Thermodynamic Properties of Al(III) Hydroxysalt in Sulfate Aqueous Solution at 333 K*

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The present investigation has been carried out to examine the thermodynamic behavior of aluminum in the hydrolysis operation of aluminum sulfate aqueous solution with sodium hydroxide solution and to determine the pH-dependence of the solubility of the precipitate produced in the hydrolysis at 333 K.

The results obtained are summarized as follows.

(1) The hydrolysis proceeds via two steps. In the case where the initial concentration of $\text{Al}_2(\text{SO}_4)_3$ was less than 0.05 kmol·m$^{-3}$, the precipitates produced in the first and second step hydrolyses were identified to be $\text{Al}_7(\text{SO}_4)_2(\text{OH})_{17}$ and $\text{Al}(	ext{OH})_3$, respectively. These hydrolysis reactions are represented by $\text{Al}_7^{3+} + \alpha\text{SO}_4^{2-} + \beta\text{HSO}_4^- + 17\text{H}_2\text{O} = \text{Al}_7(\text{SO}_4)_2(\text{OH})_{17} + (17 + \beta)\text{H}^+$, where $\alpha + \beta = 2$, and $\text{Al}_7(\text{SO}_4)_2(\text{OH})_{17} + 4\text{H}_2\text{O} = 7\text{Al}(	ext{OH})_3 + 2\text{H}_2\text{SO}_4$.

(2) For the equilibrium constant, $K$, of the first step hydrolysis at 333 K, log $K$ was calculated to be $-35.6 \pm 1.1$, from which $-8489 \pm 7$ kJ·mol$^{-1}$ was obtained as the standard free energy of formation of $\text{Al}_7(\text{SO}_4)_2(\text{OH})_{17}$ at the same temperature.

(3) The pH-dependence of the solubility of $\text{Al}_7(\text{SO}_4)_2(\text{OH})_{17}$ was determined for various choices of a parameter, which can be calculated from the composition of solutions immediately before the beginning of the first step hydrolysis reaction.

(4) A method was proposed which enables one to calculate the activity coefficients of $\text{H}^+$, $\text{HSO}_4^-$, and $\text{SO}_4^{2-}$ ions for the ternary system $\text{H}_2\text{SO}_4 - \text{Na}_2\text{SO}_4 - \text{H}_2\text{O}$ as a function of ionic strength by using $\text{H}_2\text{SO}_4$-molality as a parameter.

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I. Introduction

Most of the precious metals used as functional materials are frequently recovered as by-products from the production processes of common metals such as zinc, copper, lead, nickel, etc. In this case, their separation is often achieved by a precipitation operation through neutralization of the leaching solution containing sulfuric acid and metal sulfate. As the theoretical background for the precipitation operation, one commonly refers to the ion activity-pH diagrams of simple metal-H$_2$O systems. It is, however, questionable whether such a simple theory can be applied to more complicated systems containing sulfate ions which have a strong tendency to form sulfato-complexes with metal ions.

From this viewpoint, a series of investigations have been planned by the authors particularly to elucidate the pH-dependence of the solubility of hydroxysalts of IIIb-metals, which are, in recent years, of great value as electronic materials. As the first step to the subsequent studies on gallium and indium, aluminum was chosen in this investigation. The reason is that, in comparison with gallium and indium, more thermodynamic data required to analyze the pH-dependence of the solubility of Al(III)-hydroxysalt exist in the case of aluminum.

II. Experimental

Figure 1 is a schematic diagram of the cell assembly used in the present investigation. In
five arms of a flask of 2 dm³ are installed, (a) KCl-saturated calomel- and glass-electrodes for measuring pH-values, (b) KCl-saturated calomel-electrode and platinum-electrode (one of which is attached to the end of a impeller for agitating the solution) for measuring potentials, (c) an inlet of argon gas, (d) a tube for supplying NaOH-solution, and (e) a thermometer. The pH- and potential-values were measured on a pH-meter (Toa Electronics Ltd., HM-50AT) and on a digital multimeter (Takeda Riken Ltd., TR6843), respectively. All the chemicals used in this investigation are of reagent grade.

