases, the activity coefficient cannot remain that of the dilute solution which, for a solvent system of fixed nominal composition, is fixed also. Thus the standard state of Ag(I) is a physically unreal state in which the behavior of Ag(I) is that of an ion under conditions of essentially infinite dilution in the solvent system yet at an arbitrarily chosen fixed concentration. This fixed concentration can be selected as unity on the molarity, molality, or mole fraction scale as convenient.

The use of this electrode involves simply the measurement of its potential against any electrode of constant potential over the range of Aq(I) concentrations in which Nernstian behavior is observed. The standard condition is obtained by extrapolation using the Nernst equation to the arbitrarily fixed concentration of unity on the desired concentration scale. The potential of the cell so extrapolated is then assigned to the other electrode of constant potential, since the standard potential of $Aq(I)/Aq(\bar{0})$ is defined as zero. It is most convenient to generate a series of increasing concentrations of Ag(I) by anodic coulometry from the Ag metal present using an auxiliary cathode. At low current densities the Faradaic efficiency is 100% within experimental error; the only problem is extensive recrystallization of solid silver metal.

Comparison With Other Reference Electrodes

The reference electrode suggested is already widely used (1). The Ag(I)/Ag couple has the advantages of use of a noble and unreactive metal; a relatively high exchange current; compatibility of Ag(I) with both solvent systems (5) and apparatus materials; low vapor pressure of both components of the couple at high temperatures; operation over a wide temperature range; and definition of the standard state of both components of the couples in a manner which does not vary with melt composition except for solvent systems based on silver salts, which are not a group widely used or studied. Of greater significance is the fact that it can be constructed with a very low junction potential because the solvent system at the reference electrode differs from that elsewhere only in the presence of a relatively low concentration of Ag(I). A separator required to prevent mixing such as a glass frit, porous ceramic, or glass membrane will therefore develop across itself a junction potential of at most one or two mV, as is observed. Electrodes employing significantly different solvent melt compositions at the reference electrode than at the opposite electrode must necessarily have large, and often ill-defined, junction potentials across their separators.

References

- J.A. Plambeck. Volume X: Fused Salt Systems, Encyclopedia of Electrochemistry of the Elements, ed. A.J. Bard, Marcel Dekker, N.Y., 1976.
- G.J. Janz, F.W. Dampier, G.R. Lakshminarayanan, P.K. Lorenz, and R.P.T. Tomkins, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 15, 139 pages (Oct. 1968); G.J. Janz, C.G.M. Dijkhuis, G.R. Lakshminarayanan, R.P.T. Tomkins, and J. Wong, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 28, 116 pages (Aug., 1969); G.J. Janz, U. Krebs, H.F. Siegenthaler, and R.P.T. Tomkins, J. Phys. Chem. Ref. Data 1, 581-746 (1972); G.J. Janz, G.L. Gardner, U. Krebs, and R.P.T. Tomkins, J. Phys. Chem. Ref. Data 3, 1-115 (1974); G.J. Janz, R.P.T. Tomkins, C.B. Allen, J.R. Downey, G.L. Gardner, U. Krebs, and S.K. Singer, J. Phys. Chem. Ref. Data 4, 871-1178 (1975); G.J. Janz, R.P.T. Tomkins, C.B. Allen, J.R. Downey, and S.K. Singer, J. Phys. Chem. Ref. Data 6, 409-596 (1977).
- G.J. Janz, C.B. Allen, J.R. Downey, and R.P.T. Tomkins, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 61, Part I, 244 pages (Mar. 1978); G.J. Janz, C.B. Allen, N.P. Bansal, R.M. Murphy, and R.P.T. Tomkins, Nat. Stand. Ref. Data Ser., Nat. Bur. Stand. (U.S.), 61, Part II, 442 pages (Apr. 1979).
- S.N. Flengas and T.R. Ingraham, J. Electrochem. Soc. <u>106</u>, 714 (1959) and references cited therein.
- U. Anders and J.A. Plambeck, J. Electrochem. Soc., <u>115</u>, 598-601 (1968).

ALKALI METAL-ALKALI HALIDE SOLUTIONS : THERMODYNAMICS OF THE K-KC1 SYSTEM.

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ABSTRACT.

In order to obtain thermodynamic information on mixtures constituted with alkali metals and their halides, we investigated the K-KCl system by vapor pressure measurements.

The method chosen uses the features of both the Rodebush-Dixon and ebullition methods. The apparatus, consistent with the experimental requirements of such a system, allows one to investigate a wide temperature and pressure range.

The determination of the vapor pressure of potassium between 970 and 1140 K was a check on the operation of the apparatus.

Vapor pressure measurements above the K-KCl liquid bath between 970 K and 1140 K yielded the activity of potassium at $X_{\rm K}$ = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and 0.9.

INTRODUCTION

Solutions of alkali metals and corresponding halides are the most prevalent examples of systems in which the metal - non metal transformation is continuous and is governed by changes in composition. Many theoretical approaches have been proposed in order to explain the electronic structure and properties of these solutions but none of them is unitary in the sense that, as pointed out by Warren in his recent review (1)

- they can be classified according to their starting points as "metallic" and "non-metallic" models
- there is a further division within these broad classes into models valid only for dilute solutions and those attempting to describe concentrated solutions.

