EVALUATION OF THERMODYNAMIC DATA FOR ALUMINUM CHLORIDE HEXAHYDRATE AND ITS DEHYDRATION

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ABSTRACT

Thermodynamic data for aluminum chloride hexahydrate was evaluated from existing low temperature data and extrapolated for use at higher temperatures. Free energy minimization calculations were then used to study possible chemical systems for dehydration of aluminum chloride hexahydrate in attempts to find an efficient method for making electrochemical grade anhydrous aluminum chloride.

INTRODUCTION

Clay is the most abundant domestic resource of aluminum. The kaolin variety of clay is largely composed of aluminum silicates. Chloride leaching of clay is one of the techniques used for the production of aluminum chloride hexahydrate ACH. Methods for dehydration of ACH are of considerable interest because anhydrous aluminum chloride can be used directly to produce aluminum metal by electrowinning in a molten salt system. This approach utilizes lower temperatures than those required for the conventional Hall–Heroult cell. Furthermore, this molten salt technique is less corrosive than the cryolite bath used in electrowinning aluminum from alumina.

Free energy minimization FEM is a powerful technique for evaluation of equilibrium compositions of multicomponent systems [1,2]. The technique has found increasing applications in chemical processing industries for predicting the distributions of the products expected at thermodynamic equilibrium. The accuracy of an FEM calculation depends on the accessibility of thermodynamic data for all the relevant species existing in a system. Prediction of potential chemical dehydration processes for ACH using thermodynamic calculations are difficult to perform due to the lack of thermodynamic data for this compound above room temperature. This paper describes our approach for the evaluation of thermodynamic data for ACH from existing low temperature data and the results of our calculations for the dehydration of ACH in several systems using the FEM technique.

EVALUATION OF THERMODYNAMIC DATA OF ACH

Stull et al. reported low temperature heat capacities, entropies, and enthalpy functions for ACH from 16 to 298.15 K [3]. Based on these data, the free energy functions $(\bar{G}^{\ominus} - \bar{H}_{298}^{\ominus})/T$ of ACH were calculated. At temperatures above 100 K, there appears to be a linear relationship between the calculated free energy functions and temperature, as shown in Fig. 1. A correlation coefficient of 0.9993 and a slope of 0.1389 Gibbs mol^{-1} per degree was obtained from a least-squares linear regression analysis of the data from 100 to 298.15 K. Based on this analysis, it appears that the free energy functions of ACH above room temperature can be estimated by a linear extrapolation of the data shown in Fig. 1. The estimated free energy functions for ACH from 100 to 1000 K at 100 degree intervals are given in Table 1. These extrapolated data should be fairly reliable especially at temperatures not far above 298.15 K.

The standard heats of formation $(\Delta \bar{H}_{f,298}^{\ominus})$ and Gibbs free energies of formation $(\Delta \bar{G}_{f,298}^{\ominus})$ of ACH, AlCl$_3$(s), and H$_2$O(g) at 298.15 K are known [4,5]. The free energy functions of AlCl$_3$(s) and H$_2$O(g) are given in the JANAF Thermochemical Tables [5]. From these known data and the free energy functions of ACH estimated in Table 1, the Gibbs free energy change $(\Delta G^{\ominus})$ was calculated for the reaction

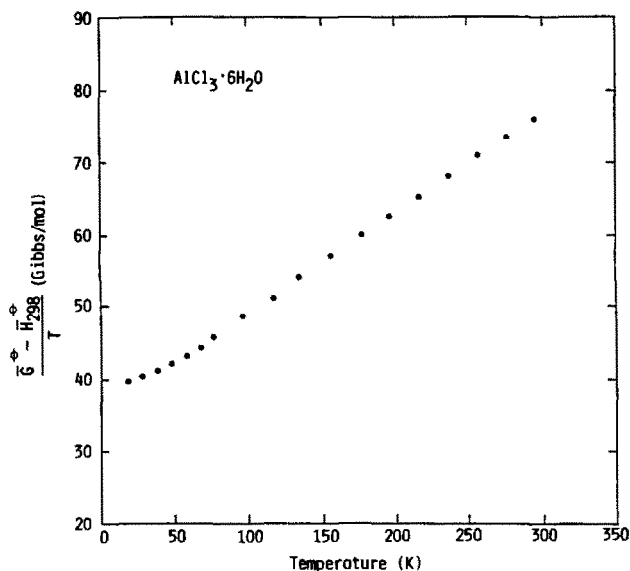$$AlCl_3 \cdot 6H_2O(s) \rightarrow AlCl_3(s) + 6H_2O \tag{1}$$

