Thermodynamic Properties of Binary Liquid Aluminium Chloride—Alkali Chloride Mixtures

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The EMF of the formation cells

has been measured in the temperature range from 200 to 600°C. M denotes Na, K, Rb, and Cs, respectively, in the present investigation.

For the systems investigated, a model characterized by the two equilibria

seems to be adaptable to the liquid mixture in a narrow concentration region around 50 mol % of aluminium chloride.

Molten mixtures of aluminium chloride and alkali chlorides are of interest both for industrial and for more fundamental research purposes. For some years these mixtures have been considered as potential electrolytes for aluminium deposition,¹⁻⁵ and as solvent electrolyte for the deposition of heavier metals.^{7,8} Recently also a new electrolysis process for the commercial production of aluminium, employing a molten alkali chloride-aluminium chloride electrolyte, has been developed. But no details have as yet been published.

As to the more fundamental aspect of the interest in these liquids they represent an extension of the field of more or less purely ionic molten salts into that of the covalent liquids.

We have for some years studied alkali and light metal reference electrodes and their application in formation cells for the study of properties of molten salt mixtures.^{9,10} The present work adds to the previous ones in its general aim.

Aluminium chloride is mainly a molecular substance in the liquid state. By melting the solid ionic layer structure is expanded by 83 %¹¹ and the liquid is constituted of Al_2Cl_6 species, corresponding to a very low specific conductance of $0.56 \times 10^{-6} \text{ Ohm}^{-1} \text{ cm}^{-1}$ at 190°C¹² and a very high vapour pressure.

By adding chloride ion to liquid aluminium chloride ionic species are formed. There is evidence that the process can be characterized by the two equilibria:

The existence of AlCl_4^- is firmly established, and the ion has been isolated in the solid state as such crystals as NaAlCl_4 ¹³ and $\text{Co}(\text{AlCl}_4)_2$.¹⁴ The Al_2Cl_7^- ion has been detected in liquid $\text{KCl} - \text{AlCl}_3$ mixtures, employing Raman spectroscopy, by Cyvin, Klæboe, Rytter and Øye.¹⁵ They have also studied the relative stability of chloroaluminate complex ions in a varying alkali cation environment.¹⁶ EMF-studies by Tremillon and Létisse¹⁷ also give indication of the presence of Al_2Cl_7^- .

In the present investigation a reversible aluminium electrode was developed, and thermodynamic data for aluminium chloride-alkali chloride mixtures evaluated from EMF measurements of formation cells of the following type:

M being Na, K, Rb, and Cs in the present investigation.

Fig. 1. Galvanic cell assembly. (A) Cl_2 inlet. (B) Cl_2 outlet. (C) Ar inlet. (D) Ar outlet. (1) Pt lead for Cl_2 electrode. (2) Chromel-Alumel thermocouple. (3) Al electrode. (4) Ampoule containing the salt mixture. (5) Rubber stopper. (6) Silica glass vessel. (7) Salt mixture. (8) Salt mixture transferred from (7). (9) Cl_2 graphite electrode. (10) Fritted silica glass diaphragm.

Fig. 2. Liquid 20 mol % Al-Ga electrode. (1) Silica glass tube. (2) Ta lead for Al-Ga electrode. (3) Alloy. (4) Fritted silica glass filter (No. 3).

EXPERIMENTAL

The arrangement of the cell is shown in Fig. 1. A pyrex crucible was used at low temperatures and a crucible of silica glass at the high temperature measurements.

The chlorine electrode consisted of a spectrographic graphite rod suspended in a concentric silica glass tube with a 0.8 mm $\varnothing$ Pt wire lead.

The aluminium electrode employed was a coiled piece of Al wire (1.0 mm $\varnothing$, 99.9 %, Johnson & Matthey) supported in silica glass tubes. For some of the measurements also a liquid Al-Ga electrode, shown in Fig. 2, was used, 99.99 % Ga (Koch-Light Laboratories) was employed.

AlCl_3 was prepared by passing dry HCl over Al metal at 400°C , and the salt mixtures were prepared on a vacuum line and filtered into ampoules, which were sealed off. The sealed ampoule was placed in the cell assembly and opened in an Ar atmosphere. By heating the cell above the melting point the mixture is transferred to the cell, as shown in Fig. 1.