One promising approach was proposed very recently by Hansen et al. and was found relevant for the description of the neutron diffraction data obtained on the K-KCl and Rb-RbBr systems (2). This was a multicomponent plasma model derived from the one-component plasma (OCP) model used successfully to describe the structure of liquid alkali metals (3); a hypernetted chain (HNC) method was used in the case of these alkali metal-halides solutions.

Like structural models, those dealing specifically with the thermodynamics of such systems were also fragmentary. Nevertheless, it should be mentionned that Pitzer (4), some twenty years ago was able to predict a priori the limiting enthalpy of dissolution of an alkali metal into its corresponding halide on the basis of a F-center model ; the recently obtained experimental values for the K-KBr (5-6) and Cs-CsX (7-8) mixtures were found in fairly good agreement with this estimation. So it is obvious that a better knowledge of the behaviour of the metal halide solutions would be afforded by : i) on the one hand, a model able to describe the thermodynamics of these systems at any concentration and temperature ii) on the other hand, a large series of experimental thermodynamic excess data.

Following our previous investigation of the K-KBr system (5-6), the present paper reports the results which were obtained for the K-KCl system.

POSITION OF THE PROBLEM

Experimental difficulties can explain the paucity of measurements -[except for phase diagrams (9-13)] - performed on the systems constituted of an alkali metal and its halide; chemical reactivity, large vapor pressure of the metal at elevated temperatures, high upper critical solution temperature etc. make measurements difficult.

Anticipating that the easiest experimental approach would be the determination of activities from vapor pressure measurements, we tested the feasibility of such a study with the complete investigation of the K-KBr system (5,6). A similar investigation was conducted for the K-KCl mixture.

ACTIVITY MEASUREMENTS

Principle

The table below indicates the vapor pressures of potassium and those of potassium chloride reported by two authors (14,15) at the experimental temperatures 970 K, 1055 K and 1140 K.

T/K		970	1055	1140
p,,∕kPa		59.21	127.66	245.43
p_{KC1}^{K}/kPa	(14)	0.01	0.065	0.295
p_{kc1}^{KC1}/kPa	(15)	0.011	0.065	0.299
· NUT				

From this table, it is obvious that :

- the vapor pressure of potassium is very high

- the difference between the vapor pressures of potassium and potassium chloride, at the same temperature, is very large.

Assuming that the vapor above a liquid bath K-KCl consists only of the more volatile component, the activity ${\rm a}_{\rm K}$ of potassium can be obtained as

 $a_K = p_K / p_K^0$

from the vapor pressures of potassium in the reference state and above the K-KCl mixture under investigation, at the same temperature T.

/1/

The temperature and concentration dependances of these activities make it possible to deduce the excess thermodynamic functions, partial or integral, of the system.

Experimental method

The method developed derived from that proposed by Rodebush and Dixon (16), was adopted to our experimental constraints.

The determination of pressure can be done

- either by recording against time the variation of pressure arising from a microleak in the gas-flow circuit above the liquid : when the pressure becomes equal to the vapor pressure there is a break in the pressure-time curve (Rodebush and Dixon's method).
- ii) or by recording the temperature T of the liquid while the pressure above it decreases linearly with time; boiling, an endothermic process, causes cooling of the liquid and hence a break in the temperature-time curve.

In practice, it is of more interest to couple these two methods so as to survey a wide experimental range.

Apparatus

A complete description of the experimental set-up was detailed in a

previous paper (6). It should only be mentioned that the thermodynamic investigation of the K-KCl system was conducted on a temperature range wider than that concerned for the K-KBr mixture (970 K<T<1140 K and 1000 K<T<1065 K respectively). Measurements were made at the potassium mole fractions $X_{\rm K}$ = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8 and and 0.9.

Experimental cares

Prior to experiments, each mixture was prepared in a dry box with all the usual care necessary to the handling of alkali metals.

Potassium and potassium chloride of reagent grade (98 and 99.5 mole per cent) were purchased from Prolabo and Merck respectively. The salt was gradually heated under vacuum up to 420 K and maintained at this temperature for 24 h. All handling of the materials was made in a dry high-purity argon atmosphere.

EXPERIMENTAL RESULTS

Relation (1) indicates that the vapor pressures of potassium in the pure state and above the liquid K, KCl₁, must be determined at the same temperatures. So, the first investigation should been devoted to the determination of the variation of p_K^{o} against temperature, $p_K^{o} = f(T)$.

Vapor pressure of pure potassium

Our experimental results between 970 K and 1140 K were fitted to the analytical expression :

 $\log_{10} p_k^0 = 5.91337 - 4016.728 T^{-1}$ /2/

with p_{K}^{O} in kPa and T in Kelvins.

Vapor pressure of potassium above liquid K_{χ} KCl_{1-X}

The mixtures of molar composition $X_K = 0.1, 0.2, 0.3, 0.4, 0.5, 0.6, 0.7, 0.8$ and 0.9 were investigated on the widest temperature ranges correponding to single-phase liquid solutions.

For each mixture, the experimental vapor pressures \textbf{p}_{K} were fitted to an analytical expression similar to /2/

 $\log_{10} p_{K} = A + B T^{-1}$

The experimental activities of potassium so obtained were corrected for dimerization according to the equilibrium :

K₂ ≤ 2K.

Figure 1 indicates the shapes of the activity curves against molar fraction, at the temperatures 1070 K, 1100 K, 1150 K and 1200 K.

