Thermodynamic Properties of Ga(III)-Hydroxysalt in Sulfate Aqueous Solution*

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The present investigation was carried out to examine the chemical composition of precipitates produced during a titration of aqueous solution containing gallium sulfate with sodium hydroxide, to obtain the standard free energy of formation of Ga(III)-hydroxysalt, and to determine the pH-dependence of its solubility at 333 K.

The results obtained are summarized as follows.

(1) The hydrolysis proceeds via two steps. The precipitates produced in the first and second step hydrolyses were identified to be \( \{Na_x{(H_2O)}_{1-x}\}Ga_3(SO_4)_2(OH)_6 \), where the value of \( x \) varies with the composition of the solution, and GaOOH, respectively. These hydrolysis reactions are represented by \( xNa^++3Ga^3++\alpha SO_4^{2-}+\beta HSO_4^-+(7-x)H_2O=\{Na_x{(H_2O)}_{1-x}\}Ga_3(SO_4)_2(OH)_6+(5+x+\beta)H^+ \), \( \alpha+\beta=2 \), and \( \{Na_x{(H_2O)}_{1-x}\}Ga_3(SO_4)_2(OH)_6+(x-1)H_2O=3GaOOH+(x/2)Na_2SO_4+{(4-x)/2}H_2SO_4 \).

(2) The standard free energies of formation of \( \{Na_x{(H_2O)}_{1-x}\}Ga_3(SO_4)_2(OH)_6 \) were obtained for the \( x \)-values of 0.13, 0.22, 0.38 and 0.66 at 333 K.

(3) The pH-dependence of the solubility of \( \{Na_x{(H_2O)}_{1-x}\}Ga_3(SO_4)_2(OH)_6 \) was determined for various choices of the parameter, which can be calculated from the initial composition of solutions.

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I. Introduction

Ion activity-pH diagrams for the metal-H_2O systems, which are often referred to as the theoretical background for precipitation operation, are not always useful for more complicated aqueous solution systems containing sulfate ions which have a strong tendency to form sulfato-complexes with metal ions. From this standpoint, the authors have planned a series of investigations, 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, and have already reported on aluminum(1)(2).

In this investigation, gallium was selected to examine its thermodynamic behavior in the hydrolysis operation of gallium sulfate aqueous solution with sodium hydroxide solution and to determine the chemical composition of precipitate produced in the first step hydrolysis, its standard free energy of formation as well as the pH-dependence of its solubility at 333 K.

II. Experimental

The apparatus used is quite similar to that described in previous papers(1)(2). In order to obtain the desired pH-value and Ga(III)-concentration in the solution, first, sulfuric acid and then gallium sulfate were added to 1 dm³ of double distilled water in a 2 dm³ flask, which has five arms to install electrodes for measuring pH- and potential-values, and impeller, a thermometer, a NaOH-solution supplying tube, etc. 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 kmol·m⁻³ NaOH-solution was

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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 precipitates were taken and chemically analysed (Ga(III) and Na(I): atomic absorption spectrochemical analysis, \((\text{SO}_4^{2-})_{\text{Tot}}\): BaSO\(_4\)-gravimetric analysis, where the subscript "Tot" is an abbreviation of "Total") to determine their chemical composition. The precipitates were also identified qualitatively by X-ray diffraction analysis. Table 1 shows the initial composition of the solutions immediately before the beginning of the first step hydrolysis reaction (see section III.2). The figures listed in the table indicate the total molarity of Na(I) added as Na\(_2\)SO\(_4\) and NaOH, that of Ga(III) added as Ga\(_2\)(SO\(_4\))\(_3\), and that of \(\text{SO}_4^{2-}\) added as Na\(_2\)SO\(_4\), Ga\(_2\)(SO\(_4\))\(_3\), and H\(_2\)SO\(_4\).

All the chemicals used in this investigation are of reagent grade.

### III. Experimental Results

1. Variations of the pH-value with time

Neutralization of the solution, as seen from the titration curves shown afterwards, proceeds in three steps; i.e. neutralization of the acid and the first and second step hydrolyses. 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 kmol\(\cdot\)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 rapidly. In contrast to this, it took about 36 ks(10 h) and 40 ks(11 h) in the first and second step hydrolyses, respectively, to attain the corresponding equilibrium pH-value. 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 the equilibrium ones.