First, sulfuric acid and then aluminum sulfate were added to 1 dm³ of double distilled water in the flask in order to obtain the desired pH-value and Al(III) concentration. The solution was agitated at a constant rotational speed by the impeller and the temperature was maintained at 333 ± 0.5 K by using a thermostated water bath. Subsequently, 2.5 N (kmol·m⁻³) NaOH-solution was added into the solution, and the variation of the pH-value with time was measured and recorded. When the pH-value became constant, this value was adopted as the equilibrium one. By repeating this procedure, titration curves were obtained. In each procedure, after the establishment of equilibrium, samples of the solution and the precipitate were taken and analysed chemically (Al(III) and Na(I): atomic absorption spectrochemical analysis, (SO₄²⁻)Tot: BaSO₄-gravimetric analysis) to determine their chemical composition. Table 1 shows the initial composition of the solutions.

### Table 1 Initial compositions of solutions.

| Run | Initial concentration/kmol·m⁻³ |
|-----|-------------------------------|
|     | Al₂(SO₄)₃ | H₂SO₄ |
| 1   | 0.0493   | 0.0375 |
| 2   | 0.0228   | 0.0938 |

### III. Experimental Results

1. **Variation of the pH-value with time**

The neutralization of the solution, as is seen from the titration curves shown later, proceeds in three steps; i.e. the neutralization of the acid and the first and second step hydrolysies. Figure 2 is an illustrative example of the variations of the pH-value of the solution with time in each step after the addition of 2.5 N (kmol·m⁻³) NaOH-solution. In the case of the neutralization of the acid, the reaction proceeded almost instantaneously and the pH-value reached equilibrium very quickly. In contrast to this, it took about 18 ks (5 h) and 194.4 ks (54 h) in the first and second step hydrolysies, respectively, to attain the corresponding equilibrium pH-values. The values which remained constant over a period of 10.8 ks (3 h) for the first step hydrolysis and 18 ks (5 h) for the second step hydrolysis were adopted as equilibrium ones.

2. **Titration curves and composition of precipitates produced by hydrolysis**

Relations between the amounts of NaOH added and the equilibrium pH-values obtained in the above way are indicated in Fig. 3. It can be seen from this figure that the hydrolysis reaction proceeds in two steps. Therefore, after the Hydrolysis reaction is generally independent of the solution potential. It was, however, recognized that not only the pH-value but also the potential of the solution became constant after the establishment of equilibrium of the hydrolysis reaction. Therefore, the electrodes for measuring the solution potential were used as a monitor to confirm the equilibrium.

† Hydrolysis reaction is generally independent of the solution potential. It was, however, recognized that not only the pH-value but also the potential of the solution became constant after the establishment of equilibrium of the hydrolysis reaction. Therefore, the electrodes for measuring the solution potential were used as a monitor to confirm the equilibrium.

‡ In the case of the pH-value remaining constant over these periods, its value did never change after 86.4 ks (24 h) also.
establishment of the first and second step hydrolyses, precipitates were taken, filtered, and washed in water at room temperature, dried slowly at around 323 K, and analysed for Na(I), Al(III), and SO$_2^-$.

The results obtained are shown in Table 2. The molar ratio of Al(III) to SO$_2^-$ in the precipitate produced in the first step hydrolysis is nearly 7 to 2 and the content of Na(I) is negligibly small. In addition, considering a mass balance and an electro-neutrality of the precipitate, it may be regarded as $\text{Al}_7\text{(SO}_4\text{)}_2\text{(OH)}_{17}$\(\text{ExH}_2\text{O}\). Excluding the crystal water from $\text{Al}_7\text{(SO}_4\text{)}_2\text{(OH)}_{17}$\(\text{ExH}_2\text{O}\), the first step hydrolysis reaction may be represented as

$$7\text{Al}^{3+} + \alpha\text{SO}_2^- + \beta\text{HSO}_4^- + 17\text{H}_2\text{O} = \text{Al}_7\text{(SO}_4\text{)}_2\text{(OH)}_{17} + (17 + \beta)\text{H}^+ \quad (1)$$

where

$$\alpha + \beta = 2. \quad (2)$$

Na(I) and SO$_2^-$ were not detected at all in the second step hydrolysis product, which was identified as Al(OH)$_3$ by the application of X-ray diffraction. This fact was also supported by the mass balance and the electro-neutrality of the product. Accordingly, the second step hydrolysis reaction may be expressed as

$$\text{Al}_7\text{(SO}_4\text{)}_2\text{(OH)}_{17} + 4\text{H}_2\text{O} = 7\text{Al(OH)}_3 + 2\text{H}_2\text{SO}_4. \quad (3)$$

IV. Discussion

For the argument on total concentration of a metal dissolved in the solution, excluding the high alkali region, the first step hydrolysis usually comes into question. The following discussion is, therefore, focused exclusively on this aspect.