Prior to the EMF measurements the mixture was electrolyzed by Al and graphite electrodes (not shown) for some minutes at lower voltages (1.6–1.8V) than the Al decomposition potential, to remove impurities. This procedure gave a clean transparent melt, and the small amounts of black substance sometimes observed, was easily coagulated around aluminium pieces at the bottom of the cell (not shown in Fig. 1). The black substance either may be finely dispersed metallic aluminium, or possibly elemental silicon that may form in the system.

After pre-electrolysis a new solid Al electrode was introduced into the melt, and the surface oxide was removed by electrolysis. This procedure was found essential to ensure the functioning of the Al electrode.

An ordinary pot furnace with Kanthal resistors was used for heating.

The measurements were carried out both at continuously decreasing and increasing temperatures in the actual temperature range, or at a few constant temperatures. The EMF of the cell and T was recorded simultaneously on a Varian G-2000 potentiometric recorder with suppressed zero point. Temperature was measured by a Chromel-Alumel thermocouple calibrated against AgNO_3 and NaNO_3 . The EMF values recorded were corrected for the thermoelectric EMF which arises in the measuring circuit due to the application of Pt and Al leads to the electrode.

RESULTS

The observed values of EMF *versus* temperature for the systems AlCl_3 – NaCl , AlCl_3 – KCl , AlCl_3 – RbCl , and AlCl_3 – CsCl are shown in Figs. 3, 4, 5, and 6, respectively. The reproduc-

Fig. 3. EMF versus T for the system $\text{AlCl}_3\text{--NaCl}$. Lines are at different N_{NaCl} .

Fig. 4. EMF versus T for the system $\text{AlCl}_3\text{--KCl}$. Lines are at different N_{KCl} .

ibility is better than 5 mV in all experiments. Reversibility is demonstrated by the agreement of the EMF values at increasing temperature with those at decreasing temperature, and the linearity of EMF versus T . The reversibility has also been checked by the application of an

external potential over the cell, the EMF of which was re-established after cutting the potential.

The cell reaction in the present case may be written as:

Fig. 5. EMF versus T for the system $\text{AlCl}_3\text{-RbCl}$. Lines are at different N_{RbCl} .

Fig. 6. EMF versus T for the system $\text{AlCl}_3\text{-CsCl}$. Lines are at different N_{CsCl} .

with a solid Al electrode, or

with a liquid Al-Ga alloy electrode.

The corresponding change in Gibbs' free energy is given by:

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_{\text{Al}_2\text{Cl}_6}}{a_{\text{Al}}^2 P_{\text{Cl}_2}^3} \quad (1)$$

Then, in a reversible electrochemical cell with the cell reaction (III), choosing as the standard states pure, liquid aluminium chloride, pure solid aluminium metal and gaseous chlorine at 1 atm:

$$E = E^\circ - \frac{RT}{6F} \ln a_{\text{Al}_2\text{Cl}_6} \quad (2)$$

where E is the observed EMF of the cell.

An experimental determination of E° by the present formation cell method is impossible, due to the high vapour pressure of AlCl_3 . The value has been calculated from the JANAF data¹⁸ to 1.973 V at 300°C.

The partial molar Gibbs' free energy of formation of Al_2Cl_6 has been calculated from the relation:

$$\Delta \bar{G}_{\text{Al}_2\text{Cl}_6} = -6F(E - E^\circ) \quad (3)$$

Some results are given in Table 1.

At the AlCl_3 -rich side of some of the AlCl_3 -NaCl and AlCl_3 -KCl mixtures, the observed EMF appeared to be slightly lower than the E° value. This seemed to be caused by a breaking of the graphite electrode by swelling, giving rise to depolarization effects. The phenomenon was only apparent at higher AlCl_3 -concentration in the remaining binary mixtures. This phenomenon is not readily explainable. A hypothesis, however, is the formation of a lamellar graphite- AlCl_3 intercalation compound. In the literature such compounds have been reported to form when graphite is exposed to liquid AlCl_3 in the presence of Cl_2 gas,¹⁹ in the temperature range between 180 and 470°C. Tremillon and Létisse¹⁷ recommend the use of a very hard glassy carbon instead of graphite for such electrodes.