2. Titration curves and composition of precipitates produced by hydrolysis

The relations between the amounts of NaOH added and the equilibrium pH-values obtained in the above way are indicated in Fig. 2. It can be seen from this figure that, as in the case of aluminium\(^{(1)(2)}\) the hydrolysis reaction proceeds in two steps. When the molar ratio of Ga(III) to Na\(_2\)SO\(_4\) in the solution is about 1.5(Run 1), the first step hydrolysis reaction begins to occur at the pH-value of around 1.4. The pH-value at which the first step hydrolysis reaction is initiated shifts to the higher pH-region as this molar ratio decreases to 0.5 (Runs 2 and 3) and 0.01 (Run 4). The second step hydrolysis reaction takes place at a pH-value of 5.4-5.7, independent of Ga(III)-concentration. After the establishment of equilibrium of the first and second step hydrolyses, the respective precipitates were taken,
decanted, washed in water and filtered at room temperature repeatedly till no sulfate ion was detected, dried slowly at a temperature of around 323 K, and analysed for Na(I), Ga(III) and SO$_4^{2-}$. The molar ratio of Na(I) and Ga(III) to SO$_4^{2-}$ obtained from their analytical values are tabulated in Table 2. For the first step hydrolysis reaction products, setting the number of moles of SO$_4^{2-}$ equal to 2, that of Ga(III) becomes nearly equal to 3, while that of Na(I) takes the value of 0.13 to 0.66. Judging from the present results, as long as the molar ratio of Na(I) to Ga(III) in the solution immediately before the beginning of the first step hydrolysis reaction is larger than 1.3, the Ga(III)-hydroxysalt of higher Na(I)-content is likely to be produced with increasing Ga(III)-concentration in the solution. The same tendency was observed with indium$^{3+}$. From the above molar ratios of the first step hydrolysis reaction products and, in addition, their mass balance and electro-neutrality, regarding them as $\{Na_x\cdot(H_3O)_{1-x}\}Ga_3(SO_4)_2(OH)_6\cdot(H_2O)$, the sum of weight percentages of their constituents; i.e. $%Na(I) + %H_2O(I) + %Ga(III) + %SO_4^{2-} + %OH^-$ results in almost 100%. Their X-ray diffraction patterns agreed with those of $Ga_3H(SO_4)_2(OH)_6\cdot H_2O$ and $NaGa_3(SO_4)_2(OH)_6\cdot H_2O$ listed in the data cards of the American Society of Testing Materials. From these results, the first step hydrolysis reaction may be represented as

$$xNa^+ + 3Ga^{3+} + aSO_4^{2-} + \beta HSO_4^- + (7-x)H_2O = \{Na_{x+\beta}\cdot(H_3O)^{1-x}\}Ga_3(SO_4)_2(OH)_6$$

$$+(5+x+\beta)H^+ \quad (1)$$

where

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

Neither Na(I) nor SO$_4^{2-}$ was analytically detected from the second step hydrolysis reaction product, which was identified as GaOOH by X-ray diffraction analysis. From these facts, the second step hydrolysis reaction may be written as

$$\{Na_{x+\beta}\cdot(H_3O)^{1-x}\}Ga_3(SO_4)_2(OH)_6 + (x-1)H_2O \rightarrow 3GaOOH + \frac{x}{2}Na_2SO_4 + \frac{4-x}{2}H_2SO_4. \quad (3)$$

By the way, the question arose whether or not the first and second step hydrolysis reaction products changed their chemical form during the washing and drying operations. To make clear this, the X-ray diffraction patterns of the products collected directly from the solution were compared with those of washed as well as washed and dried ones. There was no difference among their patterns.

### 3. Thermodynamic stability of the first step hydrolysis reaction products

In order to ascertain whether or not the first step hydrolysis reaction product was thermodynamically stable, the pH-value of the
solution of Run 4 (shown with dark circles in Fig. 2) after completion of the second step hydrolysis reaction, was brought back to the pH-region in which the first step hydrolysis reaction occurred. After standing for 260 ks (3 days), the resulting precipitate was chemically analysed. The contents of Na(I) and SO_4^{2-} in the precipitate increased 0 to 0.1% and 0 to 1.12%, respectively, through this procedure. However, their changes were too small to clearly confirm the thermodynamic stability of the first step hydrolysis reaction product. The conversion of the second step hydrolysis reaction product (GaOOH) to the first step hydrolysis reaction one is, in comparison with the backward reaction, extremely slow, particularly after the completion of the reaction on the surface of the precipitate particles, since it accompanies the incorporation of Na(I) and SO_4^{2-} into GaOOH. Accordingly, in order to obtain a more clear perception of the conversion of the second step hydrolysis reaction product to the first step hydrolysis reaction product, it is required first to make the second step hydrolysis reaction product consisting of particles as fine as possible. According to our experience, this can be realized by adding NaOH-solution into the gallium sulfate acidic aqueous solution instantaneously. Therefore, the following experiment was carried out.