The activity of KCl was obtained from that of K by integrating the Gibbs-Duhem equation :

$$X_{K} dln a_{K} + X_{KCl} dln a_{KCl} = 0$$

We made use of the Darken and Gurry (17) procedure with a polynomial expansion of the α -function.

Figure 2 reports the activities of potassium and potassium chloride against the molar fraction X_K at 1100 K and figure 3 shows the corresponding partial and integral Gibbs molar free energies $\Delta G_{K,\Delta}G_{KC1}$ and ΔG_{M} .

REFERENCES

- (1) W.W. Warren, Jr. in Advances in Molten Salt Chemistry, vol. 4, Ed. G. Mamantov and J. Braunstein, 1981, Plenum Press New-York, p. 1.
- (2) G. Chabrier, J.F. Jal, P. CHieux, J. Dupuy, J.P. Hansen Journées d'Etude des Sels Fondus, 8-9-10 June 1983, Paris.
- (3) J.P. HansenJ. Physique, Lettres, 1977, 38, L 191.
- (4) K.S. PitzerJ. Am. Soc., 1962, 84, 2025.
- (5) P. Kozoulia, J.P. Bros, M. Gaune-Escard Proc. Fourth International Symposium on Molten Salts Electrochemical Society, vol 81-9, 1981.
- (6) P. Kozoulia, J.P. Bros, M. Gaune-Escard J. Chem. Thermodynamics, 1983, 15 (in print).
- (7) H. Yokokawa, O.J. Kleppa, N.H. Nachtrieb J. Chem. Phys., 1979, 71, 4099.
- (8) H. Yokokawa, O.J. Kleppa J. Chem. Phys., 1982, 76, 5574.
- (9) M.A. Bredig, H.R. Bronstein, W.T. Smith Jr. J. Am. Chem. Soc, 1955, 77, 1454.

- (10) J.W. Johnson, M.A. Bredig J. Phys. Chem. 1958, 62, 604.
- (11) M.A. Bredig, H.R. Bronstein J. Phys. Chem. 1960, 64, 64.
- (12) A.S. Dworkin, H.R. Bronstein, M.A. Bredig J. Phys. Chem. 1962, 66, 572.
- (13) J.D. Corbett Fused Salts, Sundheim B.R., Editor, Mc Graw-Hill : New-York 1964 p. 341.
- (14) O. Kubaschewski, C.B. Alcock Metallurgical Thermochemistry 5th Edition Pergamon Press : Oxford 1979.
- (15) J.L. Barton, H. Blom J. Phys. Chem. 1959, 63, 1785.
- (16) W.H. Rodebush, A.L. Dixon Phys. Rev. 1925, 26, 851.
- (17) L. Darken, R. Gurry Physical Chemistry of Metals, Mc Graw-Hill : New York 1953.



Fig. 1 Measured activities of K at 1070K(e), 1100K, 1150K and 1200K(h).



Fig. 2 Activities of K and KCl at 1100K.



Fig. 3

- Free energies of mixing (a) Partial molar free energies of mixing of KCl
- (b) Partial molar free energies of mixing of K
- (c) Total molar free energy of mixing of the mixture

ACTIVITIES AND OTHER PARTIAL MOLAR PROPERTIES OF THE

QUARTERNARY MOLTEN SALT SYSTEM MnCl2-NaCl-KCl-CsCl

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ABSTRACT

The thermodynamic properties of the quarternary molten salt system $MnCl_2$ -NaCl-KCl-CsCl have been investigated by emf measurements using a formation cell of the type:

Mn	MnCl ₂ ((X_1)	Achector	MnCl ₂	(X ₁)	C,(Graphite)
	NaCl ((X ₂)	fibro	NaCl	(X ₂)	Cl ₂ (1 at.)
(-)	KC1 ((X ₃)	diaphragm	KC1	(X ₃)	(+)
()	CsCl ((X ₄)	draphragm	CsC1	(X ₄)	

It was found that the partial molar free energies of mixing of $MnCl_2$ in the quarternary solutions are well represented by a previously developed expression given as:

 $\overline{\Delta G}_{MnCl_2} = (1 - S) [(1 - t) \overline{\Delta G}_{MnCl_2}$ (in quarternary) $(MnCl_2 - CsCl)$ $+ t \overline{\Delta G}_{MnCl_2}] + S \overline{\Delta G}_{MnCl_2}$

+ t $\overline{\Delta G}_{MnCl_2}$] + S $\overline{\Delta G}_{MnCl_2}$ in in (MnCl_2-KCl) (MnCl_2-NaCl)

which is valid at constant X_{MnCl_2} .

In this expression, $\overline{\Delta G}_{MnCl_2}(in MnCl_2-CsCl)$ etc. refer to the corresponding partial motar free energy of MnCl_2 in the designated binary system having the same MnCl_2 content as the quarternary.

The composition parameters S and t are defined as:

$$t = \frac{X_{KC1}}{X_{KC1} + X_{CSC1}}, \qquad S = \frac{X_{NaC1}}{X_{NaC1} + X_{KC1} + X_{CSC1}}$$

INTRODUCTION

In previous publications from this laboratory(1,2), theoretical equations have been developed from which the molar and partial molar properties of ternary and quarternary molten salt solutions may be calculated from available data on the component binary systems.

