LEWIS ACID-BASE EQUILIBRIUM EFFECTS ON THE VOLATILITY OF ALUMINUM AND GALLIUM TRICHLORIDES IN MOLTEN NaCl-AlCl₃-GaCl₃ MIXTURES AND ON Ga/Al SEPARATION FACTOR

A.B. Salyulev, A.L. Bovet, and N.I. Moskalenko

Russian Academy of Sciences, Ural Division, Institute of High Temperature Electrochemistry; 620219 Ekaterinburg, Russia

ABSTRACT

The present study focuses on the separation of aluminum and gallium trichlorides by their selective evaporation from acidic molten NaCl-AlCl₃-GaCl₃ mixtures. This depends on the total concentration of trichlorides (50.1 to 67.5 mole per cent), their mole fraction ratio in the melt (N₉₈/Nₐ₅ = 0.0121-0.211), and the temperature (170 - 350 °C). The overall vapor pressure of molten NaCl-AlCl₃-GaCl₃ mixtures was calculated for a wide range of concentrations, and measured directly in melts of various compositions by a static method. The effect of the Lewis acid-base equilibrium on the volatility of aluminum and gallium trichlorides, and on the Ga/Al separation factor, is here discussed.

INTRODUCTION

Due to their special properties as acid-base solvents, chloroaluminate melts have attracted considerable interest from the point of view of their application to aluminum production, and possible use as electrolytes in rechargeable high-energy-density batteries (1,2). These melts were intensively studied by potentiometric and spectroscopic methods. The saturated vapor pressure of acidic low-melting mixtures in the NaCl-AlCl₃ system was measured by several groups of investigators. The most reliable results are presented in papers (1-7). There is significantly less information about gallium trichloride behavior in molten mixtures containing NaCl. Only one study is known, that of Petrov et al. (8), who measured the pressure of saturated vapor of molten NaCl-GaCl₃ mixtures containing 50 to 100 mole percent of GaCl₃ by a static method. The vapor pressure of acidic melts of the ternary NaCl-AlCl₃-GaCl₃ system has not previously been measured. GaCl₃, as well as AlCl₃, is a strong Lewis acid (acceptor of the Cl⁻ ions). It was therefore of great interest to study the joint behavior of aluminum and gallium trichlorides in molten mixtures containing sodium chloride (for comparing them as Lewis acids), because of the great practical importance, for example, in the selective removal (separation) of gallium and aluminum. In the present work, the relative volatility (separation factor) of aluminum and gallium trichlorides in molten NaCl-AlCl₃-GaCl₃ mixtures with total concentration of trichlorides > 50 mole percent was determined, and the vapor pressure of molten mixtures of several compositions was measured.
EXPERIMENTAL

Reagent grade NaCl was dried by gradual heating up to 400 °C under vacuum, $10^{-4}$ to $10^{-3}$ mm Hg, for several hours, and then additionally purified by zone refining. GaCl₃ and AlCl₃ were obtained through the reaction of high-purity metals with dry chlorine. The specified quantity of GaCl₃ and AlCl₃ was transferred by a flow of chlorine or pure helium into quartz ampoules containing a known quantity of NaCl. The ampoules were evacuated, sealed, and the salts then fused. Their exact chemical composition was later determined by standard analytical methods. The resulting salt mixtures of known composition were loaded into the measuring apparatus located in a glove box under a dry nitrogen atmosphere.

Vapor sampling (for determination of Ga, Al and Na content) from molten NaCl-AlCl₃-GaCl₃ mixtures employed the sealed quartz tubes in Figure 1. Initially, the whole apparatus was heated in two furnaces to a specified temperature, recorded with a Pt/Pt-Rh thermocouple (Figure 1a). Then the lower empty tube, 6, of the apparatus was heated several degrees higher than the temperature of the part of the apparatus where molten salts were contained, 3. After being held in the furnace for 20 to 30 minutes, this tube, 6, was quenched in liquid nitrogen (Figure 1b) to collect the condensate of the molten salt vapor. The conditions selected were such that the composition of the molten salt mixture changed by no more than 2 relative percent during evaporation. Thus, depending on the evaporation temperature and melt composition, the condensate sampling time was varied within from 5 to 120 min., and the pressure of the inert gas (Ar) in the sealed apparatus from $10^{-4}$ to 1 atm. After cooling, the apparatus was broken open into two pieces so that the vapor condensate and salt fusion components could be washed out separately with distilled water and analyzed for Na, Al and Ga content.