1. Relation between the total aluminum concentration in the solution and the pH-value

From eq. (2), the equilibrium constant of eq. (1),

$$K = \frac{a_{\text{Al}^{3+}}^{(17+\beta)} \cdot a_{\text{SO}_2^-} \cdot a_{\text{HSO}_4^-}^{-\beta}}{a_{\text{H}^+}^{17}} \quad (4)$$

and the dissociation equilibrium† of HSO$_4^-$ ion at 333 K,

† calculated from data\(^{(1)}\) at 298 K by using the correspondence principle proposed by Criss and Cobble\(^{(2)}\).
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\[
\text{HSO}_4^- = H^+ + \text{SO}_4^{2-} \quad (5)
\]

one obtains a relation between molality of Al\(^{3+}\) ion, \(m_{Al^{3+}}\), and the pH-value,

\[
pH = 2.42 + \log \frac{a_{\text{SO}_4^{2-}}}{a_{\text{HSO}_4^-}} \quad (6)
\]

\[
\log m_{Al^{3+}} = \left\{ -\log \gamma_{Al^{3+}} - \frac{1}{7} \left( \log K + \alpha \log a_{\text{SO}_4^{2-}} + \beta \log a_{\text{HSO}_4^-} \right) \right\} - \left[ 3 - \frac{2}{7} \left( 2 - \frac{1}{1 + \exp \{ 2.303(pH - 2.42) \} } \right) \right] \cdot pH \quad (7)
\]

where \(\alpha\) and \(\gamma\) are the molal activity and activity coefficient, respectively. Equation (7) may be approximated by the equation,

\[
\log C_{Al^{3+}} = \left\{ -\log \gamma_{Al^{3+}} - \frac{1}{7} \left( \log K + \alpha \log a_{\text{SO}_4^{2-}} + \beta \log a_{\text{HSO}_4^-} \right) \right\} - \left[ 3 - \frac{2}{7} \left( 2 - \frac{1}{1 + \exp \{ 2.303(pH - 2.42) \} } \right) \right] \cdot pH, \quad (8)
\]

since molality, \(m\), can be regarded as being nearly equal to molarity, \(C\), in dilute solutions.

According to Stability Constants\(^{(3)}\), aluminum exists in the form of three ionic species; i.e. Al\(^{3+}\), \(\text{AlSO}_4^{+}\), and \(\text{Al(}\text{SO}_4)_2\) in sulfate aqueous solutions, among which the following relationships hold,

\[
\text{Al}^{3+} + \text{SO}_4^{2-} = \text{AlSO}_4^{+} \quad \frac{C_{\text{AlSO}_4^+}}{C_{\text{Al}^{3+}} \cdot C_{\text{SO}_4^{2-}}} = 20 \quad (9)
\]

\[
\text{AlSO}_4^{+} + \text{SO}_4^{2-} = \text{Al(}\text{SO}_4)_2\) \quad \frac{C_{\text{Al(}\text{SO}_4)_2\)}}{C_{\text{AlSO}_4^+} \cdot C_{\text{SO}_4^{2-}}} = 10 \quad (10)
\]

in NaClO\(_4\)-containing aqueous solution with an ionic strength, \(I\), of 0.6 at 298 K. The ionic strength of the solutions used in the present investigation is within the range 0.25 to 0.31. However, the temperature dependence of eqs. (9) and (10) is unknown. Therefore, assuming the validity of eqs. (9) and (10) at 333 K also, the total concentration, \(C_{Al}^V\), of aluminum dissolved in sulfate aqueous solutions may be represented as

\[
C_{Al}^V = C_{Al}^{3+} + C_{\text{AlSO}_4^+} + C_{\text{Al(}\text{SO}_4)_2\} = \{ 1 + 20C_{\text{SO}_4^{2-}}(1 + 10C_{\text{SO}_4^{2-}}) \} C_{Al}^{3+}. \quad (11)
\]