The thermodynamic properties of binary fused salt solutions have been the object of several systematic investigations and extensive compilations of thermodynamic data are available. However, similar information on ternary fused salt solutions is limited to only a few selected systems, and for quarternary solutions there is hardly any information at all. Yet, systems of metallurgical importance are usually multicomponent and the application of the thermodynamic approach to high temperature equilibria is restricted by the lack of experimental data. Thus, it is evident that expressions from which the thermodynamic properties of ternary and quarternary systems may be predicted from available information on the related binary systems should be of considerable theoretical and practical importance.

In the present investigation, the thermodynamic properties of $MnCl_2$ in the quarternary molten salt system $MnCl_2$ -NaCl-KCl-CsCl, have been obtained from emf measurements using a formation cell of the type:

Mn	MnCl ₂ (X ₁) NaCl (X ₂)	Asbestos	MnCl ₂ (X ₁) NaCl (X ₂)	C (graphite) Cl ₂ (1 at.)
(-)	KC1 (X ₃) CsC1 (X ₄)	diaphragm	$\begin{array}{c c} KC1 & (X_3) \\ CsC1 & (X_4) \end{array}$	(+)

For this system, the thermodynamic and structural properties of the binary solutions $MnCl_2$ -NaCl, $MnCl_2$ -KCl, $MnCl_2$ -CsCl, as well as of the ternary $MnCl_2$ -NaCl-CsCl, have been investigated in this laboratory and elsewhere (3,4,5,6).

It is of interest that the MnCl₂-NaCl system is characterized by relatively low exothermic enthalpies of mixing which reach the maximum value of -1900 cal/mole at a composition of about 35 mole % MnCl₂. Also, the change of volume on mixing indicates only slight positive deviations from additivity(6,7). On the contrary, in the MnCl₂-KCl and the MnCl₂-CsCl systems, the enthalpies of mixing are strongly exothermic and the changes of volume on mixing show pronounced positive deviations from additivity, which is indicative of compound formation. For example at 33 mole % CsCl the integral enthalpy of mixing in the MnCl₂-CsCl system has a value of -5,400 cal/mole at 700°C. Because of such pronounced differences in the properties of the binary systems, the quarternary system MnCl₂-NaCl-KCl-CsCl should be considered as a

test system for establishing the validity of the proposed theoretical expressions (1,2).

EXPERIMENTAL

The alkali chlorides employed in the present work were reagent grade materials, and the anhydrous $MnCl_2$ was 99.5 wt% pure. These salts were further dehydrated by heating under vacuum for several days at 200°C. The materials were handled and weighed in a dry box filled with anhydrous argon gas.

The cell design was similar to that used in the previous work(7). It consisted of a Mn indicator electrode immersed in the $MnCl_2-NaCl-KCl-CsCl$ molten solution of known composition, and a graphite-chlorine electrode which also dipped into a molten salt solution of the same composition. The two cell compartments were separated by an asbestos fibre diaphragm fused into silica glass(8).

The chlorine electrode was continuously flushed with anhydrous research grade chlorine gas. The Mn electrode was made by placing a tungsten rod, 1/8" in diameter, and crushed electrolytic manganese metal, in a stabilized zirconia ceramic tube closed at one end which was heated to about 1400°C under an argon atmosphere. The molten Mn was allowed to solidify very slowly to avoid cracking as it passed through its crystallographic transformation(9). This electrode was about 10 mm in diameter by 4 cm in length and was acid polished prior to use. During a run the Mn electrode was operated under an atmosphere of de-oxygenated argon gas.

The asbestos diaphragm had a resistance in the range of 1000 to 2,000 ohms and its construction has been described elsewhere(8).

During a run, emf readings were taken at intervals of about 25°C, up to approximately 850°C. Potentials were fully reproducible to within 2mV during a temperature cycle and cell reversibility was also established through polarization tests at currents of about 1 mA.

Volatility of $MnCl_2$ for the salt compositions used in this work, was insignificant and did not affect the reproducibility of the emf measurements during a temperature cycle.

DATA TREATMENT AND RESULTS

Compositions in a quarternary system are represented(10) by points within the volume of an equilateral tetrahedron, as shown in Figure 1, in which the four apexes correspond to the pure components $MnCl_2$, NaCl, KCl and CsCl, and the edges represent the six binary systems $MnCl_2$ -NaCl, $MnCl_2$ -KCl, $MnCl_2$ -CsCl, KCl-NaCl, KCl-CsCl and NaCl-CsCl.

The triangular faces represent the four ternary systems MnCl₂-NaCl-KCl, MnCl₂-NaCl-CsCl, MnCl₂-KCl-CsCl and NaCl-KCl-CsCl.

It is a property of all equilateral tetrahedra that lines originating from any internal point P, drawn parallel to the four different faces have a total length equal to one edge, and each of these segments may be taken to define the mole fraction of a particular component occupying an apex.

In view of the complexity of such three dimensional plots useful composition paths have been defined mathematically(2), and the composition parameters, y, t and S have been defined by the following expressions:

$$y = 1 - X_{MnCl_2}$$
, where $1.0 \ge y \ge 0$ (1)

$$t = \frac{X_{KC1}}{X_{KC1} + X_{CSC1}}, \quad where 1.0 \ge t \ge 0$$

$$t = 1 \text{ along the } MnCl_2-KC1 \quad (2)$$

binary, and

$$t = 0 \text{ along the } MnCl_2-CsC1$$

binary

$$S = \frac{^{NaCl}}{X_{NaCl} + X_{KCl} + X_{CsCl}}$$
(3)

where X's are mole fractions.