The vapor pressure above the molten mixtures of several compositions was measured by a static method (quartz membrane pressure gauge). The pre-melted NaAlCl₄ was loaded into the apparatus in a glove box, and known quantities of AlCl₃ and GaCl₃ added and transferred by chlorine or helium flow. The salt vapor pressure on the membrane was counter-balanced by argon, using a U-tube manometer, containing dibutyl phthalate or mercury, and a standard pressure gauge. The total percentage error in measuring pressure was 1.0 to 1.5 percent. The temperature of the molten salt was controlled using a Pt/Pt-Rh thermocouple with an accuracy of ±1°C. A more detailed description of the measurement procedure has been given elsewhere (9). The weights of salts used in the experiments, (10 - 20g), were enough to minimize changes in the composition of salt mixtures by no more than 1 relative per cent owing to vaporizing during trials.

The Ga, Al and Na contents in the salt fusions and vapor condensates were determined by dissolving completely the chloride salt in distilled water. The solutions were acidified by HCl up to 2 % vol. An Inductively Coupled Plasma (ICP) Spectrometer coupled with an Optical Emission Spectrometer (ICP-OES) JY48, Jobin Yvon (France), with appropriate gallium and aluminum standards was used. Na was determined by atomic-absorption in the air-acetylene flame using a PE 403
spectrophotometer, Perkin Elmer (USA). The relative error of the Ga, Al and Na content did not exceed 3%.

RESULTS AND DISCUSSION

At moderate temperatures of around 200 - 300°C in the NaCl-AlCl₃ systems homogeneous melts can only exist within a limited concentrations range (Figure 2). Here the compositions of the vapors above molten NaCl-AlCl₃ mixtures with small additions of GaCl₃ were studied at temperatures within the range of 170 - 350°C. The total mole fraction (N⁺) of the trichlorides in the melts was varied from 0.501 to 0.675, and their ratio (N_{Ga}/N_{Al} ) was changed within the range 0.0121 to 0.211. Experimental results fitted the function:

\[ K = \frac{[N_{Ga}/N_{Al}]_{vapor}}{[N_{Ga}/N_{Al}]_{melt}} \]  

and are presented in Figs.3 and 4, as a function of temperature and melt composition. The separation factor K (relative volatility coefficient) shows that the mole fraction ratio of gallium and aluminum chlorides in the vapor phase depends on the melt composition (and temperature). We note that, from the analysis of the data, the sodium content in the vapor was insignificant (< 1 per cent). The sodium content increased up to 10 to 20 mole percent, but only when melts with the lowest concentrations of aluminum and gallium trichlorides were employed. Within the temperature ranges and molten mixtures compositions that have been studied (1-8), the pressure of saturated vapors of gallium and aluminum trichlorides changed by several orders of magnitude. This is seen, for example, in Figure 4, where an isotherm of saturated aluminum trichloride vapor pressure above molten NaCl-AlCl₃ mixtures is given for comparison. The isotherm was obtained on the basis of the most reliable published data (2,4,6). With a good precision this isotherm (e.g., at 235 °C) approximates to the following equation:

\[ \log P = a + b \times \left[ 1 - \exp\left( -\left( \frac{N + d \times [\ln(2)]^{(1/e)} - c}{d} \right) \right) \right] \pm \Delta \]  

where P is the vapor pressure in mm Hg, and K, the separation factor determined as follows:

\[ K = a + b \times \left[ 1 - \exp\left( -\left( \frac{N^2 + d \times [\ln(2)]^{(1/e)} - c}{d} \right) \right) \right] \pm \Delta \]  

Numerical values of the coefficients in these equations are summarized in Table I. Here N and N², are the mole fraction of AlCl₃ and the total mole fraction of AlCl₃ and GaCl₃, respectively, in the melt. When the trichloride content in the melt is less than 50 mole percent, the overall vapor pressure (and separation factor K) are independent of concentration (Figure 4), because the heterogeneous mixture (NaCl(liquid) + melt with
constant composition) is formed in the aluminum and sodium chloride systems at moderate temperature under these conditions, Figure 2.

