Lewis Acid-based Equilibrium Effects on Volatility of Aluminum and Gallium Tetrachlorides in Molten NaCl-$AlCl_3$-$GaCl_3$ Mixtures and on Ga/Al Separation Factor

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Chloroaluminate melts have attracted considerable interest because of their special properties as acid-based solvents. According to Lewis, $GaCl_3$ as well as $AlCl_3$ is a strong acid. Therefore there is currently great interest in studying their joint behavior in molten mixtures with alkali metals chlorides. It may be of great practical importance, for example, in selective removal (separation) of gallium and aluminum.

Molten NaCl-$AlCl_3$-$GaCl_3$ mixtures containing 50 to 68 mole percent of $AlCl_3$ with variable gallium concentration (up to 7 mass percent) have been studied at the temperatures within the range 170 to 300°C. The vapor pressure above molten mixtures of several compositions was measured using static method (membrane pressure gauge was used) and chemical composition of vapors was studied. It was found out that overall pressure increases when a part of $AlCl_3$ in the melt is replaced with $GaCl_3$. The less the total concentration of tetrachlorides is in the melt, the stronger this effect is.

It was established that the Ga/Al separation factor

$$K = \frac{(N_{Ga}/N_{Al})vapor}{(N_{Ga}/N_{Al})melt},$$

where N – mole fraction, increases several times, up to K = 5÷15, as the total concentration of $AlCl_3$+$GaCl_3$ in the melts decreases, and also the temperature goes up. Thus the vapor is enriched in gallium tetrachloride. Conversely the volatility of pure molten AlCl3 is approximately 2.5 times higher than that of molten GaCl3.

The obtained experimental data can be explained as due to the appearance of step-type acid-based Lewis equilibria in molten salts:

$$A_2Cl_6 + Cl^- \leftrightarrow A_2Cl_7^- \quad (1)$$

$$+\ A_2Cl_7^- + Cl^- \leftrightarrow 2ACl_4^- \quad (2)$$

$$A_2Cl_6 + Cl^- \leftrightarrow 2ACl_4^- \quad (3),$$

where A is Al(III) and Ga(III). It follows from our data that in the equations (1)÷(3) Al_2Cl_6 and $Al_2Cl_7^-$ are stronger acceptors of the Cl^- ions than Ga_2Cl_6 and $Ga_2Cl_7^-$ respectively. When the concentration of the Cl^- free ions increases (that is at the melt acidity decrease according to Lewis) due to reduction of total concentration of $AlCl_3$+$GaCl_3$, the Ga/Al separation factor grows. This factor increases at the temperature growth as well.

It was demonstrated that as a result of selective evaporation of aluminum and gallium tetrachlorides, the gallium content in molten NaCl-$AlCl_3$-$GACl_3$ mixtures can be two to four times decreased.