Considering Figure 1, in which MnCl₂ is placed at the apex of the tetrahedron, constant "t" represents the pseudo-quarternary composition surface BeC. All compositions along that surface have in common the constant ratio of $\frac{X_{KC1}}{X_{KC1} + X_{CSC1}}$.

Also, constant "y" represents compositions along a pseudo-ternary surface parallel to the base of the equilateral tetrahedron having a constant X_{MnCl_2} content.

The intersection of the planes, t and y, defines the line "S" which has the following limiting values; within the binary $MnCl_2$ -NaCl at point "b", S = 1, and at point e' within the ternary $MnCl_2$ -KCl-CsCl, S = 0.

The relationship between primary mole fractions and the composition parameters y, t and S, is readily found as,

$$X_{CSC1} = y(1 - t)(1 - S)$$
 (4)

$$X_{NaC1} = yS$$
(5)

 $X_{KC1} = ty(1-S)$ (6) $X_{MnC1_2} = 1-y$ (7)

Considering the S-path be', within the quarternary tetrahedron shown in Figure 1, which is defined by the intersection of the y- and t-planes, all compositions along be' have the same X_{MnCl_2} content and the same ratio of KCl to CsCl. However, as S changes $^{(1)}$ from 0 (point e') to 1 (point b) the amount of NaCl in the quarternary changes in proportion to S (eq. 5), and the value of any thermodynamic property measured along such an S-composition path should reflect the reactivity of NaCl towards MnCl₂. In this melt the ratio of KCl/CsCl remains constant, but the absolute amounts of these two components decrease as they are replaced by NaCl.

It follows that the y, S and t parameters, proposed in this paper, define quarternary composition paths along which it is possible to follow the relative contributions of the various salt components to the magnitude of the thermodynamic properties of the solutions.

Compositions investigated in this study are given in Table 1 and cover the alkali chloride rich section of the quarternary up to $X_{MnCl_2} = 0.4$.

This composition range represents a region of increased thermodynamic stability for $MnCl_2$ because of the predominance of the complex $MnCl_4^2$ species, the formation of which requires an excess of chloride anions.

The results of the emf measurements for various X $_{MnC1_2}$, S and t values are summarized in Table 1 in the form of linear MnC1_2 equations of the form

 $E - E^{\circ} = AT + B \tag{8}$

where,	Е	is the measured cell potential in millivolts
	Е°	is the "standard" potential of MnCl2, i.e., the
		formation potential of pure molten $MnCl_2$ at the
		temperature of the measurement, and
	т	is the absolute temperature in degrees K.

Values for the standard potentials of molten $MnCl_2$ at various temperatures have been obtained in a previous investigation(3).

Thus for the reaction:

 α -Mn(s) + Cl₂(g, 1 at) \rightarrow MnCl₂(liquid)

For, 990 K > T > 923 K

$$E^{\circ} (in mV) = 2387.7 + 0.4043 T \log T - 0.3729 x 10^{-4} T^{2} - \frac{1.1138 x 10^{3}}{T} - 1.7179 T$$
(9)

For the reaction:

 β -Mn(s) + Cl₂(g,1 at) = MnCl₂(liquid)

For, 1200 K > T > 900 K

E° (in mV) = 2372.6 + 0.2721 T log T - 0.78 x
$$10^{-5}$$
 T²
+ $\frac{7.32 \times 10^2}{T}$ - 1.3381 T (10)

The partial molar free energies, enthalpies and entropies of mixing may be readily calculated as:

 $\overline{\Delta G}_{MnCl_2} = -Z F (E - E^{\circ})$ (11)

$$\overline{\Delta H}_{MnCl_2} = -Z F B$$
(12)

$$\overline{\Delta S}_{MnCl_2} = Z F A \tag{13}$$

where, A and B are the constants given in Table 1, $E - E^{\circ}$ is given in millivolts, Z is the valence of the metal cation and F is the Faraday constant expressed as 23.060 cal/mV equivalent.

The activities of $MnCl_2$ are calculated from the measured cell emf's using the well known Nernst equation written as:

$$E_{cell} = E_{MnCl_2}^{\circ} - \frac{RI}{ZF} \ln a_{MnCl_2}$$
(14)

where, E and E°_{MnC12} are expressed in millivolts, and the ideal gas constant R = 1.987 cal/mol. K.

Activities of the $MnCl_2$ calculated for equation (14) refer to pure molten $MnCl_2$ as the standard state of reference.

Partial molar heats of mixing, entropies of mixing and activities of MnCl₂ calculated from the data, are also included in Table 1. Plots of $E - E^{\circ}$ versus temperature, for various X_{MnCl_2} , S and t values are given in Figures 2 to 14.