The aluminum and gallium trichlorides have the properties of Lewis acids (strong acceptors of chloride ions), and in molten mixtures containing sodium chloride they form the stable complex anions $\text{ACL}^-$ and $\text{A}_2\text{Cl}_7^-$ (A=Al or Ga) (1,11-14). In acidic melts of the NaACL$_4$+ACL$_3$ composition acid-base equilibria arise, and depend on the concentration of aluminum and gallium trichlorides present:

$$\text{A}_2\text{Cl}_6 + \text{Cl}^- \leftrightarrow \text{A}_2\text{Cl}_7^- \quad [4]$$

$$\text{A}_2\text{Cl}_7^- + \text{Cl}^- \leftrightarrow 2\text{ACL}_4^- \quad [5]$$

$$\text{A}_2\text{Cl}_6 + 2\text{Cl}^- \leftrightarrow 2\text{ACL}_4^- \quad [6]$$

The concentration of the Cl$^-$ ions present can serve as a measure of acidity. This concentration can vary by several orders of magnitude (pCl $\sim 3$ to 8) in NaCl-AlCl$_3$ melts with the concentration within the range of 50 to 70 mole percent of AlCl$_3$ and the temperature ranging from 175 to 375°C. The acidity of the melt increases with AlCl$_3$ or GaCl$_3$ increase and temperature decrease (1,11-13). The dramatic effect of Lewis acidity decrease (when the trichloride concentration decreases in molten mixtures containing NaCl) on the volatility of aluminum and gallium species and the separation factor K (Figure 4) has been established. The changes in the saturated vapors pressure of the trichlorides, the relative volatility coefficient, K, are greatest when the concentration of the trichlorides in the melt approaches 50 mole percent. Near this composition the acid-base properties change dramatically, and equilibria [5] and [6] shift to the right (1,11-14) towards the formation of Lewis bases, ACI$_4$. Temperature increase has a considerably smaller effect on the increase in the relative volatility coefficient (Figure 3), and this correlates with the weaker effect of temperature increase on the decrease of melt acidity (12). In melts with low concentrations of the trichlorides, the effect of temperature on the K factor is greater.

The saturated vapor pressure of the trichlorides must correlate with the concentration of the neutral dimeric molecules Al$_2$Cl$_6$ and Ga$_2$Cl$_6$ in the molten mixtures. The high relative volatility of gallium trichloride (Figure 3 and 4) indicates that in molten mixtures with sodium chlorides, Al$_2$Cl$_6$ and Al$_2$Cl$_7$ are stronger acceptors of Cl$^-$ ions (Lewis acids) than Ga$_2$Cl$_6$ and Ga$_2$Cl$_7$, respectively. When the concentration of the free Cl$^-$ ions increases in the melt, the relative volatility coefficient of Ga/Al also increases. We note that in pure molecular melts of Al$_2$Cl$_6$ and Ga$_2$Cl$_6$, aluminum chloride is more volatile (15,16).

The increase in ratio of mole fractions of $N_{Ga}$ and $N_{Al}$ from 0.0121 to 0.211 in molten NaCl-AlCl$_3$-GaCl$_3$ mixtures leads to an increase in the $N_{Ga}$ and $N_{Al}$ ratio in the vapor. However, it has practically no effect on the separation factor K when the total concentration of the trichlorides in the melt remains constant. For example, it can be observed in Figure 4 that the experimental points for different mixtures can be approximated by a single isotherm.
In order to obtain more specific information on the effect of the changes in the \(N_{Ga}/N_{Al}\) ratio in the melt (with small additions of GaCl\(_3\)) on the overall vapor pressure at constant total concentration of the trichlorides, we carried out direct tensimetric measurements in molten mixtures of different composition. The results are presented in Figure 5 and 4. Depending on the temperature, the overall vapor pressure can be approximated by the equations of the following type:

\[
\log P = A - \frac{B}{T}.
\]

[7]

The values of the coefficients \(A\) and \(B\) are given in Table II.

The experimental data of the most reliable studies (2-7) on the saturated vapor pressure of molten NaCl-AlCl\(_3\) mixtures vary by a factor of 2 to 3. A more detailed analysis is presented in these papers. The values of vapor pressure of NaCl-AlCl\(_3\) melts, measured in this work, agree best with those of Viola et al. (4) and Dewing (3) (Figure 4). Replacement of about 10 percent of AlCl\(_3\) by GaCl\(_3\) in their molten mixtures containing NaCl leads to increase in overall vapor pressure (Figure 4 and 5). A more significant pressure increase is observed in melts with a lower total concentration of the trichlorides. This increase correlates with the dependence of the relative volatility coefficient \(K\) of the gallium and aluminum trichlorides on concentration (Figure 4.).