Table 1. Experimental EMF and partial molar Gibbs' free energy values. E° (300°C) = 1.973 V and E° (450°C) = 1.890 V, calculated from JANAF data.¹⁸ The precision in the Gibbs' free energy values (kcal/mol) has been evaluated to ± 0.25 kcal/mol from the experimental data.

N_{AlCl_3}	E	$E - E^\circ$	$\Delta G_{\text{Al}_2\text{Cl}_6}$
AlCl_3 - NaCl at 300°C or 450°C			
0.475	2.064*	0.174	-24.1
0.488	2.058*	0.168	-23.2
sat.	2.129	0.156	-21.6
0.500	2.065	0.092	-12.7
AlCl_3 - KCl at 300°C or 450°C			
0.450	2.167*	0.277	-38.3
0.476	2.163*	0.273	-37.8
0.500	2.185	0.212	-29.3
0.501	2.075	0.102	-14.1
AlCl_3 - RbCl at 450°C			
0.476	2.176	0.286	-39.5
0.500	2.094	0.204	-28.2
0.526	2.004	0.104	-14.4
0.550	1.959	0.069	-9.55
AlCl_3 - CsCl at 450°C			
0.301	2.270	0.380	-52.6
0.401	2.246	0.356	-49.3
0.448	2.221	0.331	-45.8
0.476	2.191	0.301	-41.7
0.500	2.152	0.262	-36.3
0.525	2.022	0.132	-18.3
0.552	1.983	0.093	-12.9

* at 450°C.

DISCUSSION

The results obtained at the saturation point of NaCl in NaCl- AlCl_3 is in good agreement with results by Tremillon and Létisse.¹⁷ Other EMF data from formation cell studies of the present system do not seem to have entered chemical literature.

The vapour pressure of liquid mixtures containing aluminium chloride has been measured by several investigators. Thus Dewing²⁰ and Rao²¹ have studied the AlCl_3 -NaCl and AlCl_3 -RbCl systems, respectively. It is generally recognized that the vapour on the AlCl_3 -rich side probably only consists of Al_2Cl_6 molecules, and the activity of Al_2Cl_6 in the melt, therefore,

Fig. 7. Partial molar Gibbs' free energy of Al_2Cl_6 . Full drawn curves: This investigation; filled circles, AlCl_3 -NaCl at 300°C or 450°C; double open circles, AlCl_3 -saturated NaCl at 300°C; filled triangles, AlCl_3 -KCl at 300°C or 450°C; filled squares, AlCl_3 -RbCl at 450°C; open triangles, AlCl_3 -CsCl at 450°C. Open circles: From vapour pressure measurement by Dewing²⁰ AlCl_3 -NaCl, Half filled circle: From vapour pressure measurement by Rao²¹ AlCl_3 -NaCl at 300°C. Half filled squares, from vapor pressure measurement by Rao AlCl_3 -RbCl at 450°C; Dotted curves, calculated from complex molecular model; (a) $K_1 = 3 \times 10^8$, $K_2 = 3 \times 10^5$, (b) $K_1 = 3 \times 10^8$, $K_2 = 3 \times 10^5$, (c) $K_1 = 3 \times 10^7$, $K_2 = 3 \times 10^5$, (d) $K_1 = 3 \times 10^6$, $K_2 = 3 \times 10^5$, (e) Ideal mixture of Al_2Cl_6 - MAlCl_4 , (f) Ideal mixture of Al_2Cl_6 -MCl.

may be calculated from the ratio of the total vapour pressure of the mixture to that of pure aluminium chloride. The values calculated from the cited vapour pressure data connect smoothly to those of the present investigation, as shown in Fig. 7.

In the AlCl_3 -NaCl and AlCl_3 -KCl phase diagrams, the liquidus rises steeply around the composition $N_{\text{AlCl}_3} = 0.5$. Consequently, a study of thermodynamic properties at the same temperature for both sides of the equimolar composition is difficult. The calculation was, therefore, carried out at 300°C and 450°C, in the aluminium chloride rich region and on the

alkali chloride side, respectively. For the mixture AlCl_3 -RbCl and AlCl_3 -CsCl, however, values are presented at 450°C for the whole concentration range.