DISCUSSION

The previously derived expression(2) for the calculation of the partial molar free energies of mixing in the quarternary system is:

$$\frac{\overline{\Delta G}}{MnCl_2} = (1-S) \left[(1-t) \overline{\Delta G}_{MnCl_2} + t \overline{\Delta G}_{MnCl_2} \right]$$
(in quarternary)
(in quarternary)
(MnCl_2-KCl)
(MnCl_2-KCl)
(MnCl_2-KCl)
(15)
(16)
(17)
(MnCl_2-NaCl)

The quantities, $\overline{\Delta G}_{MnCl_2}$ (in MnCl₂-CsCl), $\overline{\Delta G}_{MnCl_2}$ (in MnCl₂-KCl) and $\overline{\Delta G}_{MnCl_2}$ (in MnCl₂-NaCl) are the partial molar free energies of mixing of MnCl₂ in the designated binary systems having the same MnCl₂ content and temperature as the quarternary.

From equations (11) and (15), $E - E^{\circ}$ values were calculated and are given as dotted lines in Figures 2 to 14.

The quantities $\overline{\Delta G}_{MnCl_2}$, for the three binary systems, plotted as $E - E^\circ$ versus X_{MnCl_2} , were available from previous measurements(3) and are given in Figure 15.

From Figures 2 to 14, it is evident that the agreement between the experimental and calculated partial molar free energies of mixing expressed by the $E - E^{\circ}$ quantities, is better than 3% over the investigated composition range of the quarternary system.

From equation (15) the expression for the activity of MnCl₂ in the quarternary system is readily derived as:

 $a_{MnCl_2} = a_{MnCl_2}^{(1-S)(1-t)} \cdot a_{MnCl_2}^{(1-S)t} \cdot a_{MnCl_2}^{S}$ (16) (in quarternary) in in in (MnCl_2-CsCl) (MnCl_2-KCl) (MnCl_2-NaCl)

In terms of activity coefficients equation (16) may be written as:

$$\gamma_{MnCl_{2}} = (\gamma_{MnCl_{2}})^{(1-S)(1-t)} \cdot (\gamma_{MnCl_{2}})^{(1-S)t}$$
(in quarternary)
in in in
(MnCl_{2}-CsCl) (MnCl_{2}-KCl)

$$\cdot (\gamma_{MnCl_{2}})^{S}$$
(17)
in
(MnCl_{2}-NaCl)

where the quantities in parentheses represent activity coefficients in binary systems at compositions having the same $\rm X_{MnCl_2}$ values as in the quarternary.

Plots of the partial molar free energies of mixing of $MnCl_2$ as functions of the parameter S, at constant y and t values are given in Figures 16 to 19.

Activities of MnCl₂ in the quarternary system, calculated from equation (16), are plotted as a function of X_{MnCl_2} at constant temperature and constant S and t values. The MnCl₂ various curves correspond to different t-values, and the composition path followed in this case starts from solutions very dilute in MnCl₂ and moves upwards through the quarternary to $X_{MnCl_2} = 0.4$.

These plots are given in Figure 20 and include the few experimental points available for such a composition path. Again, agreement is indicated between equation (16) and the experimental values.

The partial molar enthalpies of mixing, $\overrightarrow{AH}_{MnC1}$ shown in Table 1, become more exothermic as t decreases, i.e. when the CsCl content of the melt increases. $\overrightarrow{AH}_{MnC1}$ becomes less exothermic as S increases, i.e. when the NaCl content of these melts increases. As expected the activities of MnCl₂, indicate pronounced negative deviations from ideality, particularly for the CsCl rich melts.

Equations (15), (16) and (17), should be strictly valid for charge asymmetric molten salt solutions(2) like the system $MnCl_2$ -NaCl-KCl-CsCl, in which the charge asymmetric component $MnCl_2$, is known to react with the alkali metal chlorides. Although an exact knowledge of the structure of such complexes is not necessary for a thermodynamic treatment there are certain indirect indications regarding their probable configuration. For example, recent structural evidence(11) as well as measurements of electrical conductivities and molar volumes(6,12) suggest that solutions of $MnCl_2$ in alkali chloride melts appear to contain tetrahedrally coordinated complexes of the type $MnCl_4^{2^-}$.

For a tetrahedral configuration the following reaction is expected to occur upon mixing:

 $MnCl_2 + 2Cl \rightarrow MnCl_4^2$ (from ACl)

and the enthalpies of mixing in binary melts containing alkali metal chlorides, should reach maximum values at a $MnCl_2$ content of 33 mole %. Deviations from ideality may be attributed to the relative stability, or strength, of such complexes. Experimental evidence(3) indicates that the observed negative deviation in the activities of $MnCl_2$ increases with increasing size of the alkali metal cations in the order Li \rightarrow Na \rightarrow K \rightarrow Rb \rightarrow Cs.

Such trends reflect the effects of competing interactions between the Mn^{2^+} and A^+ cations for the same Cl $\,$ anions in which the alkali

chloride acts as a ligand donor and the reactive metal chloride $MnCl_2$ is the ligand acceptor. Alkali metal cations like Na⁺, because of their small size, are strongly attracted to their chloride anions and effectively the NaCl salt is less "dissociated" than the other alkali metal chlorides containing larger cations like K⁺ or Cs⁺. The difference in the strength of the complexes which are formed when the reactive metal chloride, $MnCl_2$, is mixed with either of the alkali chlorides of the type ACl or BCl, is simply reflected by the difference in the bond distances in configurations of the type Mn-Cl-A or Mn-Cl-B.

