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Solubility and Activity of Aluminum Chloride in Aqueous Hydrochloric Acid Solutions

By R. R. Brown, G. E. Daut, R. V. Mrazek,
and N. A. Gokcen

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SOLUBILITY AND ACTIVITY OF ALUMINUM CHLORIDE IN AQUEOUS HYDROCHLORIC ACID SOLUTIONS

by

R. R. Brown,[1] G. E. Daut,[2] R. V. Mrazek,[3] and N. A. Gokcen[4]

ABSTRACT

The solubility and the activity of aluminum chloride hexahydrate, $AlCl_3 \cdot 6H_2O$, in aqueous solutions were determined as a part of the Bureau of Mines, U.S. Department of the Interior, research to improve mineral processing technology for recovering alumina from low-grade domestic resources. The solubility of $AlCl_3$ in pure water was found to be 31.09 and 31.77 wt-pct at 25° and 85° C, respectively, and decreased drastically to 10 and 0.1 wt-pct when the respective amounts of 20.3 and 37 wt-pct hydrochloric acid (HCl) were added in solution. The equilibrium constant for the solubility of hexahydrate, activities, and activity coefficients of $AlCl_3$ and H_2O were calculated and compared with the results from the available methods of estimation. The results were shown to be useful in leaching nonbauxitic ores for extraction of alumina by changing the solubilities of component salts upon addition of HCl.

Simultaneous solubilities of $AlCl_3$, $FeCl_3$, KCl, and NaCl in solutions of HCl-H_2O were also determined and their effects on the purity of $AlCl_3 \cdot 6H_2O$ crystallized from mixed salt solutions are briefly discussed.

INTRODUCTION

The Bureau of Mines, U.S. Department of the Interior, is currently conducting an extensive research program to improve processing technology for extracting alumina from nonbauxitic, domestic resources. The success of this program will provide the technology necessary for producing an adequate supply of high-grade alumina from domestic sources, thus meeting national economic and strategic needs relative to aluminum production.

The hydrochloric acid process for recovering alumina from low-grade ores is one of the processes being investigated in the Bureau research program.

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One phase of this process uses the effect of chloride-ion concentration on the solubility of aluminum ion in solution. At 25° C, the solubility of $AlCl_3$ in pure water is approximately 31 pct by weight, and decreases with increasing concentration of hydrochloric acid (HCl), becoming 0.1 pct when the HCl concentration is increased to 37 pct. This behavior has been the subject of numerous investigations, processes, and patents (1, 7-9, 13-16, 18).[5] Thus it is possible to leach a nonbauxitic ore with HCl, decant and filter the liquor, and add gaseous HCl to precipitate out $AlCl_3 \cdot 6H_2O$. The remaining acid solution can then be used for leaching additional ore and the precipitated $AlCl_3 \cdot 6H_2O$ can be calcined to obtain Al_2O_3. An extensive discussion and evaluation of this process is presented by Peters, Johnson, and Kirby (16). Thermodynamic data, such as the ionic activities and the solubilities, required for complete analysis, interpretation, and improvement of this process are scarce, and the existing solubility data (12) are limited to a narrow range of temperature. Therefore, the aims of this investigation were (1) to determine the solubility of $AlCl_3$ in a temperature range of 25° to 85° C with HCl concentration from 0.0 to 37.2 pct; (2) to calculate the activities of $AlCl_3$ and of H_2O in solutions containing various electrolytes, and the equilibrium constant for the dissolution of $AlCl_3 \cdot 6H_2O$; and (3) to suggest areas of research for generating useful data.

APPARATUS

The apparatus used for measurements of solubilities is shown in figure 1. A 100-ml flask, A, contains a solution of electrolytes and some excess salt. A fritted glass filter, B, fused on a 6-mm-OD Pyrex[6] tube is joined to an outer tube attached to two Teflon stopcocks, D and E. The top assembly is attached to A at C by a threaded nylon compression fitting with a neoprene O-ring. A 6-mm-OD polyethylene tube, F-L, delivers a sample of solution filtered at B into the second flask, K, when A is pressurized through stopcock D, and E is opened. The fitting at J is similar to that at C. The flasks are clamped on a bar, G, which is attached to a rocking mechanism, with H as the axis of rocking for shaking the flasks, A and K, alternately up and down. A covered thermostat, O, is controlled to within ±0.2° C. A closer temperature control is unnecessary since the solubility is a very weak function of temperature.

EXPERIMENTAL PROCEDURE

Measurements of solubilities at 25°, 45°, 65°, and 85° C were made under conditions of phase equilibrium with analytical reagent-grade materials. Appropriate amounts of $AlCl_3 \cdot 6H_2O$, 37-pct HCl solution, and distilled water were placed in flask A to form approximately 90 ml of solution with a small amount of excess salt crystals (hereafter "salt" refers to aluminum chloride hexahydrate). The amounts of materials were estimated from the existing solubility data (12) on the ternary system $AlCl_3 \cdot 6H_2O$-HCl-H_2O. After the solution was formed in flask A and the apparatus was assembled, it was immersed in the water to level N, and the thermostat was set to the desired temperature. A continuous mechanical agitation of the flasks was used during each run lasting 2 to 3 days. Periodically, vigorous manual agitation was also used to assure

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[5] Underlined numbers in parentheses refer to items in the list of references at the end of this report.

