THERMODYNAMICS OF THE FORMATION OF GALLIUM CHLORIDES IN LiCl-KCl-CsCl EUTECTIC MELT

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ABSTRACT

The equilibrium between metallic gallium and its chlorides in the eutectic LiCl-KCl-CsCl, (57.5 : 16.5 : 26.0) at 300-400°C in an inert gas atmosphere was studied by measuring its EMF at various concentrations. It is shown that upon anodic dissolution of gallium into the melt the formation of a mixture of its ions of oxidation state +1 and +3 takes place. The temperature dependence of the standard potentials of metallic gallium for mono and trivalent ions in this melt, and the formal redox potential of such melts are obtained. The equilibrium reduction constant by metal gallium of its trichloride down to its monochloride is established. The thermodynamics of the formation of gallium chlorides and their decomposition potentials in this melt system are calculated.

INTRODUCTION

In the literature there are data on the behavior of gallium and its ions in various solvents. McMullen and Corbett (1) determined from Raman-spectra that Ga_2Cl_4 dissolves in benzene to form the ionic species Ga^+ and (GaCl)^-. Carpenter and Verbrugge (2) established by voltammetric methods that both Ga and GaAs deposit on the cathode from solutions based on 1-methyl-3-ethylimidazolium chloride upon reduction of Ga ions, having oxidation state +3. Other workers (3, 4, 5, 6) used EMF measurements to obtain the conventional standard potentials of Ga in the LiCl-KCl eutectic melt. Laitinen and Liu (3) and Shafir and Plambeck (4) determined E*(Ga^{3+}/Ga) at 450°C. Yacenko et al (5, 6) reported the coexistance in such melts of Ga ions with oxidation states +1 and +3 and calculated the thermodynamics of formation of the corresponding Ga chlorides. Anders and Plambeck (7) similarly pointed out the existence of both Ga ions in a AlCl_3-NaCl-KCl melt. The published data (3-6) on the value of E*(Ga^{3+}/Ga) at 450°C range from -1.096 to -1.443V.

The purpose of the present work was to determine the thermodynamics of gallium chloride formation in the LiCl-KCl-CsCl eutectic.
EXPERIMENTAL

The equilibrium between gallium metal and its chlorides in the molten eutectic mixture LiCl-KCl-CsCl, (57.5 : 16.5 : 26.0) at 300-400°C was studied using EMF measurements in an inert gas atmosphere. Ga was added into the melt by anodic dissolution. The reagents were purified specifically to be free from moisture and oxygen-containing impurities. A diagram of an experimental cell used is shown in Figure 1. Before making measurements the gas space of the cell was first purified by zirconium getter at 750°C, after which the getter was raised into a cold zone of cell and a melt was cooled down to a desired temperature.

The cell investigated can be represented as follows:

$$\text{Ga} \mid \text{LiCl - KCl - CsCl - GaCl}_2 \mid \text{LiCl - KCl - CsCl, Cl}_2 (g) \mid \text{C}$$  \[1\]

where \(z\) is the average oxidation state of the ions. The techniques for calculating the ionic composition of a melt in equilibrium with metal, developed in Professor Smirnov's publications over thirty years ago (8, 9), have been employed here.

The above techniques are applicable in the situation when reliable data on the total concentration of metal ions in melt is not available. In this case, it is calculated using Faraday's law by a successive approximation method (9).

Knowledge of the conditional standard potentials \(E^*(\text{Me}^{m+})/\text{Me}\) and \(E^*(\text{Me}^{n+})/\text{Me}\) enables the calculation of the conventional standard redox potential \(E^*(\text{Me}^{m+}/\text{Me}^{m-+})\), the decomposition voltage of diluted solutions of chlorides and \(\Delta G^*\) of gallium chloride formation.

RESULTS AND DISCUSSION

The results are presented in Figure 2. The values of \(E^*(\text{Me}^{m+})/\text{Me}\) and \(E^*(\text{Me}^{n+})/\text{Me}\), obtained (under calculation under each isotherm), were averaged. These averaged \(E^*\) values were improved using the linearity of dependence \(E^* = f (T)\) over a wide range of temperatures (9). The improved \(E^*\) values were used for the calculation of the disproportionation reaction constant.