Fig. 1. Variation of the free energy function with respect to temperature for aluminum chloride hexahydrate from 16 to 298.15 K.

TABLE 1

Estimated Gibbs free energy functions and standard Gibbs free energies of formation of aluminum chloride hexahydrate, $AlCl_3 \cdot 6H_2O$, from 100 to 1000 K

T (K)	$(\bar{G}^{\ominus} - \bar{H}_{298}^{\ominus})/T$ $(J\ mol^{-1}\ K^{-1})$	$\Delta \bar{G}_f^{\ominus}$ $(kJ\ mol^{-1})$
100	-203.2	-2507
200	-262.3	-2386
298.15	-318.1	-2262
300	-319.2	-2259
400	-378.1	-2133
500	-436.2	-2010
600	-494.4	-1891
700	-552.5	-1778
800	-610.6	-1672
900	-668.7	-1572
1000	-726.8	-1479

From the known Gibbs free energies of formation of $AlCl_3(s)$ and $H_2O(g)$, we also calculated the standard Gibbs free energy of formation of ACH from 100 to 1000 K (Table 1). The thermodynamic data were then fitted into temperature dependent polynomial equations and stored in a data bank compatible with the free energy minimization program written by Gordon and McBride [6]. In addition to ACH, the data bank contains all the chemical species relevant to this calculation listed in the JANAF Thermochemical Tables and Supplements [5].

FEM CALCULATIONS FOR THE DEHYDRATION OF ACH

Using the estimated Gibbs free energy of ACH, our calculations indicate that the predominant products resulting from the direct heating of ACH are $Al_2O_3(s)$, $HCl(g)$, and $H_2O(g)$. The decomposition temperature depends on the partial pressures of the products. At a total partial pressure of 0.1 atm for the gaseous products, the decomposition temperature of ACH was found to be 389 K. If the pressure of the gaseous products is kept at 1 atm, the decomposition temperature of ACH is raised to 448 K.

The difficulty in the dehydration of ACH by direct heating is primarily related to the structure of this compound. Aluminum chloride hexahydrate has a complex rhombohedral structure in which each water molecule is adjacent to two chloride ions [7]. The oxygen atom is at the center of an irregular tetrahedron with two hydrogen atoms and two chloride ions at the four corners. Probably the most important feature of the ACH structure is that the water molecules lie between the Al(III) ion and the chloride ions. This structural feature is largely responsible for the impossibility of dehy-

drating the compound by direct heating which leads to the preferential evolution of hydrogen chloride molecules and eventually to the formation of alumina. There are, however, reports in the literature indicating that chemical dehydration of ACH is feasible [8,9]. For example, aluminum chloride is reported to have been prepared by spreading ACH on the hearth of a furnace made of suitable refractories and heated by a burning mixture of hydrogen and chlorine [8]. Phosgene or a mixture of carbon monoxide and chlorine gases were also reported to cause dehydration of ACH [9].

CHEMICAL DEHYDRATION OF ACH

A number of compounds were considered in this thermodynamic study of the chemical dehydration of ACH. These compounds were initially chosen because of their reactive nature toward water. Simple thermochemical calculations were carried out to evaluate the Gibbs free energy changes ($\Delta G^{\ominus}$) of the possible dehydration reactions at room temperature. These potential dehydration reactions and their free energy changes are given in Table 2. Most of the listed reactions have negative $\Delta G^{\ominus}$ values at 298.15 K indicating that the reactions are thermodynamically favored as written. A few reactions with small positive $\Delta G^{\ominus}$ values were also considered.