[6] Reference to specific trade names is made for identification only and does not imply endorsement by the Bureau of Mines.

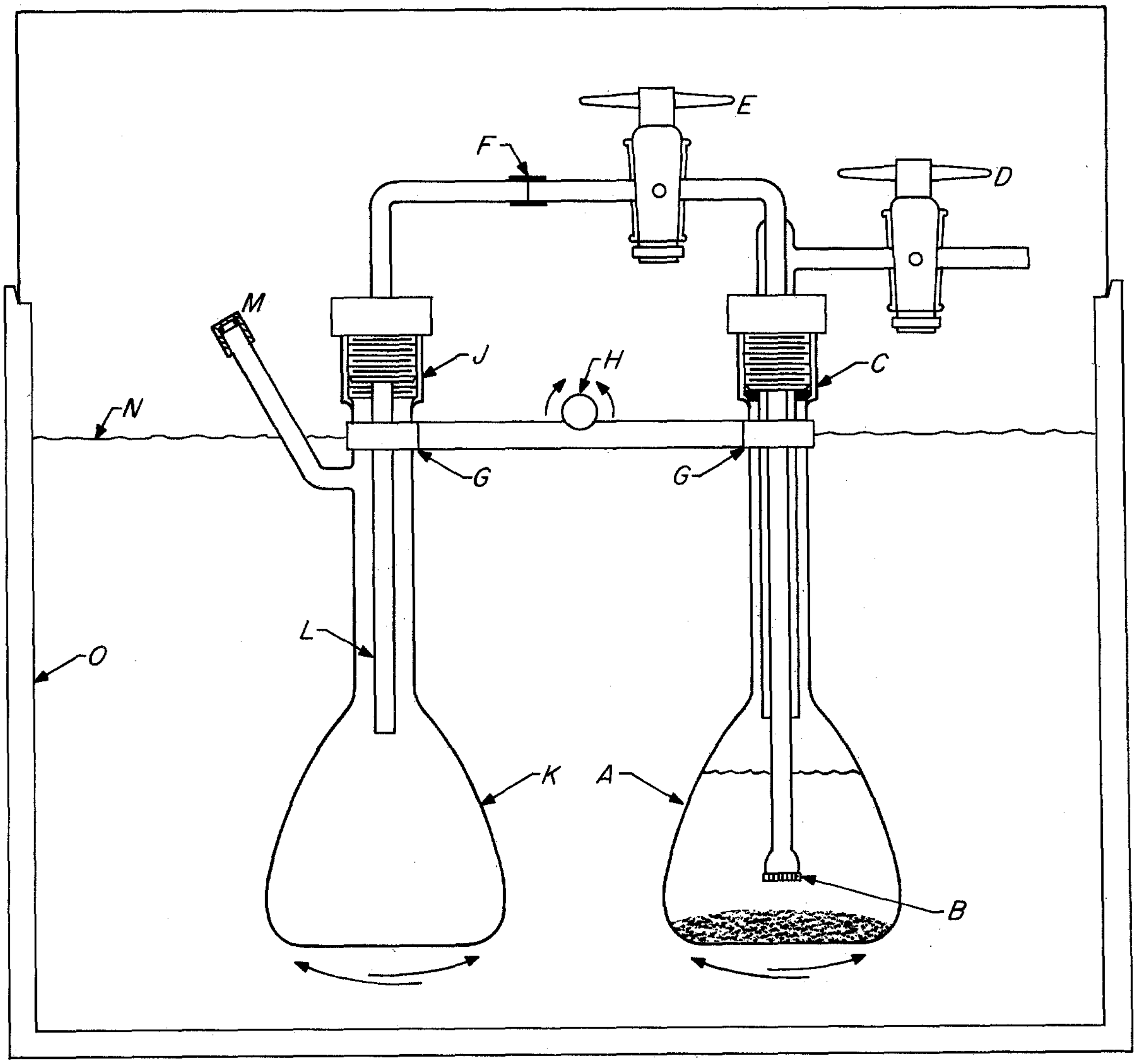

FIGURE 1. - Apparatus for measurement of solubilities.

equilibrium, particularly if the salt could form a complex solid salt with HCl. At the end of the equilibration period, the flasks were allowed to remain motionless in an upright position for 1 hour to insure settling of solid particles. Stopcocks D and E were then opened to transfer approximately half of the solution into the sampling flask, K. The level of B below the liquid in A usually determined the amount of solution transferred into K. The weight of the solution in K was determined by weighing the flask before assembling and after admitting the solution and disassembling. A known amount of distilled water was injected into the flask through L to dilute the sample and dissolve any vapor in the gas phase. The partial pressure of HCl in pure water exceeds 1 torr at 25° C at molalities in excess of 8 m (m after a number in a sentence denotes molal); therefore, at concentrations less than 8 m it is doubtful that any loss of HCl could occur during sampling. For this reason, some of the runs at 25° C, containing less than 4 m HCl, were made with a single stoppered flask, and, after equilibration, a portion of the solution was carefully decanted and filtered for sampling.