Taking logarithms of eq. (11) and substituting eq. (8) in it gives

\[
\log C_{Al}^V = \left[ \log \{ 1 + 20C_{\text{SO}_4^{2-}}(1 + 10C_{\text{SO}_4^{2-}}) \} - \log \gamma_{Al^{3+}} - \frac{1}{7} \left( \log K + \alpha \log a_{\text{SO}_4^{2-}} + \beta \log a_{\text{HSO}_4^-} \right) \right] - \left[ 3 - \frac{2}{7} \left( 2 - \frac{1}{1 + \exp \{ 2.303(pH - 2.42) \} } \right) \right] \cdot pH. \quad (12)
\]

Furthermore, assuming the term which does not include pH in eq. (12) to be constant, one obtains finally

\[
\log C_{Al}^V = \text{const.} - \left[ 3 - \frac{2}{7} \left( 2 - \frac{1}{1 + \exp \{ 2.303(pH - 2.42) \} } \right) \right] \cdot pH. \quad (13)
\]

Introducing a parameter, \(\varepsilon\), defined by

\[
\varepsilon = \log \{ 1 + 20C_{SO_4^{2-}}(1 + 10C_{SO_4^{2-}}) \} - \log \gamma_{Al^{3+}} - \frac{1}{7} \left( \alpha \log a_{\text{SO}_4^{2-}} + \beta \log a_{\text{HSO}_4^-} \right), \quad (14)
\]

\(\dagger\dagger\) under the postulation that \(\alpha\) and \(\beta\) are proportional to \(a_{\text{SO}_4^{2-}}\) and \(a_{\text{HSO}_4^-}\), respectively, and that both proportionality constants are equal.
the term "const." can be expressed as

\[ \text{const.} = e^{-\frac{1}{7} \log K} \quad (15) \]

which is a constant adjustable to suit the experimental data.

Figure 4 shows the relation between \( \log C_A^\ell \) and pH-value in the first step hydrolysis. Solid portions and open circles whose longitudinal lengths indicate the scatters of chemical analysis, correspond to Runs 1 and 2, respectively. By fitting eq. (13) most closely on all the points, the value of const. was determined to be 6.79 (standard deviation = 0.03). Equation (13) with the value of const. = 6.79 is shown by a solid line in Fig. 4. The value of const. has been determined in this way. If it is possible to estimate the value of \( \varepsilon \), one can obtain the value of the equilibrium constant, \( K \), for the first step hydrolysis reaction (eq. (1)). In order to estimate the value of \( \varepsilon \), the molalities and activity coefficients of \( \text{SO}_3^2^- \) and \( \text{HSO}_4^- \) ions, the activity coefficient of \( \text{Al}^{3+} \) ion, and the ionic strength of the solution are required to be known.

2. Ionic strength of the solution and molalities of \( \text{SO}_3^- \) and \( \text{HSO}_4^- \) ions

Strictly speaking, \( \text{H}_2\text{SO}_4, \text{NaOH}, \text{Na}_2\text{SO}_4 \), and \( \text{Al}_2(\text{SO}_4)_3 \) exist in the solution. However, since the first step hydrolysis proceeds in an acidic region, the existence of \( \text{OH}^- \) ion is negligible. In this case, ions existing in the solution may be considered to be \( \text{H}^+, \text{HSO}_4^-, \text{SO}_4^{2-}, \text{Na}^+, \text{Na}_2\text{SO}_4^{-1}, \text{AlSO}_4^+, \text{Al}(\text{SO}_4)^-2 \). Their molalities can be calculated from a combination of the following relations (A)–(H).