Adding chloride ions to aluminium chloride may be considered as a stepwise titration, involving the two previously mentioned equilibria I and II.

Considerable amounts of Al_2Cl_7^- are formed in the concentration range $0.33 < N_{\text{AlCl}_3} < 0.50$. When N_{AlCl_3} exceeds 0.5, AlCl_4^- will tend to be the dominating complex anion species. The corresponding equilibrium quotients are:

$$K_1 = N_{\text{Al}_2\text{Cl}_7^-} / N_{\text{Cl}^-} N_{\text{Al}_2\text{Cl}_6} \quad (4)$$

$$K_2 = N^2_{\text{AlCl}_4^-} / N_{\text{Cl}^-} N_{\text{Al}_2\text{Cl}_6} \quad (5)$$

The quotients K_1 and K_2 are probably not true constants, as shown previously for the corresponding MgCl_2 -Alk. Cl systems.¹⁰

Øye and Gruen²² introduced the mol fraction of each species as the activity and compared the activity of Al_2Cl_6 with that obtained from the vapour pressure data of Dewing²⁰ on the assumption that the mol fraction of chloride ion is negligibly small at higher aluminium chloride concentrations. This assumption definitely is valid at $N_{\text{AlCl}_3} > 0.5$. The applicability of this model will be tested in the following.

Consider a mixture of $2N$ mol of aluminium chloride corresponding to N mol of Al_2Cl_6 , and $1 - N$ mol of alkali chloride. Then:

$$1 - N = n_{\text{Cl}^-} + n_{\text{Al}_2\text{Cl}_7^-} + n_{\text{AlCl}_4^-} \quad (6)$$

$$N = 2n_{\text{Al}_2\text{Cl}_6} + 2n_{\text{Al}_2\text{Cl}_7^-} + n_{\text{AlCl}_4^-} \quad (7)$$

n denotes the molar amounts of the constituent species. By combining (4), (5), (6), and (7) the following relation between the weighed-in mol fraction N and the activity x (taken as the mol fraction of Al_2Cl_6) is obtained:

$$N = \frac{4Ax + (1-x)(A-1/K_1x)}{A(1+3x) + (1-x)(A-1+K_1x)} \quad (8)$$

$$\text{Here } A = 1 + K_1x + (K_1K_2x)^{\frac{1}{2}} \quad (9)$$

Some solutions of this equation are shown in Fig. 7 for a few combinations of the equilibrium quotients K_1 and K_2 . This model seems to fit the observed values rather well around $N_{\text{AlCl}_3} = 0.5$.

The equilibrium quotient, K_2 , for the reaction:

has been taken as constant, $K_2 = 3 \times 10^5$, which can be taken as true over a narrow concentration range. This value, combined with $K_1 = 3 \times 10^9$ seems to fit the AlCl_3 – CsCl data rather well. The corresponding value given by Tremillon *et al.* amounts to $K_2 = 2.9 \times 10^5$.

It is seen from Fig. 7 that this model demands the value of K_1 to decrease when going from the CsCl – AlCl_3 to the NaCl – AlCl_3 . The system KCl – AlCl_3 seems to be rationalized fairly well with the combination $K_1 = 3 \times 10^7$, $K_2 = 3 \times 10^5$.

Øye *et al.*²³ have evaluated the dissociation equilibrium constant for the reaction

from spectroscopic data on molten KCl – AlCl_3 mixtures, and arrived at value $K_V = (4 \pm 2) \times 10^{-3}$ in the temperature range 170–240°C. In the present work $K_V = K_2/K_1$, which for the same system at 300°C should amount to $K_V = 3 \times 10^5/3 \times 10^7 = 10^{-2}$. This seems to be in fair agreement with the value given by Øye *et al.*

The precision of the present data, and the tabulated JANAF data on the standard Gibbs' free energy of formation as well, does not permit sufficiently precise entropy values to be calculated from the slope of the EMF *versus* T curve.

An estimate from the present data gives values around –20 e.u., being somewhat lower for the NaCl – AlCl_3 than for the CsCl – AlCl_3 system.

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