ANALYSIS

The solutions were analyzed after appropriate dilutions for total chloride-ion and aluminum-ion concentrations. The total chloride-ion concentration was determined by potentiometric titration with Ag^+. The Al^{+++} concentration was determined by first complexing with an excess of ethylenediamine-tetraacetic acid (EDTA) and then back titration of the excess EDTA with Cu^{++} at a pH of 3.8.

The $AlCl_3$ content was calculated from the Al^{+++} analysis. Subtraction of the chloride-ion in the calculated amount of $AlCl_3$ from the total chloride-ion concentration allowed calculation of the HCl concentration in the saturated solutions.

This method of calculation was used for all analyses except those in which the HCl concentration was known to be zero, that is, when $AlCl_3$ was the only electrolyte in pure water. For these analyses, the $AlCl_3$ concentration was simply calculated from the chloride-ion analysis, which was the more accurate of the two analyses, although both Al^{+++} and Cl^- analyses were still completed for these samples.

The difference in Cl^- analysis computed from the total Cl^- analysis and Cl^- from Al^{+++} analysis for experiments without added HCl was ±0.2 wt-pct Cl^- This indicates that, on the average, the analysis of Al^{+++} was subject to ±0.05 wt-pct error, since the Cl^- analysis was known to be considerably more accurate than the Al^{+++} analysis. In solutions containing HCl, an error of ±0.05 percent in Al^{+++} content was reflected as ±0.20 pct in HCl content; this was because, while the total Cl^- content was very accurate, the Cl^- contributed by added HCl and, hence the molality of HCl, was computed by difference as mentioned earlier.

RESULTS

The results are summarized in table 1 and shown in figure 2. The maximum HCl concentration for the data given in table 1 for 85° C is approximately 30 wt-pct. Measurements were stopped at this concentration because of the excessive equilibrium pressures in the system at higher concentrations. It should also be noted that fewer determinations were carried out at 65° and 85° C than at 25° and 45° C. Replicates were run at the two lower temperatures to give an indication of satisfactory repeatability of results. Figure 2 shows that the solubility of aluminum salt decreases drastically with increasing HCl concentration. Therefore, leaching nonbauxitic ores with HCl solution and precipitating out the pure salt for extraction of aluminum by adding HCl is a feasible process; such a process has been the subject of several patents (1, 14). The results show that the solubility does not greatly change with temperature, and for a temperature increase of 60° C (25° to 85° C), the solubility of pure salt alone in water increases only 2.2 pct relative to solubility at 25° C.

TABLE 1. - Solubility of $AlCl_3 \cdot 6H_2O$ in HCl-H_2O solutions

Wt-pct $AlCl_3$	m, $AlCl_3$ moles/kg	Wt-pct HCl	n, HCl moles/kg	Ionic strength	Wt-pct $AlCl_3$	m, $AlCl_3$ moles/kg	Wt-pct HCl	n, HCl moles/kg	Ionic strength
		25° C					45° C		
31.08	3.382	0.00	0.00	20.292	31.17	3.396	0.00	0.00	20.376
31.10	3.385	.00	.00	20.310	31.18	3.398	.00	.00	20.388
28.73	3.110	1.99	.788	19.448	28.85	3.128	1.98	.785	19.553
28.95	3.147	2.06	.819	19.701	29.03	3.164	2.17	.865	19.849
24.20	2.620	6.52	2.581	18.301	25.02	2.701	5.52	2.180	18.386
23.66	2.558	6.96	2.751	18.099	24.24	2.623	6.45	2.552	18.290
18.78	2.016	11.36	4.460	16.556	16.78	1.812	13.76	5.433	16.305
18.58	2.001	11.79	4.644	16.650	16.68	1.799	13.79	5.440	16.284
13.47	1.443	16.52	6.472	15.130	14.73	1.584	15.52	6.103	15.607
12.47	1.333	17.35	6.780	14.778	14.12	1.529	16.64	6.591	15.765
9.60	1.0361	20.91	8.253	14.470	9.98	1.081	20.81	8.247	14.733
8.87	.9530	21.36	8.397	14.115	7.21	.779	23.36	9.228	13.902
4.87	.5234	25.35	9.964	13.104	3.47	.3795	27.95	11.178	13.455
5.05	.5467	25.67	10.162	13.442	3.46	.3799	28.23	11.334	13.613
1.05	.1177	32.04	13.133	13.839	1.51	.1691	31.53	12.915	13.930
1.06	.1190	32.13	13.190	13.904	1.45	.1631	31.86	13.103	14.082
.10	.0119	37.12	16.217	16.931	.20	.0237	36.49	15.808	15.950
.10	.0120	37.19	16.265	16.337	.22	.0263	36.94	16.122	16.280
		65° C					85° C		
31.29	3.415	0.00	0.00	20.490	31.77	3.492	0.00	0.00	20.952
21.52	2.332	9.27	3.674	17.666	25.45	2.790	6.14	2.462	19.202
20.86	2.267	10.13	4.026	17.628	18.55	2.019	12.56	5.000	17.114
13.39	1.452	17.47	6.930	15.642	13.68	1.501	17.99	7.221	16.227
6.76	.739	24.66	9.862	14.296	7.00	.772	25.02	10.094	14.726
2.14	.238	30.39	12.354	13.782	3.22	.3625	30.16	12.416	14.591
.79	.0902	33.50	13.982	14.523					

NOTE.--m refers to the molality of $AlCl_3$, n refers to the molality of HCl and molality is moles in 1 kg of water.