(A) Ionic strength

\[
I = \frac{1}{2} (m_{\text{H}^+} + m_{\text{HSO}_4^-} + 4m_{\text{SO}_4^{2-}} + m_{\text{Na}^+} + m_{\text{Na}_2\text{SO}_4^{-1}} - 9m_{\text{Al}^{3+}} + m_{\text{AlSO}_4^+} + m_{\text{Al}(\text{SO}_4)^-2}) \quad (16)
\]

(B) Dissociation quotient \( \left( \frac{m_{\text{H}^+} \cdot m_{\text{SO}_4^{2-}}}{m_{\text{HSO}_4^-}} \right) \) of \( \text{HSO}_4^- \) ion

Baes\(^{(5)}\) has analyzed the relation between the bisulfate ion dissociation quotient at 298 K and the ionic strength provided by the Raman measurements of Young and co-workers\(^{(6)}\) by using an equation of the form

\[
\text{log} \left( \frac{m_{\text{H}^+} \cdot m_{\text{SO}_4^{2-}}}{m_{\text{HSO}_4^-}} \right)_{298K} = \text{log} D + A \sqrt{I} / (1 + B \sqrt{I})
\]

In order to extend the application of eq. (17) to the temperature (333 K) used in this investigation, the values of \( A, B \) and \( D \) were determined as follows. The antilogarithm of the first term on the right-hand side of eq. (17); i.e. the value, 0.0102, approximately agrees with the equilibrium constant of eq. (5) calculated from the standard free energies of formation of \( \text{HSO}_4^- \) and \( \text{SO}_4^{2-} \) ions at 298 K. Therefore, the value of \( D \) for 333 K also was similarly determined from the standard free energies of formation of \( \text{HSO}_4^- \) and \( \text{SO}_4^{2-} \) ions at 333 K calculated from the data at 298 K by using the correspondence principle\(^{(2)}\). On the other hand, the second term, assuming \( \gamma_{\text{H}^+} = \gamma_{\text{HSO}_4^-} \)

\[ \frac{2.036 \sqrt{I}}{1 + 0.4 \sqrt{I}} \quad (17) \]

\(^{\dagger}\) In the previous paper\(^{(4)}\) NaSO\(_4^-\) ion was not considered.
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(when comparing Fig. 5 with Fig. 9 shown below, this assumption may be considered to be valid under the condition of sulfuric acid concentration around 0.1 mol·kg⁻¹ and ionic strength of around 0.3), corresponds to a Debye-Hückel expression, \( A \sqrt{I} / (1 + B \sqrt{I}) \), concerning the activity coefficient of the SO₄²⁻ ion. Then, the values of \( A \) and \( B \) are proportional to \( (\eta T)^{-3/2} \) and \( (\eta T)^{-1/2} \), respectively, where \( \eta \) is the dielectric constant of water and \( T \) the absolute temperature. The dissociation quotient of eq. (5) for 333 K obtained in this way may be represented as

\[
\log \left( \frac{m_{H} \cdot m_{SO_{4}}}{m_{HSO_{4}}} \right)_{333 \, K} = -2.420 + \frac{2.188 \sqrt{I}}{1 + 0.41 \sqrt{I}}.
\]  

(C) pH-value of the solution

Awakura et al.\(^{(7)}\) have measured the activity of the H⁺ ion for the ternary system H₂SO₄-Na₂SO₄-H₂O at 298K. Analysing their results on the basis of

\[
\log \gamma_{H^+} = \frac{A \sqrt{I}}{1 + \sqrt{I}} + bI + c,
\]  

one obtains the following relations for \( b \) and \( c \) (see the next section):

\[
b = -0.516m_{H_{2}SO_{4}}^{0.264} + 0.283. 
\]  

\[
c = 0.683m_{H_{2}SO_{4}}^{0.593} + 0.144. 
\]  

The numerical value of \( A \) is 0.5471\(^{(8)}\) at 333 K. Equations (20) and (21) are assumed to be applicable to the temperature of 333 K also, because the temperature dependencies of \( b \) and \( c \) are unknown.

(D) Mass balance of SO₄²⁻

\[
m_{HSO_{4}} + m_{SO_{4}} + m_{NaSO_{4}} + m_{AlSO_{4}} + 2m_{Al(SO_{4})_{2}} = m_{SO_{4}}^{T}
\]  

where \( m^{T} \) is the total molality determined by the chemical analysis.

(E) Mass balance of Al(III)

\[
m_{Al^{3+}} + m_{AlSO_{4}} + m_{Al(SO_{4})_{2}} = m_{Al}^{T}.
\]  

(F) Mass balance of Na(I)

\[
m_{Na^{+}} + m_{NaSO_{4}} = m_{Na}^{T}.
\]  

(G) Stepwise formation constant of Na(I) sulfato complex\(^{(3)}\)

\[
\frac{C_{NaSO_{4}}}{C_{Na^{+}} \cdot C_{SO_{4}}^{2-}} = 5.25.
\]  

(H) Stepwise formation constants of Al(III) sulfato complexes

Equations (9) and (10) are used.