The dependence of calculated values of \(z\) on total Ga concentration is shown in Figure 3. Ga ions have two oxidation states, +1 and +3. Here it can be seen that the monochloride fraction increases regularly with increasing of temperature and decreasing of concentration of the dissolved metal. The average oxidation state of Ga ions thus has an inverse temperature and concentration relationship. The similar legitimacies in aquimolarity a melt NaCl-KCl are obtained P.M. Usov, et al. (6). The temperature dependencies of the main thermodynamic values obtained are presented in Table I.
Table I. Temperature dependencies of the main thermodynamic values for 57.5 LiCl – 16.5 KCl – 26.0 CsCl at 573-673 K

| Temperature dependence | Units       |
|------------------------|-------------|
| $E^{\circ}_{Ga^{+}/Ga}$ = (-2.165 + 1.5 x $10^{-3}$T) ± 0.001 | V           |
| $E^{\circ}_{Ga^{3+}/Ga}$ = (-2.211+1.1 x $10^{-3}$T) ± 0.002 | V           |
| $E^{\circ}_{Ga^{3+}/Ga^{+}}$ = (-2.234+0.9 x $10^{-3}$T) ± 0.004 | V           |
| $\log K_{p}^{*} = -4.98 – 703/T$ ± 0.1 {Ga$^{3+}$(sol.)+2Ga $\leftrightarrow$ 3 Ga(sol.)} | -           |
| $\Delta G^{*}_{GaCl} = -208.86 + 144.32 x 10^{-3} x T$ ± 0.1 | KJ/mol     |
| $\Delta G^{*}_{GaCl_{3}} = -640.03 + 327.09 x 10^{-3} x T$ ± 0.6 | KJ/mol     |
| $E_{\text{destroy of GaCl}} = 2.165 - 1.5 x 10^{-3} x T$ ± 0.001 | V           |
| $E_{\text{destroy of GaCl}_{3}} = 2.211 - 1.1 x 10^{-3} x T$ ± 0.002 | V           |

Comparison of $\Delta G^{*}$ values for the reaction of gallium mono- and trichloride with standard values of $\Delta G^{0}$ for pure its liquid chlorides calculated from tabulated data (6,10):

$$\Delta G^{0}_{GaCl} = (- 153.82 + 68.1 x 10^{-3} x T), \text{KJ/mol}$$ [2]

$$\Delta G^{0}_{GaCl_{3}} = (-506.34 +162.7 x 10^{-3} x T), \text{KJ/mol}$$ [3]

reveals that the solutions of gallium chlorides do not behave ideally, and that the interaction of components takes place.

CONCLUSION

It has been established that gallium in the molten chloride eutectic LiCl-KCl-CsCl consists of a mixture of ions in both oxidation state +1 and +3. The fraction of the trichloride is reduced upon increasing temperature and decreasing of gallium concentration in the melt. The temperature dependence of conventional standard potentials have also been obtained. The equilibrium reaction constants for the reduction of the trichloride by metal to the monochloride have been calculated. The thermodynamics of gallium chlorides formation and their potentials as a function of temperature in melts are also reported.
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Figure 1. Diagram of experimental cell. 1, rubber stoppers; 2, chlorine electrode; 3, cover from SiO2; 4, Pt-Pt/Rh thermocouple; 5, microsection; 6, test tube from SiO2; 7, suspension from Mo; 8, BeO crucible; 9, BeO tube; 10, SiO2 crucible; 11, Ga metal; 12, current lead from Mo; 13, explored melt; 14 – melt bath; 15, SiO2 crucible.
Figure 2. Equilibrium potentials of gallium for LiCl-KCl-CsCl eutectic melt. Quantity of electric spent on anodic dissolution of Ga referred to unit mass of a solvent: 1, 4.8 x 10³ C/kg; 2, 3.6 x 10³ C/kg; 3, 2.4 x 10³ C/kg.

Figure 3. Average oxidation state of gallium ions in LiCl-KCl-CsCl eutectic melt. Temperature: 1- 573 K; 2 - 623 K; 3 - 673 K; 4 - 723 K; 5 - 773 K