It should be pointed out that although a reaction may have a negative $\Delta G^{\ominus}$ value, it does not necessarily mean that this is the only reaction channel that can occur. In reality, other reactions between the reactants and the products may also occur leading to a variety of products at final equilibrium. In free energy minimization calculations, all possible combinations of reaction products, which are contained in the data bank, are considered. The final equilibrium composition of the system is the composition which gives the minimum Gibbs free energy.

TABLE 2

Potential aluminum chloride hexahydrate dehydration reactions

	$\Delta G^{\ominus}_{298.15}$ (kJ)
(1) $AlCl_3 \cdot 6H_2O + 6COCl_2 \rightarrow AlCl_3 + 6CO_2 + 12HCl$	-650.1
(2) $AlCl_3 \cdot 6H_2O + 6CO + 6Cl_2 \rightarrow AlCl_3 + 6CO_2 + 12HCl$	-1054.5
(3) $AlCl_3 \cdot 6H_2O + 6SOCl_2 \rightarrow AlCl_3 + 6SO_2 + 12HCl$	-122.7
(4) $AlCl_3 \cdot 6H_2O + 6S_2Cl_2 + 9O_2 \rightarrow AlCl_3 + 12SO_2 + 12HCl$	-2922.9
(5) $AlCl_3 \cdot 6H_2O + 6COS \rightarrow AlCl_3 + 6CO_2 + 6H_2S$	80.8
(6) $AlCl_3 \cdot 6H_2O + 6SO_2Cl_2 \rightarrow AlCl_3 + 6SO_3 + 12HCl$	182.3
(7) $AlCl_3 \cdot 6H_2O + 4PCl_3 + 2O_2 \rightarrow AlCl_3 + P_4O_{10} + 12HCl$	-1137.8
(8) $AlCl_3 \cdot 6H_2O + 2.4PCl_5 \rightarrow AlCl_3 + 0.6P_4O_{10} + 12HCl$	-397.9
(9) $AlCl_3 \cdot 6H_2O + 4POCl_3 \rightarrow AlCl_3 + P_4O_{10} + 12HCl$	-157.3
(10) $AlCl_3 \cdot 6H_2O + 12NOCl \rightarrow AlCl_3 + 6N_2O_3 + 12HCl$	532.5

The results of our FEM calculations for the systems listed in Table 2 over the temperature range 300–500 K are separately described in the following sections.

The ACH + 6COCl$_2$ system

According to our FEM calculations, phosgene ($COCl_2$) appears to be an effective dehydration agent for ACH. Our calculations indicate that the condensation temperature of $AlCl_3$(s) is 404 K. The predominant products over the temperature range 300–404 K are $AlCl_3$(s), CO_2(g), and HCl(g) indicating that the main reaction channel in this system is the dehydration of ACH as shown in eqn. (1) of Table 2. Al_2Cl_6(g) is not present in significant amounts at low temperatures (mole fraction approximately 2×10^{-7} at 300 K) but becomes increasingly important as the temperature is raised (mole fraction approximately 2.5×10^{-2} at 404 K). Alumina is present in trace amounts (mole fraction $< 10^{-7}$) in this temperature range and is always present as a contaminant. At 405 K, Al_2Cl_6 becomes the predominant aluminum-containing species in the system.

The ACH + 6CO + 6Cl$_2$ system

When carbon monoxide and chlorine gas are used in the same elemental ratios as in the phosgene case, the results of FEM calculations are essentially identical. In both cases, the reactants $COCl_2$ or CO and Cl_2 react to form the same products. The distribution of the products which gives the minimum free energy of the system is expected to be the same.