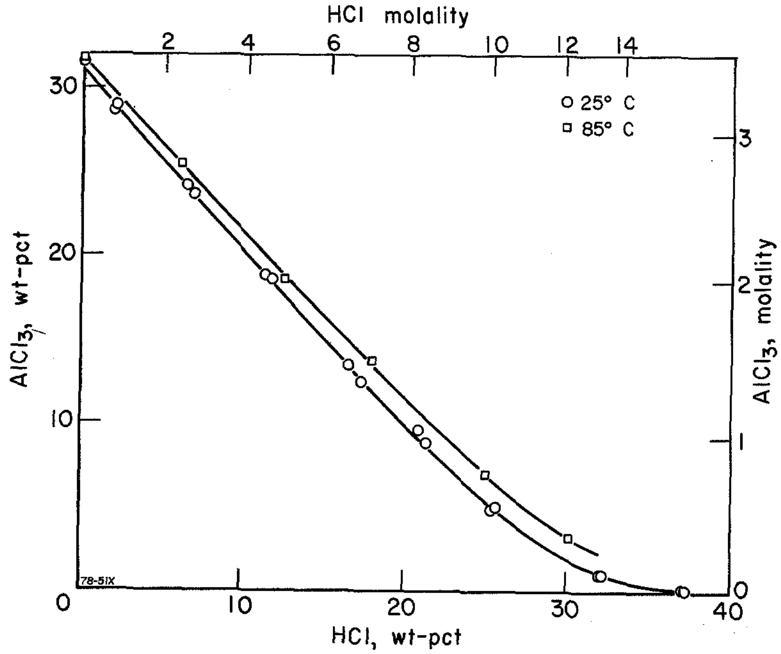

FIGURE 2. - Variation of solubility of $AlCl_3 \cdot 6H_2O$ in water at various concentrations of HCl at 25° and 85° C. (Data at 45° and 65° C listed in table I are not plotted for clarity.)

COMPARISON WITH OTHER DATA

The solubility of pure salt in water at 25° C was found to agree exactly with the data of Palitzch and with Ehret and Frere (12).[7] Results given by Malquori are about 10 pct higher (12). The solubility obtained by Tanaka (12) is about 3.3 pct higher than in the present investigation at 45° and at 65° C.

The effect of HCl in water on the solubility of salt has been investigated by Seidel and Fisher (18) at 0° C and by Malquori (12) at 25° C. The results of the former investigators at 0° C agree very closely with the data in table 1, extrapolated to 0° C, whereas those of the latter investigator at 25° C scatter somewhat and disagree roughly by 3 pct at low HCl concentrations; however, the agreement in the range of 5 to 30 wt-pct HCl is within 1 pct.

THERMODYNAMIC TREATMENT

Solubility Product and Activities in $AlCl_3 \cdot 6H_2O$-H_2O System

The ionic activity[8] coefficient γ_{12} of $AlCl_3$ in water has been measured up to 1.8 m by Mason (13), and recalculated values are given by Robinson and Stokes (17). Since the activity coefficient from 1.8 m to the saturation value of 3.3835 m is expected to increase more than fivefold, the saturation value is used for calculation by the method described in detail in a previous report (4) (1 m = 1 mole in 1 kg of solvent). The method, with its appropriate novel application, is briefly summarized in this report. The mean ionic activity of $AlCl_3$, designated as a_{12}, is expressed by the following power series in terms of molality m:

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[7] The experimental data of Palitzch, Ehret, Frere, and Malquori are summarized by Linke in his detailed compilation of solubility data (12). This compilation gives references for the original published work.

[8] All thermodynamic methods are discussed and all properties and terms are defined in detail in a previous report (4).

$$\ln a_{12}^{4} = -34.402m^{0.5} - 2Cm - (5/3)Dm^{1.5} - 1.5\,Em^{2} - 1.4\,Fm^{2.5} - (4/3)Gm^{3} - (9/7)Hm^{3.5} + \ln(3^{3}m^{4}). \quad (1)$$

where $\gamma_{12}^{4} = a_{12}^{4}/3^{3}m^{4}$ by definition.

The corresponding equation for the activity of water a_w, is obtained by the application of the Gibbs-Duhem relation; the result is

$$55.508 \ln a_w = -4m + 11.46733m^{1.5} + Cm^{2} + Dm^{2.5} + Em^{3} + Fm^{3.5} + Gm^{4} + Hm^{4.5}. \quad (2)$$

Note that the exponents of m with the same coefficients of C, D, etc., are 1 higher in equation 2 than in equation 1, and the coefficient of $m^{1.5}$ in equation 2 originates from the Debye-Hückel theory as discussed by Gokcen (4). The reaction for dissolution of the salt is

$$AlCl_3{\cdot}6H_2O\ (s) = Al^{+++} + 3Cl^{-} + 6H_2O\ (\ell), \quad (3)$$

where (s) means solid and (ℓ) liquid.