The spatial arrangement of such complexes within the ionic melt structure should be compatible with the requirement of local electrical neutrality and with the concept of interlocking anionic and cationic "quasi-lattices" as proposed by Temkin(13).

CONCLUSIONS

It has been shown that the thermodynamic properties of non-ideal and non-regular charge asymmetric fused salt systems may be calculated from data on component binary systems along composition paths representing constant content of the charge asymmetric component $MnCl_2$. Although the derivation of equation (15) was based on the formation of complex species in the binary solutions, its application depends only on the availability of experimental data on binary systems.

Regarding quarternary systems, the introduction of the composition parameters y, t and S, serves in the planning of experiments and in reducing the large number of compositions to be studied in order to characterize a quaternary system adequately.

Also, the use of these composition parameters makes it possible to plot thermodynamic data along well defined composition paths and to identify the effects of competing interactions on a charge asymmetric cation. For example, the complexing effects of CsCl or KCl on $MnCl_2$ become evident as the quaternary solutions become richer in CsCl, or in KCl, respectively.

The successful application of equations (15), (16) and (17) to such non-ideal charge asymmetric fused salt solutions indicates that in quaternary and possibly even in higher order systems, reactions within the binary solutions account for most of the deviations from ideality. Thus, the formation of a higher order system represents mixing of such pre-reacted binary systems and the properties of the multicomponent system should be predictable.

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REFERENCES

- 1. D.R. Sadoway, S.N. Flengas, J. Electrochem. Soc., 122, 515, 1975.
- S.N. Flengas, D.R. Sadoway, Proceedings of 3rd International Symposium on Molten Salts, p.68-94, 1981, The Electrochem. Soc., Inc., Pennington, N.J. 08534, Gleb Maniantou, Milton Blander and G.P. Smith, eds.
- A.S. Kucharski, S.N. Flengas, J. Electrochem. Soc., <u>119</u>, 1170, 1972.
- 4. S.N. Flengas, J. Skeaff, Can. J. Chem., 50, 1345, 1972.
- 5. G.N. Papatheodorou and O.J. Kleppa, J. Inorg. Nucl. Chem., <u>33</u>, 1249, 1971.
- N.R. Carmichael, S.N. Flengas, J. Electrochem. Soc., <u>128</u>, 2098, 1979.
- A.S. Kucharski, S.N. Flengas, J. Electrochem. Soc., <u>121</u>, 1298, 1974.
- 8. S.N. Flengas, High Temperatures-High Pressures, 5, 551, 1973.
- 9. O. Kubaschewski, C.B. Alcock, "Metallurgical Thermochemistry", Pergamon Press, 5th Ed., 1979, p.294.
- A. Prince, "Alloy Phase Equilibria", Elsevier Publishing Co., N.Y., 1966.
- 11. K. Tamemoto, T. Nakamura, Chem. Lett., 351, 356, 1975.
- N.R. Carmichael, S.N. Flengas, J. Electrochem. Soc., <u>126</u>, 2104, 1979.
- 13. M. Temkin, Zhur. Fiz. Khim., 20, 105, 1946.

TABLE	1	

Summary of emf Measurements

X.MaCl ₂			E - E° • in	AT+B mV	Standard*	Temperature	MnC12**	AS MnCl ₂	a MnCL2
	3		A	В	(±mV)	(K)	cal.mol ⁻¹	** ¹ S _{McCl₂} ⁴ mcC ₁ ⁴ mc (973 J e.u (973 J 0 3.79 3.50) 0 4.50 4.70 0 4.95 6.60 0 4.93 8.80 0 5.61 5.90 0 5.62 6.80 0 5.27 1.10 0 5.20 1.20 0 4.97 7.90 0 5.77 1.10 x	(973 K)
0.05	0.1	0.2	0.0822	350.38	5.78	940-1130	-16,160	3.79	3.50 x 10 ⁻⁵
		0.4	0.0975	322.78	7.39	940-1140	-14,390	4.50	4.70 x 10 ⁻⁵
		0.6	0.1073	299.36	8.33	935-1140	-13,810	4.95	6.60 x 10 ⁻⁵
		0.8	0.1069	287.69	7.28	970-1145	-13,270	4.93	8.80 x 10 ⁻⁵
	0.2	0.2	7/ 0.1271	289.60	8.23	930-1090	-13,360	5.61	5.90 x 10 ⁻⁵
		0.4	0.1263	279.52	9.24	930-1120	-12,390	5.82	6.80 x 10 ⁻⁵
		0.6	0.1142	2 78 . 38	7.76	950-1130	-12,580	5.27	1.10 x 10 ⁻⁴
		0.8	0.1128	268.88	7.73	950-1135	-12,400	5.20	1.20 x 10 ⁻⁴
	0.3	0.2	0.1078	290.98	7.09	940-1110	-13,420	4.97	7.90 x 10 ⁻⁵
		0.4	0.1134	275.75	8.15	940-1135	-12,720	5.23	1.00 x 10 ⁻⁴
		0.6	0.1251	252.69	8.25	940-1120	-11,650	5.77	1.10 x 10 ⁻⁴
		0.8	0.1232	244.45	8.36	950-1130	-11,270	5.68	1.70 x 10 ⁻⁴
0.05	0.4	0.2	0.1194	261.35	8.51	935-1125	-12,050	5.51	1.20 x 10 ⁻⁴
		0.4	0.1190	252.48	8.27	940-1130	-11,640	5.49	1.50 x 10 ^{-*}
		0.6	0.1272	235.93	7.78	960-1125	-10,380	5.87	1.90 x 10 ⁻⁴
		0.8	0.1346	221.29	8.09	970-1130	-10,200	6.21	2.20 x 10 ⁻⁴
	0.5	0.2	0.1249	238.90	8.48	945-1120	-11,020	5.76	1.90 x 10
		0.4	0.1294	226.52	7.72	950-1110	-10,450	5.97	2.20 x 10 ⁻¹
		0.5	0.1315	217.89	7.98	945.1110	-10,050	6.07	2.70 x 10
		0.3	0.1302	211.02	9.14	950-1130	-9,730	6.00	3.20 x 10 ⁻⁴
0.15	0.2	0.1	0.0745	251.09	5.42	930-1130	-11,580	3.44	4.40 x 10 ⁻⁴
		0.4	0.0812	227.82	6.00	935-1130	-10,510	3.75	6.60 x 10
	0.4	0.1	0.0805	213.94	6.16	940-1130	-9,870	3.71	9.70 x 10 ⁻¹
		0.4	0.0849	195.83	5.68	950-1120	-9,030	3.97	1.30 × 10 ⁻³