3. Activity coefficients of H⁺, HSO₄⁻ and SO₄²⁻ ions for the ternary system H₂SO₄-Na₂SO₄-H₂O at 298 K

Awakura et al.\(^{(7)}\) have reported the activities of H⁺, HSO₄⁻ and SO₄²⁻ ions for the ternary system H₂SO₄-Na₂SO₄-H₂O at 298 K. The corresponding molalities of those ions can be obtained by solving the following simultaneous equations:

\[
I = \frac{1}{2}(m_{H^{+}} + m_{HSO_{4}^{-}} + 4m_{SO_{4}^{2-}} + m_{Na^{+}} + m_{NaSO_{4}^{-}}),
\]  

\[
\log \left( \frac{m_{H^{+}} \cdot m_{SO_{4}^{2-}}}{m_{HSO_{4}^{-}}} \right)_{298 \, K} = -1.991 + \frac{2.036 \sqrt{I}}{1 + 0.4 \sqrt{I}}.
\]  

\[
m_{H^{+}} + m_{HSO_{4}^{-}} = 2m_{H_{2}SO_{4}},
\]  

\[
m_{Na^{+}} + m_{NaSO_{4}^{-}} = 2m_{Na_{2}SO_{4}},
\]  

\[
m_{HSO_{4}^{-}} + m_{SO_{4}^{2-}} + m_{NaSO_{4}^{-}} = m_{H_{2}SO_{4}} + m_{Na_{2}SO_{4}},
\]  

\[
\frac{m_{NaSO_{4}^{-}}}{m_{Na^{+}} \cdot m_{SO_{4}^{2-}}} = 5.25.
\]  

Accordingly, the activity coefficients of those ions can be calculated from both activity and molality.

(I) Activity coefficient of the H⁺ ion

Figure 5 indicates the relation between the activity coefficients of the H⁺ ion obtained in the above described manner and the ionic strengths. By using \( m_{H_{2}SO_{4}} \) as a parameter, this relation was analysed on the basis of eq. (19), in which the value of \( A \) is 0.5092\(^{(8)}\) at 298 K. Equation (19) reveals that a plot of \( \log \gamma_{H^{+}} + \{0.5092 \sqrt{I} / (1 + \sqrt{I})\} \) against \( I \) for a given molality of H₂SO₄ yields a linear relationship. Figure 6 shows the results obtained for six different molalities of H₂SO₄. There are
good linear relationships between them, except for the regions of relatively high ionic strength at each molality of H$_2$SO$_4$. Plots of the values of the slope (b) and the intercept (c) of each straight line determined by the method of least squares against $m_{H_2SO_4}$ are shown with dark circles in Figs. 7 and 8, respectively, which were regressed by using an equation of the

Fig. 5 Relation between activity coefficient of H$^+$ ion and ionic strength for the system H$_2$SO$_4$-Na$_2$SO$_4$-H$_2$O at 298 K.

Fig. 6 \( \log \gamma_{H^+} + 0.5092 \sqrt{I/(1+\sqrt{I})} \) vs $I$ for the system H$_2$SO$_4$-Na$_2$SO$_4$-H$_2$O at 298 K.

Fig. 7 Dependence of $b$-value in the eqs. (19), (32) and (35) on $m_{H_2SO_4}$.

Fig. 8 Dependence of $c$-value in the eqs. (19), (32) and (35) on $m_{H_2SO_4}$. 
form of $b$ or $c = a_q m_{H_2SO_4} + q$ as
\[ b = -0.516 m_{H_2SO_4}^{-0.264} + 0.283. \tag{20} \]
\[ c = 0.683 m_{H_2SO_4}^{0.593} + 0.144. \tag{21} \]

From eqs. (19)–(21), one can obtain by calculation the value of $\gamma_{H^+}$ at any molality of $H_2SO_4$ for the ternary system $H_2SO_4-Na_2SO_4-H_2O$.