The corresponding equilibrium constant is

$$K_p = a_w^{6}a_{12}^{4}/[a(\text{solid})], \quad (4)$$

where the denominator, the activity of solid, is taken as unity since its composition remains unchanged when other electrolytes are added in solution. We substitute for a_{12} in $\ln K_p$ directly from equation 1 and for a_w from equation 2 after multiplying equation 2 by 0.108093 to make the coefficient of $\ln a_w$ equal to 6. Since K_p is composition independent, it is evident that

$$d \ln K_p/dm = d \ln(a_w^{6} \cdot a_{12}^{4})/dm = 0. \quad (5)$$

After the required substitutions from equations 1 and 2 and then the substitution of the average value m = 3.3835 from the first two runs in table 1, one equation is obtained for solving the six unknown coefficients in equation 1, and the remaining five equations are obtained by substituting each of the five experimental values of the mean ionic activity coefficient of $AlCl_3$, γ_{12} in table 2, into

$$a_{12}^{4} = \gamma_{12}^{4}\ (3^{3}m^{4}), \quad (6)$$

and then substituting each result in equation 1. Six simultaneous equations obtained in this manner are then solved by computer. The results are as follows:

$C = -57.5723,$

$D = +142.0288,$

$E = -202.5581,$

$F = +161.1919,$

$G = -67.7831,$

and $H = +11.6880.$

Substitution of these values in equations 1, 2, and 4 yields the values of γ_{12}, a_w, and K_p. The results are listed in table 3 under the heading "Bureau results:" It should be noted that the activity of water can now be calculated from equation 2, and the vapor pressure of water over the solution, P, from

$$a_w = P/P^\circ, \tag{7}$$

where P° is the vapor pressure of pure water at the same temperature. Note that the vapor pressure of water over the saturated solution is a little more than half of that over pure water since $a_w = 0.509$. The foregoing results constitute the first set of data on activities based on the solubility of the salt.

TABLE 2. - Activity coefficients of $AlCl_3$ and HCl in their binary solutions in water at 25° C

			$AlCl_3$-H_2O			
m[1]	0.2	0.6	1.0	1.4	1.8	[2]3.3835
γ_{12}......	.305	.356	.539	.936	1.819	[2]10.251
			HCl-H_2O			
n[3]	0.1	0.5	1.0	2.0	6.0	13.0
γ_{32}......	.796	.757	.809	1.009	3.22	21.8

[1] Data from compilation in (17).

[2] Data as used in equations 4 and 5, average of two close values in table 1; all other data for $AlCl_3$-H_2O system are from (17).

[3] Data from (5); see also (3, 17).

NOTE.--In this table, m refers to the molality of $AlCl_3$; n refers to the molality of HCl; and molality is moles in 1 kg of water.

TABLE 3. - Activity and activity coefficient of $AlCl_3$ and H_2O, and solubility product for solutions saturated with $AlCl_3 \cdot 6H_2O(c)$ at 25° C[1]

	Bureau results	Estimated[2]	Bureau results	Estimated[2]	Bureau results	Estimated[2]
m........	[3]3.3835	[3]3.3835	2.620	2.62	1.0361	1.0361
n........	0	0	2.581	2.581	8.253	8.253
γ_{12}.......	10.251	9.94	30.54	11.25	28.43	15.7
a_{12}.......	79.1	76.7	225.7	83.1	177.5	98.0
a_w........	.509	.47	.253	.42	.309	.35
$10^{-5}K_p$....	6.80	3.7	6.81	2.6	[4]8.64	1.7

[1] Data selected from table 1.

[2] Estimated by authors using Kusik-Meissner method (10-11).

[3] Average of two close values from table 1.

[4] Small changes in molality at low values of m ($m < 0.5$) greatly affect the values of K_p; therefore, computations have not been made for $m < 0.5$. For example, a likely error of -0.05 pct in molality on the fifth column for the same activity coefficients causes a decrease of 20 pct in K_p and makes it nearly identical with the remaining values obtained by the authors.

NOTE.--In this table, m refers to the molality of $AlCl_3$, n refers to the molality of HCl, and molality is moles in 1 kg of water.

Estimation of Activities in $AlCl_3 \cdot 6H_2O$-H_2O System

Two existing reliable methods of estimation are used to obtain the activities in $AlCl_3 \cdot 6H_2O$-H_2O system beyond the existing direct experimental data at m = 1.8. The first method, as described by Kusik and Meissner (10-11), gives an estimated value of $\gamma_{12} = 9.94$ at 3.3835 m.[9] This estimated value is in close agreement with 10.251, the value obtained in the present investigation. The corresponding estimated value of the activity of water, a_w, is 0.47, again in close agreement with the value of 0.509 found in the present investigation. The equilibrium constant K_p calculated from these values is not far from 6.8×10^5, considering the fact that the fourth power of a_{12} and the sixth power of a_w are multiplied to obtain K_p.