 Standard deviations based on a maximum of 10 experimental points for each composition.

TABLE 1	(cont'd)
---------	----------

			E-E° =	AT + B mV	Standard*	Iemperature	Δ	AS MOCIO	8.WmC1r
MnCl ₂	5	£	A	В	Deviation (±mV)	Range (K)	cal.mol ⁻¹	e.u	PLICE_
0.15	0.6	0.1	0.0853	178.53	5.89	935-1120	-8,240	3.93	2.00 x 10 ⁻¹
		0.4	0.0861	168.30	6.44	940-1140	-7,760	3.97	2.50 x 10 ⁻³
	0.8	0.1	0.0846	147.99	5.96	935-1125	-6,830	3.90	4.10 x 10 ⁻¹
		0.4	0.0885	139.21	6.53	935-1125	-6,420	4.08	4.60 x 10 ⁻³
0.25	0.2	0.2	0.0579	189.82	6.47	940-1130	-8,750	2.67	2.90 × 10 ⁻⁹
		0.8	0.0813	135.16	5.87	930-1110	-6,230	3.75	6.00 x 10 ⁻⁵
	0.4	0.2	0.0478	174.62	7.12	935-1130	-8,050	2.20	5.10 x 10 ⁻³
		0.8	0.0603	137.94	6.54	935-1120	-6,360	2.78	9.20 x 10 ⁻³
	0.6	0.2	0.0477	150.28	3.27	940-1135	-6,930	2.20	9.20 x 10 ⁻⁵
		8.0	0.0585	123.58	3.56	955-1135	-5,700	2.70	1.35 x 10 ⁻¹
	0.8	0.2	0.0458	128.31	2.79	930-1110	-5,920	2.11	1.62 x 10 ⁻²
		0.8	0.0521	114.85	2.99	945-1115	-5,300	2.40	1.93 x 10 ⁻²
0.40	0.2	0.3	0.0495	108.25	3.33	940-1120	-4,990	2.28	2.41 x 10 ⁻²
		0.6	0.0532	91.94	3.56	940-1125	-4,240	2.45	3.24 x 10 ⁻²
		0.9	0.0474	84.57	3.16	940-1130	-3,900	2.19	4.43 x 10 ⁻²
	0.4	0.3	0.0486	92.71	3.60	930-1130	-4,280	2.24	3.50 x 10 ⁻²
		0.6	0.0445	91.63	2.94	930-1130	-4,230	2.05	4.00 x 10 ⁻²
		0.9	0.0405	90.51	3.08	930-1130	-4,080	1.87	4.74 x 10 ⁻²
	0.6	0.3	0.0410	83.00	2.74	950-1130	-3,830	1.89	5.33 x 10 ⁻²
		0.6	0.0402	77.68	2.79	950-1130	-3,580	1.85	6.16 x 10 ⁻²
		0.9	0.0369	72.93	2.36	940-1130	-3,360	1.70	7.46 x 10 ⁻²
	0.8	0.3	0.0377	68.81	2.36	930-1115	-3,170	1.74	8.07 x 10 ⁻²
		0.6	0.0362	66.95	2.56	940-1140	-3,090	1.66	8.74 x 10 ⁻²
		0.9	0.0336	67.40	2.36	940-1140	-3,110	1.55	9.18 x 10 ⁻²

** Calories may be converted to the S.I. units, Joules, by multi-plying with the factor 4.184.



Figure 1. Representation of compositions in a quarternary system in terms of the parameters y, t, and S, where:

$$y = 1 - X_{MnCl_2}$$
$$t = \frac{X_{KCl}}{X_{KCl} + X_{CsCl}}$$
$$S = \frac{X_{NaCl}}{X_{NaCl} + X_{KCl} + X_{CsCl}}$$

Any composition P lies on a S line which represents the intersection of y and t planes.



Figure 3

Figure 2

















Figure 11



73g





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Figure 15. Plots of E - E° for the three binary systems(3)
MnCl₂-NaCl, MnCl₂-KCl and MnCl₂-CsCl, at 700°C
and 800°C.







Figures 16 to 19.





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