The method that enables evaluation of the overall saturated vapor pressure of molten NaCl-AlCl\(_3\)-GaCl\(_3\) mixtures and its dependence on temperature and total mole fraction of gallium and aluminum trichlorides \((N^2)\) has been developed. The calculations are based on our experimental data on relative volatility coefficient of gallium and aluminum trichlorides, as well as on published data on the pressures of Al\(_2\)Cl\(_6\) vapors above NaCl-AlCl\(_3\) melts (2,4,6) and equilibrium constants of gas molecules dissociation reactions:

\[
\text{Al}_2\text{Cl}_6 \leftrightarrow 2 \text{AlCl}_3 \quad [8] \quad \text{and} \quad \text{Ga}_2\text{Cl}_6 \leftrightarrow 2 \text{GaCl}_3 \quad [9]
\]

This method presupposes that the value of the saturated vapor pressure is known at each temperature for at least one composition of the melt. For example, at a temperature of 235°C (mean temperature of our measurement range) four calculated isotherms are presented in the coordinates of \(\log P-N^2\) axis. Changes of \(N^2\) within the boundaries of each curve occur due to changes in the Ga/Al ratio, when the gallium trichloride concentration remains constant. It is evident from Figure 6 that the calculated values of the overall vapor pressure for similar melt compositions are in good agreement with the data experimentally measured by a static method in this work.

Partial replacement of aluminum chloride by gallium chloride in molten NaCl-AlCl\(_3\) mixtures results in an increase in the overall vapor pressure (Figures 5 and 6). This effect is most clearly observed in the melts, the total concentration of AlCl\(_3\) and GaCl\(_3\) in
which is the least when compared with the other melts studied. This can be explained upon considering that when the stronger acceptors of the Cl⁻ ions (Al₂Cl₆, Al₂Cl₇) are partially replaced by weaker ones (Ga₂Cl₆, Ga₂Cl₇) in the equations [4] - [6], the equilibria are shifted to the left (vapor phase becomes enriched in gallium chloride, leading to an increase in overall pressure). In case of such replacement, the difference in acid-base properties (and in the ratio of the trichlorides volatilities) significantly increases when the composition of the melts becomes close to NaAl(Ga)Cl₄, where small changes in composition result in pronounced changes of pCl⁻ and thermodynamic properties (1-8, 10-13).

We carried out technological studies on the evaporation of gallium and aluminum trichlorides from molten NaCl-AlCl₃-GaCl₃ mixtures with the total concentration of the trichlorides from 60 to 68 mole percent, and the NGaCl₃/NaAlCl₃ ratio of 0.02 to 0.25 at temperatures within the range 190 to 300°C. The evaporation was performed in the apparatus shown in Figure 1, or in the inert gas flow. The final total concentration of the trichlorides in the melts after evaporation was 50 to 55 mole %. It has been demonstrated that as a result of selective evaporation of aluminum and gallium trichlorides, the gallium content in molten NaCl-AlCl₃-GaCl₃ mixtures can be decreased by a factor of 2 to 5.

ACKNOWLEDGEMENTS

The authors are grateful to the U.S. Civilian Research and Development Foundation for the Independent States of the Former Soviet Union (CRDF) for financial support.

REFERENCES

1. L.E. Ivanovsky, V.A. Khokhlov and G.F. Kazantsev, Physical Chemistry and Electrochemistry of Chloroaluminate Melts, Nauka, Moscow (1993).
2. H.A. Hjuler, A. Mahan, J.H. von Barner and N.J. Bjerrum, Inorg. Chem., 21, 402 (1982).
3. E.W. Dewing, J. Amer. Chem. Soc., 77, 2639 (1955).
4. J.T. Viola, L.A. King, A.A. Fannin, Jr. and D.W. Seegmiller, J. Chem. Eng. Data, 23, 122 (1978).
5. T. Narita, T. Ishikawa and R. Midorikawa, Denki Kagaku, 36, 300 (1968).
6. R. A. Sandler, A. A. Larionov and A. Kh. Ratner, Proc. VIII Conf. on Molten Salts, V.1, p.119, Nauka, Leningrad (1983).
7. K. Grande, Thermodynamics and Mathematical Modelling of Chloroaluminate Melts: Thesis, Trondheim, Norway (1987).
8. V.N. Arbekov and E.S. Petrov, Proceedings of the Siberia Department of the USSR Academy of Science, Series Chemical Science, 11, 55 (1964).
9. M.V. Smirnov, A.B. Salyulev and V.Ya. Kudyakov, Electrochim. Acta, 29, 1087 (1984).
10. A.A. Fannin, L.A. King, D.W. Seegmiller and H.A. Øye, J. Chem. Eng. Data, 27, 114 (1982).
11. A.A. Fannin, L.A. King and D.W. Seegmiller, J. Electrochem. Soc., 119, 801 (1972).
12. L.G. Boxall, H.L. Jones and R.A. Osteryoung, J. Electrochem. Soc., 120, 223 (1973).
13. K.W. Fung and G. Mamantov, in Advances in Molten Salt Chemistry, J. Braunstein, G. Mamantov and G.P. Smith, Editors, V.2, p.199, Plenum Press, New York (1973).
14. M.H. Brooker and G.N. Papatheodorou, in Advances in Molten Salt Chemistry, G. Mamantov, Editor, V.5, p.26, Elsevier, Amsterdam, Oxford (1983).
15. J.T. Viola, D.W. Seegmiller, A.A. Fannin, Jr. and L.A. King, J. Chem. Eng. Data, 22, 367 (1977).
16. P.I. Fyodorov, M.V. Mokhosoyev and F.P. Alekseev, Chemistry of Gallium, Indium and Thallium, Nauka, Novosibirsk, USSR (1977).
17. A. Smits and J.L. Meijering, Z. Physikal. Chem. Abt. B, 41, 98 (1938).
18. O.N. Komshilova, O.G. Polyachenok and G.I. Novikov, Russian Journal of Inorganic Chemistry, 15, 251 (1970).