(2) Activity coefficient of the $HSO_4^-$ ion

Figure 9 indicates the relations between $\gamma_{HSO_4^-}$ and $I$, which are undistinguished from each other at $m_{H_2SO_4} \leq 0.2 \text{ mol} \cdot \text{kg}^{-1}$. As in the case of the $H^+$ ion, $\log \gamma_{HSO_4^-} + \{A \sqrt{I}/(1 + \sqrt{I})\}$ was plotted against $I$ as shown in Fig. 10. In the case of $m_{H_2SO_4} \leq 0.2 \text{ mol} \cdot \text{kg}^{-1}$, the relation between them may be approximated by a straight line common to any molality of $H_2SO_4$; i.e. $m_{H_2SO_4} \leq 0.2$:

\[ \log \gamma_{HSO_4^-} = -\frac{0.5092 \sqrt{I}}{1 + \sqrt{I}} + 0.276I - 0.0823. \tag{31} \]

The following relations were obtained for

$m_{H_2SO_4} = 0.5 - 2.0 \text{ mol} \cdot \text{kg}^{-1}$, respectively:

\[ \log \gamma_{HSO_4^-} = -\frac{0.5092 \sqrt{I}}{1 + \sqrt{I}} + bI + c \tag{32} \]

where

\[ b = 0.288 \tag{33} \]
\[ c = 0.285 m_{H_2SO_4}^{-1.04} - 0.737. \tag{34} \]

(3) Activity coefficient of the $SO_4^{2-}$ ion

In the case of the $SO_4^{2-}$ ion also, the relations corresponding to Fig. 5 for $H^+$ ion and Fig. 9 for $H_2SO_4$ ion are shown in Fig. 11, and those corresponding to Fig. 6 for $H^+$ ion and Fig. 10 for $HSO_4^-$ ion, in Fig. 12. In this case, the activity coefficient of the $SO_4^{2-}$ ion is expressed as

\[ \log \gamma_{SO_4^{2-}} = \frac{-AZ^2 \sqrt{I}}{1 + \sqrt{I}} + bI + c \tag{35} \]

where $z$ is the electric charge on ions which is $-2$ for the $SO_4^{2-}$ ion. Plots of the value of $b$ and $c$ against $m_{H_2SO_4}$ are represented by the symbol, ▲, in Figs. 7 and 8, respectively, from which the following relations can be obtained between $b$ or $c$ and $m_{H_2SO_4}$:

![Fig. 9 Relation between activity coefficient of $HSO_4^-$ ion and ionic strength for the system $H_2SO_4-Na_2SO_4-H_2O$ at 298 K.](image)
b = 0.0260 m_{H_{2}SO_{4}}^{0.976} + 0.348. \quad (36)

c = -1.39 m_{H_{2}SO_{4}}^{0.686} - 0.166. \quad (37)

4. Activity coefficients of the H\(^{+}\), HSO\(^{-}\)\(_{4}\) and SO\(^{2-}\)\(_{4}\) ions of the solution at 333 K used in this investigation

In the calculation, the following were assumed.

(i) The solution used in this investigation may be regarded approximately as the ternary system H\(_{2}\)SO\(_{4}\)-Na\(_{2}\)SO\(_{4}\)-H\(_{2}\)O, since the concentration of aluminum is much less than that of sodium in the first step hydrolysis.

(ii) The value of \(A\) of the Debye-Hückel expression depends only on temperature, while the values of \(b\) and \(c\) are independent of temperature.

Under these assumptions, the activity coefficients of the H\(^{+}\), HSO\(^{-}\)\(_{4}\), and SO\(^{2-}\)\(_{4}\) ions of the solution at 333 K used in this investigation can be calculated from eqs. (19), (20), (21), (35), (36) and (37).