The ACH + 6SO + 6Cl$_2$ system

Thionyl chloride, $SOCl_2$, is a strong dehydration agent frequently used in certain inorganic reactions. However, thermodynamic data for this compound are not available in the JANAF Tables. Therefore, SO and Cl_2 were used to test whether or not the expected dehydration would take place. Condensation of $AlCl_3$(s) takes place at 404 K. Over the temperature range 300–404 K, the major products observed in this system are $AlCl_3$(s), HCl(g), and SO_2(g) as indicated in eqn. (3) in Table 2. As in the phosgene case, the dimer Al_2Cl_6(g) becomes increasingly important as the temperature is raised above 300 K and becomes the predominant aluminum-containing species at approximately 400 K due to the vaporization of $AlCl_3$(s). In addition, Al_2O_3(s) is also present in the system with mole fractions less than 10^{-3}. Small amounts (mole fractions between 10^{-3} and 10^{-7}) of $AlCl_3$(g), Cl_2(g), SCl_2(g), SO_2Cl_2(g), and S_2Cl_2(g) are also found in this system.

The ACH + 6S$_2$Cl$_2$ + 9O$_2$ system

Dichlorodisulfane, S$_2$Cl$_2$, can also cause dehydration of ACH in the presence of oxygen, according to our FEM calculations. In this system, condensation of AlCl$_3$(s) occurs at 401 K. As before, Al$_2$O$_3$(s) is present over the entire temperature range with mole fractions of less than 10^{-3}. The reaction proceeds as predicted in eqn. (4) of Table 2 to form primarily AlCl$_3$(s), SO$_2$(g), and HCl(g). A small fraction of unreacted S$_2$Cl$_2$ is always present in the system.

The ACH + 6COS system

Apparently, dehydration of ACH would not occur in this system. At 300 K, ACH remains essentially unreacted in the presence of carbonyl sulfide, COS. The condensation temperature of ACH is 383 K and Al$_2$O$_3$(s), C(s), CO$_2$(g), COS(g), HCl(g), H$_2$S(g), and S(s and l) are all important products observed in this system.

The ACH + 6SO$_2$Cl$_2$ system

According to the results of our study, sulfuryl chloride, SO$_2$Cl$_2$, reacts with ACH to form Al$_2$O$_3$(s). Other major products observed in the system include Cl$_2$(g), HCl(g), H$_2$SO$_4$(l and g), SO$_2$(g), and SO$_2$Cl$_2$(g).

The ACH + 4PCl$_3$ + 2O$_2$ system, the ACH + 2.4PCl$_5$ system, and the ACH + 4POCl$_3$ system

None of the phosphorus compounds appear useful for the dehydration of aluminum chloride hexahydrate. Phosphoryl chloride, POCl$_3$, phosphorus trichloride, PCl$_3$, and phosphorus pentachloride, PCl$_5$, all convert ACH into Al$_2$O$_3$. Other major products which appear in all the systems are HCl(g), POCl$_3$(g), and P$_4$O$_{10}$(g). P$_4$O$_{10}$ is not an important species at low temperatures, but its mole fraction increases as the temperature increases. Over the temperature range 300–500 K, however, its mole fraction is never greater than the mole fraction of POCl$_3$. Apparently, AlCl$_3$ and P$_4$O$_{10}$ are less stable than Al$_2$O$_3$ and POCl$_3$ in the mixture and hence the latter combination prevails at equilibrium.

The ACH + 12NOCl system

According to our calculation, dehydration of ACH would not occur in this system. In this system, the condensation temperature of ACH is 381 K and the major products are Al$_2$O$_3$(s), Cl$_2$(g), HCl(g), H$_2$O(g), N$_2$(g), and O$_2$(g).

CONCLUSION

The Gibbs free energy functions $(\overline{G}^{\ominus} - \overline{H}_{298}^{\ominus})/T$ of ACH vary linearly with respect to temperature from 100 to 298.15 K. This relationship provides a basis for extrapolation to obtain data at higher temperatures (from 298.15 to 1000 K). The Gibbs free energies of formation $(\Delta \overline{G}_f^{\ominus})$ of ACH in this temperature range were also calculated. FEM calculations based on the extrapolated data showed that direct heating of ACH would result in the formation of Al_2O_3, HCl, and H_2O. Chemical dehydration of ACH is feasible in the presence of $COCl_2$, $SOCl_2$, and $S_2Cl_2 + O_2$.

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