

**Lewis Acid-based Equilibrium Effects on
Volatility of Aluminum and Gallium
Tetrachlorides in Molten NaCl-AlCl₃-GaCl₃
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, GaCl₃ as well as AlCl₃ 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.

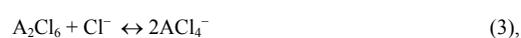
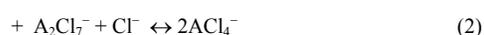
Molten NaCl-AlCl₃-GaCl₃ mixtures containing 50 to 68 mole percent of AlCl₃ with variable gallium concentration (up to 7 mass percent) have been studied at the temperatures within the range 170 to 300°C. The vapor pressure above molten mixtures of several compositions was measured using static method (membrane pressure gauge was used) and chemical composition of vapors was studied. It was found out that overall pressure increases when a part of AlCl₃ in the melt is replaced with GaCl₃. 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 $K = 5\div 15$, as the total concentration of AlCl₃+GaCl₃ 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:



where A is Al(III) and Ga(III). It follows from our data that in the equations (1)-(3) Al₂Cl₆ and Al₂Cl₇⁻ are stronger acceptors of the Cl⁻ ions than Ga₂Cl₆ and Ga₂Cl₇⁻ 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 AlCl₃+GaCl₃, 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-AlCl₃-GaCl₃ mixtures can be two to four times decreased.

