MOLECULAR AND IONIC ASSOCIATES IN SATURATED VAPOR OVER RbCl-$CeCl_3$ SYSTEM[†]

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The systematic investigations of the composition and thermochemistry of the equilibrium vapor constituents over metal halides and their binary systems $MX–LnX_3$ are very important for metal halide lamps (e.g. Ref. 1).

The study of RbCl–$CeCl_3$ system presented here supplements our investigation of the pure RbCl and $CeCl_3$ substances (Ref. 2,3). A Knudsen effusion cell mass spectrometric technique was used. A unique ion source permitted to analyze the neutral vapor species by means of electron impact ionization (*EI*) method and charged components (both positive and negative) were analyzed in the thermal emission regime (*TE*). In the latter the ions produced *via* self-surface thermal ionization inside the effusion cell were drawn out from it by a weak electric field.

The RbCl–$CeCl_3$ system with the molar ratio of the constituents 0.8 : 0.2 (I) and 0.15 : 0.85 (II) were studied in the temperature range 848–1177 K. The phase diagram of the system (Ref. 4) is shown in the Fig. 1.

The ions Rb^+ (100), $RbCl^+$ (6.2), Rb_2Cl^+ (2.3), $RbCeCl_3^+$ (1.2), $RbCeCl_2^+$, $Rb_2CeCl_4^+$, Ce^+ (0.2), $CeCl^+$ (0.3), $CeCl_2^+$ (0.8), $CeCl_3^+$, $Ce_2Cl_5^+$ have been registered in the *EI* mass spectra at the electron ionization energy of 50 eV. The relative intensities of the ion currents corrected for the isotopic abundances are given in parenthesis for the system (I) at 1035 K. The assignment of the ions to their neutral precursors was made. The dimmers Rb_2Cl_2, Ce_2Cl_6 and heterocomplex $RbCeCl_4$, Rb_2CeCl_5 molecules was proved to be present along with the monomers RbCl and $CeCl_3$ molecules in the saturated vapor.

The various positive and negative ions Rb^+ ($>10^3$), Rb_2Cl^+ (100), $Rb_3Cl_2^+$ (0.1), $Rb_4Cl_3^+$, $Rb_5Cl_4^+$, $Rb_2CeCl_4^+$ (0.07), $Rb_3CeCl_5^+$ (0.002), $Rb_4CeCl_6^+$ ($<10^{-3}$); Cl^-(0.08), $RbCl_2^-$, $CeCl_4^-$(100), $Ce_2Cl_7^-$ (0.9), $Ce_3Cl_{10}^-$, $RbCeCl_5^-$, $RbCe_2Cl_8^-$ (0.007) have been identified in the *TE* mass spectra.

To determine the formation enthalpies of neutral and charged associates the different reactions involving the molecules and ions observed were studied (Table 1). The equilibrium constants of the reactions were calculated on the basis of the partial pressures of molecules and ion current intensities measured in *EI* and *TE* regimes, respectively. The reaction enthalpies and formation enthalpies of molecules and ions (Table 1) have been determined by the third law of thermodynamics.

The thermodynamic functions of molecules and ions were computed in the rigid rotator – harmonic oscillator approximation on the basis of molecular parameters taken from literature (Rb_2Cl^+, $Rb_3Cl_2^+$) or estimated by us ($RbCeCl_4$, $Rb_4Cl_3^+$, $Rb_5Cl_4^+$, $CeCl_4^-$, $Ce_2Cl_7^-$, $Ce_3Cl_{10}^-$). The thermodynamic functions of more complex molecules and ions (Rb_2CeCl_5, $Rb_2CeCl_4^+$, $Rb_3CeCl_5^+$, $Rb_4CeCl_6^+$, $RbCe_2Cl_8^-$) were calculated using the additive rule. The thermodynamic functions for Cl^- was taken from Ref. 5.

The formation enthalpies of associates were determined by combination of the reaction enthalpies with the formation enthalpies from Ref. 2 (Rb_2Cl^+, RbCl), Ref. 3 ($CeCl_3$) and Ref. 5 (Cl^-).

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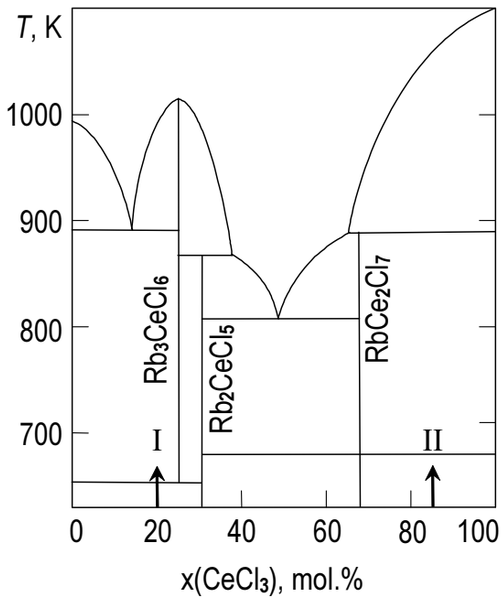

Fig. 1. The phase diagram of the RbCl–$CeCl_3$ system

Reaction		
ΔT/K; N	$\Delta_r H°$(298 K)	$-\Delta_f H°$(298 K)
$RbCeCl_4$ = RbCl + $CeCl_3$		
1036–1151; 12	247 ± 27	1201 ± 28
Rb_2CeCl_5 = 2RbCl + $CeCl_3$		
1035–1066; 2	457 ± 32	1635 ± 33
$Rb_3Cl_2^+$ = Rb_2Cl^+ + RbCl		
871–1035; 6	135 ± 24	265 ± 26
$Rb_4Cl_3^+$ = Rb_2Cl^+ + 2RbCl		
934–986; 2	329 ± 41	682 ± 43
$Rb_5Cl_4^+$ = Rb_2Cl^+ + 3RbCl		
934; 1	531 ± 51	1108 ± 52
$Rb_2CeCl_4^+$ = Rb_2Cl^+ + $CeCl_3$		
1036–1151; 7	149 ± 29	787 ± 31
$Rb_3CeCl_5^+$ = Rb_2Cl^+ + RbCl + $CeCl_3$		
1151; 1	394 ± 38	1255 ± 40
$Rb_4CeCl_6^+$ = Rb_2Cl^+ + 2RbCl + $CeCl_3$		
1035; 1	659 ± 42	1743 ± 44
$CeCl_4^-$ = Cl^- + $CeCl_3$		
1066–1151; 7	293 ± 18	1258 ± 19
$Ce_2Cl_7^-$ = Cl^- + 2$CeCl_3$		
1066–1151; 7	510 ± 30	2206 ± 31
$Ce_3Cl_{10}^-$ = Cl^- + 3$CeCl_3$		
1036–1151; 5	785 ± 39	3211 ± 40
$RbCe_2Cl_8^-$ = Cl^- + RbCl + 2$CeCl_3$		
1062–1078; 3	732 ± 38	2651 ± 39

Table 1. The reaction enthalpies and formation enthalpies of associates (in kJ·mole^{-1}). The values of $\Delta_f H°$ correspond to the molecules and ions printed in bold type. Overall uncertainties follow the «±» sings.

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