The second method of estimation due to Bromley (2) yields 10.42 for γ_{12}, a value closer than that obtained by the preceding method. The activity coefficient of water has been obtained by the present authors, by integrating the Gibbs-Duhem equation in which the values of a_{12} estimated by the Bromley method were used. The result is $a_w = 0.540$. The average of both methods is 0.505, which is in very good agreement with the Bureau's value of 0.509. The Bromley method, however, does not contain a convenient method for determination of a_w included in the Kusik-Meissner method.

The agreement of the estimated values with the values from the solubility data is not always as good as shown here for every electrolyte at every

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[9] The Kusik-Meissner method is summarized in a previous report (4).

composition. For example, even for $AlCl_3$ at 1 m, the two estimates of γ_{12} differ by only 13 percent from each other.

Solubility product and activities in $AlCl_3 \cdot 6H_2O$-HCl-H_2O system

The effect of increasing concentration of HCl on the solubility of the salt is largely due to the increasing concentration of the chloride ions. The equilibrium constant in this case with the activities a_1 and a_2 of individual ions is

$$K_p = 6.80 \times 10^5 = a_1 a_2^3 = \gamma_1 \gamma_2^3 \, m(3m + n)^3 a^6 = \gamma_{12}^4 \, m(3m + n)^3 a_w^6 , \qquad (8)$$

where $\gamma_{12}^4 = \gamma_1 \gamma_2^3$ by definition of γ_{12} from the individual ionic activities γ_1 (for Al^{+++}) and γ_2 (for Cl^-), and n is the molality of HCl. The value of K_p is the same as that for equation 4 but the right side in equation 8 is different from that in equation 4. It may be noted that as n increases, m, the concentration of Al^{+++}, must decrease, provided that γ_{12} and a_w do not decrease greatly; therefore, the salt precipitates out, which is known as the salting out effect.

The calculation of the activities in the ternary solution requires an equation similar to equation 1 for HCl. Since the data for HCl are known accurately over a wide range of concentration, it is possible to take an equation with as many variables as desired. The following equation gives an accurate representation of the data for the activity coefficient of HCl, γ_{32}, where the subscript 3 is for H^+ and 2 for Cl^-:

$$\ln \gamma_{32}^2 = -2.342 n^{0.5} - 2Jn - (5/3)Kn^{1.5} - 1.5Ln^2$$
$$- 1.4Mn^{2.5} - (4/3)Nn^3 - (9/7)Pn^{3.5} . \qquad (9)$$

The data selected for this purpose from Haase, Naas, and Thumm (5) are listed on the third and fourth rows of table 2. The values of the coefficients calculated from these data are as follows:

$J = -1.88416$,

$K = +2.24342$,

$L = -1.98545$,

$M = +1.00091$,

$N = -0.25934$,

and $P = +0.02634$.

The equations for the activities of $AlCl_3$ and of H_2O contain these coefficients as well as the coefficients of the cross products $(m^{h/2})(n^{k/2})$, where h and k are integers, and these equations are as follows:

$$\ln a_{12}^4 = [\mathrm{Eq}(1) - \ln(3^3 m^4)] - Qn - 2/3Sn^{1.5} - 0.5Un^2$$
$$-Vm^{0.5}n - 0.75Wm^{0.5}n^{1.5} + \ln[m(3m + n)^3], \qquad (10)$$

$$55.508\ln a_w = [\mathrm{Eq}(2)] + 0.780667n^{1.5} + Jn^2 + Kn^{2.5} + Ln^3$$
$$+ Mn^{3.5} + Nn^4 + Pn^{4.5} + Qmn + Smn^{1.5} + Umn^3$$
$$+ Vm^{1.5}n + Wm^{1.5}n^{1.5}. \qquad (11)$$

The five additional coefficients in these equations are determined by adding equation 10 and 6 ln a_w from equation 11 to obtain ln K_p and by using the following selected solubility data from table 1:

m: 2.620, 2.016, 1.333, 0.953, and 0.535.

n: 2.581, 4.460, 6.780, 8.397, and 10.063.

The resulting calculations yield the following values of the coefficients in equations 10 and 11:

$Q = +23.27027$,

$S = -22.47064$,

$U = +4.29102$,

$V = -9.76081$,

and $W = +4.60246$.

The results for γ_{12}, a_{12}, a_w, and K_p calculated from the preceding equations are listed in table 3. The values of γ_{12} from equation 9 are in agreement with those by Harned and Gary (6) at very low concentrations of HCl and $AlCl_3$.

The partial pressure of HCl(g), P_{32}, over a solution can be calculated from the following equation (4):

$$K_p(\mathrm{HCl}) = 4.94 \times 10^{-7} = P_{32}/a_{32}^2, \qquad (12)$$

where K_p(HCl) is the equilibrium constant at 25° C for $H^+ + Cl^- = HCl(g)$, and a_{32} is the mean ionic activity of HCl in solution (3-4). For this purpose, it is necessary to write an equation for a_{32}, similar to equation 10, by using the parameters in equation 11, as shown elsewhere in detail (4).

The effect of temperature on the solubility of the salt is small, as shown in table 1. The effect on the ionic activities is therefore expected to be small since all the parameters in equation 11 could have been obtained from the solubility data if the experimental error were smaller than ±0.01 wt-pct for aluminum analysis. In general, for a range of temperature up to approximately 80° C, each parameter is a linear function of temperature, and this dependence can be determined if equation 11 were known at another temperature at least 50° C higher than 25° C.