5. Activity coefficient of the Al\(^{3+}\) ion

As mentioned in the section IV.2, the solution used in this investigation can be regarded as the Al\(_{2}\)(SO\(_{4}\))\(_{3}\)-Na\(_{2}\)SO\(_{4}\)-H\(_{2}\)SO\(_{4}\)-H\(_{2}\)O system. By applying Meissner’s empirical procedure\(^{(9)-(12)}\) to this system, the total mean activity coefficient of Al\(_{2}\)(SO\(_{4}\))\(_{3}\), and hence its activity in the solution can be estimated. This activity, \(a\), is related to molalities, \(m\), of free Al\(^{3+}\) and SO\(^{2-}\)\(_{4}\) ions and their free mean activity coefficients, \(\gamma\), by the equation,

\[ a_{Al_{2}(SO_{4})_{3}} = \gamma_{Al^{3+}} \cdot \gamma_{SO_{4}^{2-}} \cdot m_{Al^{3+}} \cdot m_{SO_{4}^{2-}}, \quad (38) \]

from which the value of \(\gamma_{Al^{3+}}\) can be determined by calculating the values of \(m_{Al^{3+}}\) and \(m_{SO_{4}^{2-}}\) and \(\gamma_{SO_{4}^{2-}}\) with the aid of the methods described in the sections IV.2 and IV.3, respectively.

6. Equilibrium constant of the first step hydrolysis reaction, standard free energy of formation of Al\(_{2}\)(SO\(_{4}\)(OH))\(_{7}\) and pH-dependence of its solubility

The value of \(\varepsilon\) calculated from the molalities and/or activity coefficients of H\(^{+}\), HSO\(^{-}\)\(_{4}\), SO\(^{2-}\)\(_{4}\) and Al\(^{3+}\) ions obtained in the above way is
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listed in Table 3. The deviation of $\varepsilon$ from its mean value in the first step hydrolysis is 9% or so. This fact demonstrates the validity of the assumption, made in the section IV.1, that the term not including pH in eq. (12) is constant. From the value of $\varepsilon$ obtained, the equilibrium constant of the first step hydrolysis reaction and the standard free energy of formation of Al$_7$(SO$_4$)$_2$(OH)$_{17}$ at 333 K were calculated and their values are also listed in Table 3.

The value of $\varepsilon$, as mentioned above, remains almost constant throughout the first step hydrolysis. Therefore, as long as the composition of the solution immediately before the beginning of the first step hydrolysis reaction is known, the value of const. can be estimated from the value of the standard free energy of formation of Al$_7$(SO$_4$)$_2$(OH)$_{17}$ listed in Table 3. Accordingly, from eqs. (13) and (15), one can determine the pH-dependence of the solubility of Al$_7$(SO$_4$)$_2$(OH)$_{17}$ by using the value of const. as a parameter. The results obtained for various values of const. are shown with dashed lines in Fig. 4. That is to say, if the composition of the solution prior to the first step hydrolysis reaction is known, it is possible to judge which solubility line should be used.

## V. Conclusions

From the present thermodynamic investigation on the behavior of aluminum during the hydrolysis operation of aluminum sulfate aqueous solution containing Al$_2$(SO$_4$)$_3$ less than 0.05 kmol·m$^{-3}$ with sodium hydroxide solution, it was found that (i) the hydrolysis proceeded in two steps, (ii) Precipitates produced in the first and second step hydrolysies were Al$_7$(SO$_4$)$_2$(OH)$_{17}$·xH$_2$O and Al(OH)$_3$, respectively. (iii) the first and second step hydrolyses were represented by $7\text{Al}^{3+} + \alpha\text{SO}_4^{2-} + \beta\text{HSO}_4^- + 17\text{H}_2\text{O} = \text{Al}_7(\text{SO}_4)_2(\text{OH})_{17} + (17 + \beta)\text{H}^+$, where $\alpha + \beta = 2$, and Al$_7$(SO$_4$)$_2$(OH)$_{17}$ + 4H$_2$O = Al(OH)$_3$ + 2H$_2$SO$_4$, respectively, (iv) log $K = -35.6 \pm 1.1$, where $K$ is the equilibrium constant of the first step hydrolysis at 333 K, and (v) the standard free energy of formation of Al$_7$(SO$_4$)$_2$(OH)$_{17}$ at 333 K was $-8489 \pm 7$ kJ·mol$^{-1}$. In addition, the pH-dependence of the solubility of Al$_7$(SO$_4$)$_2$(OH)$_{17}$ was also determined. Furthermore, a method was proposed which enables one to calculate the activity coefficients of H$^+$, HSO$_4^-$ and SO$_4^{2-}$ ions in the ternary system H$_2$SO$_4$-Na$_2$SO$_4$-H$_2$O as a function of ionic strength by using H$_2$SO$_4$-molality as a parameter.

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