**Table I.** Coefficients of approximation of equations logP = f(N) and K = f(N²) at 235°C

| Dependence | a     | b      | c      | d      | e      | Δ    |
|------------|-------|--------|--------|--------|--------|------|
| logP(mm Hg) = f(N) | -1.00039 | 8.76528 | 0.730869 | 0.488793 | 0.486946 | 0.037 |
| K = f(N²) | 12.65372 | -12.8820 | 0.522479 | 0.0457891 | 0.380730 | 0.128 |

**Table II.** Saturated vapor pressures of molten NaCl-AlCl₃-(GaCl₃) mixtures

| Melt | Temperature range, K | logP(mmHg) = A – B / T ± Δ |
|------|----------------------|-----------------------------|
| NE = NAlCl₃ + NGaCl₃ | A | B | Δ |
| Nₐ/NaI | | | | |
| 0.551 | 0 | 424-575 | 5.599±0.037 | 2152±19 | 0.017 |
| 0.550 | 0.1000 | 416-559 | 5.782±0.051 | 2176±25 | 0.021 |
| 0.682 | 0 | 437-538 | 6.737±0.032 | 1896±16 | 0.010 |
| 0.6825 | 0.1017 | 432-529 | 6.792±0.044 | 1910±21 | 0.012 |

360  Electrochemical Society Proceedings Volume 2002-19
Figure 1. Apparatus for sampling vapor from molten NaCl-AlCl$_3$-GaCl$_3$ mixtures. 1, sealed (after loading salts) quartz tube; 2, furnace; 3, molten salt mixture; 4, quartz apparatus; 5, furnace; 6, tube with a condensate of the salts vapor; 7, liquid nitrogen.
Figure 2. NaCl-AlCl₃ phase diagram (10).
Figure 3. Temperature dependence of the relative volatility coefficients (separation factors) of gallium and aluminum trichlorides.

Total mole fraction of trichlorides in molten NaCl-AlCl_{3}-GaCl_{3} mixtures:
1, 0.501; 2, 0.505; 3, 0.515; 4, 0.534; 5, 0.540; 6, 0.572; 7, 0.581;
8, 0.601; 9, 0.615; 10, 0.635; 11, 0.675
for \( \text{Ga}/\text{Na} \): 1, 0.0432; 2, 0.0640; 3, 0.0121; 4, 0.145; 5, 0.155;
6, 0.146; 7, 0.130; 8, 0.158; 9, 0.211; 10, 0.0947; 11, 0.113.
Figure 4. ■, variation in the relative volatility coefficients (separation factors) K of gallium and aluminum trichlorides with their total mole fraction in NaCl-AlCl₃-GaCl₃ melts; ▲, x, variation in the saturated vapor pressure P, on the mole fraction of AlCl₃ in NaCl-AlCl₃ melts at 235°C (x and O, our P-dates, Table II).

Figure 5. Temperature dependence of the overall saturated vapor pressure above NaCl-AlCl₃ melts with NaAlCl₃: 1, 0.551; 2, 0.682 and NaCl-AlCl₃-GaCl₃ with N² = NaAlCl₃+NgGaCl₃: 3, 0.550; 4, 0.6825 and with Ng/NaAl: 3, 0.1000; 4, 0.1017.
Figure 6. Calculated curves of the overall saturated vapor pressure $P$ above NaCl-AlCl$_3$-GaCl$_3$ melts as a function of the total mole fraction of Al and Ga trichlorides at 235°C.

1, $\text{NGaCl}_3 = 0.0196$; 2, $\text{NGaCl}_3 = 0.0500$; 3, $\text{NGaCl}_3 = 0.0630$; 4, $\text{NGaCl}_3 = 0.1071$
♦, experimental results (Table II)