Estimation of Activities in $AlCl_3 \cdot 6H_2O$-HCl-H_2O System

The values of activities, activity coefficient, and the solubility product estimated in the present report according to the method devised by Kusik and Meissner (10-11), are listed in table 3. The activity coefficient γ_{12} for $AlCl_3$ is roughly twice as high as the estimated value for the selected solutions containing HCl. The activity of water, a_w, however, agrees well with the estimated values except for m = 2.620. It is evident that the calculations would have been considerably more reliable if the vapor pressure of water, a_w, were measured because a_w enters in K_p as a_w^6, so that small errors in a_w cause large errors in γ_{12} and K_p. For this purpose, a limited number of vapor pressure measurements are recommended to test the accuracy of the present calculations and the methods of estimation.

The temperature dependence of the thermodynamic properties listed in table 3 can be estimated as described by Kusik and Meissner (10-11). However, the estimate is likely to yield a higher degree of temperature dependence than that indicated by the weak temperature dependence of the solubility. No attempt could be made to calculate the effect of temperature by the Bureau's method because (1) a_{12} at low concentrations of $AlCl_3$ is not known at various temperatures, (2) the solubility of $AlCl_3$ could not be determined with an accuracy approaching 0.01 pct in Al^{+++}, and (3) the range of concentration of HCl at 65° and 85° C is too small for selecting a sufficient number of widely differing solubility data for $AlCl_3$ to determine accurately the parameters in equations 10 and 11.

THE $AlCl_3$-$FeCl_3$-KCl-NaCl-HCl-H_2O SYSTEM

Preliminary data on solubilities of $AlCl_3$, $FeCl_3$, KCl, and NaCl in aqueous solutions containing 24 to 31 wt-pct HCl at 25° C were obtained to assess contamination of $AlCl_3 \cdot 6H_2O$ extractable from nonbauxitic ores. For this purpose, 2 liters of a solution containing known amounts of salts were prepared, 90 ml of this solution were placed in a flask for each run and then a known amount of gaseous HCl was admitted to attain 24 to 31 wt-pct of dissolved HCl. In this range of HCl in solution, colorless anisotropic crystals of $AlCl_3 \cdot 6H_2O$, bright anisotropic crystals of $FeCl_3 \cdot 2KCl \cdot H_2O$, and cubic isotropic transparent crystals of KCl and NaCl were precipitated and identified by microscopic examination (15). The procedure and analyses for aluminum-ion and chloride-ion concentrations were the same as those used for the $AlCl_3 \cdot 6H_2O$-HCl-H_2O system presented earlier in this report. In addition, the ferric-ion concentration was determined by standard $K_2Cr_2O_7$ titration, the sodium-ion concentration was determined by atomic absorption techniques, and the potassium-ion concentration was determined by subtraction of the sodium-ion concentration from a determination of the combined potassium-ion plus sodium-ion concentrations after separation by ion-exchange. The results are listed in table 4 and plotted in figure 3. Similar results by Miles (15) are also plotted in

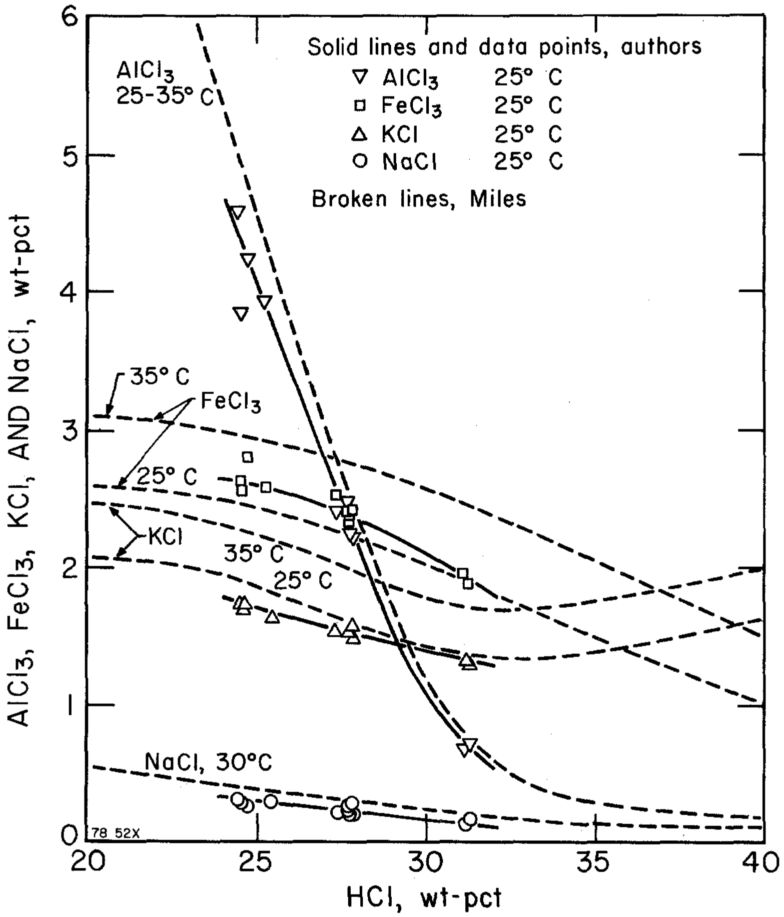

FIGURE 3. - Solubilities of $AlCl_3 \cdot 6H_2O$, $FeCl_3 \cdot 2KCl \cdot H_2O$, KCl, and NaCl in HCl-H_2O solutions at 25° C. (Results by Miles (15) at 25° and 35° C are presented for comparison.) Solutions saturated simultaneously with respect to the four salts ($AlCl_3 \cdot 6H_2O$), ($FeCl_3 \cdot 2KCl \cdot H_2O$), (KCl), and (NaCl).

figure 3 to show that the agreement is excellent. Published data for related simpler systems containing fewer components have been compiled by Linke (12).

In the evaporative or HCl gas sparging crystallization processes for producing pure aluminum chloride hexahydrate, contamination by other metallic chlorides becomes a problem as impurity levels build up in leaching solutions. Figure 3 shows the concentration levels that impurities such as NaCl, KCl, and $FeCl_2 \cdot 2KCl \cdot H_2O$ will also crystallize from solution as distinct separate phases, thus causing contamination of the $AlCl_3 \cdot 6H_2O$ crystals. For example, at less than 2.4 wt-pct $FeCl_3$ in the presence of 1.6 wt-pct KCl at 25° C, the concentration of HCl must be less than 28 wt-pct to avoid contamination of $AlCl_3 \cdot 6H_2O$ by the double salt, $FeCl_3 \cdot 2KCl \cdot H_2O$. Figure 3 is also useful in redissolving the precipitate for fractional recrystallization to purify the aluminum salt. In addition, some of the transition element salts, such as $FeCl_3$, can be minimized by partial electrolysis to plate out a sufficient amount of iron prior to acidification with HCl.

A thermodynamic treatment of the system with the usual error of ±0.05 wt-pct in chloride-ion concentration is not feasible, particularly in the absence of vapor pressure data for $H_2O(g)$ and $HCl(g)$. However, rough estimates of the activities can be made by the Kusik-Meissner method. It is anticipated that such estimates could give only rough values of the activities for the hydrated and complex salts and for the water.

TABLE 4. - Solubility data for $AlCl_3$-$FeCl_3$-KCl-NaCl in solutions of HCl-H_2O at 25° C[1]

$AlCl_3$		HCl[2]		$FeCl_3$		KCl		NaCl	
Wt-pct	Molality	Wt-pct	Molality	Wt-pct	Molality	Wt-pct	Molality	Wt-pct	Molality
4.59	0.5190	24.44	10.1071	2.63	0.2445	1.70	0.3438	0.32	0.0826
3.84	.4291	24.53	10.0249	2.54	.2333	1.69	.3378	.29	.0739
4.23	.4781	24.65	10.1894	2.76	.2564	1.73	.3497	.28	.0722
3.94	.4468	25.40	10.5343	2.58	.2405	1.63	.3306	.32	.0828
2.39	.2715	27.33	11.3554	2.52	.2354	1.53	.3109	.22	.0570
2.48	.2830	27.62	11.5247	2.38	.2232	1.53	.3122	.26	.0677
2.38	.2717	27.73	11.5777	2.40	.2252	1.51	.3083	.29	.0755
2.29	.2610	27.73	11.5583	2.41	.2258	1.54	.3139	.23	.0598
2.35	.2680	27.79	11.5922	2.33	.2185	1.48	.3019	.30	.0781
2.21	.2520	27.81	11.5952	2.41	.2259	1.57	.3201	.22	.0572
.70	.0811	31.18	13.2071	1.93	.1838	1.30	.2693	.14	.0370
.72	.0835	31.25	13.2490	1.88	.1792	1.28	.2654	.18	.0476

[1] Total ionic strength, not listed in this table, ranges from 14.4 to 15.1.

[2] Data arranged in increasing concentration of HCl.

AREAS RECOMMENDED FOR RESEARCH

The measurements of activities are useful in interpreting thermodynamics and kinetics of leaching, precipitating, and purifying desired components of various ores. There are two reasons that the activities can be determined accurately from the measurements of vapor pressure of water: (1) The vapor pressure can be measured with a high degree of precision by differential pressure transducers to obtain a_w by equation 7 and then to calculate the values of the parameters in equation 11 so that all the related properties can be computed as discussed previously in detail (4). (2) The solubility product and the activities can both be determined accurately for multivalent salts that contain large numbers of water molecules in their hydrated crystals. The second reason arises from the fact that the exponent of the activity of water in equation 4 is equal to the moles of water in the hydrated crystal.

Another interesting type of experiment for the ternary system discussed here is the measurement of the partial pressure of HCl(g) over various solutions containing sufficiently large amounts of dissolved HCl. The experimental procedure for this purpose is described elsewhere (4). Group IIA, IIIA, and transition metal salts are excellent candidates for these types of investigations since electrolytes with higher valences than 1:1 usually form hydrated salts.

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