A solution was made up from gallium sulfate and sulfuric acid to contain Ga(III) of 0.099 kmol·m^{-3} and (SO_4^{2-})_Tot of 0.182 kmol·m^{-3} and to have a pH-value of 1.56. The amount of 2.5 kmol·m^{-3} NaOH-solution required for completion of the first step hydrolysis reaction only was added instantaneously into this solution which was agitated by the impeller at a constant rotational speed and maintained at 333 K in argon atmosphere. Figure 3 shows the changes of the pH-value, Ga(III)-concentration in the solution, and SO_4^{2-} content in the precipitate with time. The pH-value immediately after the addition of NaOH-solution was ca. 3.4, which was in the region bringing about the first step hydrolysis reaction. After that, the pH-value gradually decreased during the first 9 ks, had a minimum during the period of 9-14.4 ks, then slowly rose over a period of about 190 ks, and finally reached a constant value. The Ga(III)-concentration in the solution fell down to 1.0-1.2 mol·m^{-3} rapidly after the addition of NaOH-solution, and was then lowered exponentially to approach zero in about 60 ks. The SO_4^{2-} content in the precipitate increased with time, while the rate of its increase was gradually lowered.

The changes mentioned above can be explained by using the experimental results shown in Fig. 2. In time period ranging from zero to about 60 ks in which the Ga(III)-concentration in the solution is lowered exponentially, the first step hydrolysis reaction (eq. (1)); i.e. the reaction producing the acid may be reasonably considered to occur from the corresponding pH-region, and in addition, the backward reaction of eq. (3); i.e. the reaction consuming the acid, proceeds simultaneously, because the instantaneous addition of NaOH-solution permits the second step hydrolysis reaction precipitate; i.e. GaOOH, to be produced. While the rate of the acid producing reaction is greater than that of the acid consuming one, the pH-value of the solution is lowered, takes the minimum when the rates are balanced, and is raised after the rate of the acid producing reaction becomes smaller than that of the acid consuming one. When both reactions come to a halt, the pH-value remains constant again. The SO_4^{2-} content in the precipitate is increased by both acid producing and consuming reactions. Particularly, the increase of the SO_4^{2-} content in the precipitate with time even after the Ga(III)-concentration in the solution reached almost zero reveals that the acid consuming reaction; i.e. the conver-
sion of the second step hydrolysis reaction product to the first step hydrolysis reaction one must have surely occurred. As is seen from the above, the experimental results shown in Fig. 3 cannot be consistently explained without considering the conversion of the second step hydrolysis reaction product to the first step hydrolysis reaction one. It is, therefore, reasonable to consider that the first step hydrolysis reaction product is thermodynamically stable in a certain pH-region.

IV. Discussion

For arguing 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 gallium concentration and pH-value in the solution

From eq. (4); i.e. the equilibrium constant of eq. (1),

$$K_i = \frac{a_{\text{Ga}^{3+}}(5+x+y)}{a_{\text{Na}^+} \cdot a_{\text{Ga}^{3+}} \cdot a_{\text{SO}_4^{2-}} \cdot a_{\text{HSO}_4^-}}$$

and eq. (6) representing the dissociation equilibrium of HSO$_4^-$ ion at 333 K,

$$\text{HSO}_4^- = \text{H}^+ + \text{SO}_4^{2-}$$

one obtains a relation between molality of Ga$^{3+}$ ion, $m_{\text{Ga}^{3+}}$, and the pH-value,

$$\log m_{\text{Ga}^{3+}} = \left\{ -\log \gamma_{\text{Ga}^{3+}} - \frac{1}{3} (\log K_i + x \log a_{\text{Na}^+} + \alpha \log a_{\text{SO}_4^{2-}} + \beta \log a_{\text{HSO}_4^-}) \right\}$$

$$- \left[ \frac{5 + x}{3} + \frac{2}{3[1 + \exp \{2.303(pH - 2.42)\}]} \right] \cdot \text{pH},$$

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

$$\log C_{\text{Ga}^{3+}} = \left\{ -\log \gamma_{\text{Ga}^{3+}} - \frac{1}{3} (\log K_i + x \log a_{\text{Na}^+} + \alpha \log a_{\text{SO}_4^{2-}} + \beta \log a_{\text{HSO}_4^-}) \right\}$$

$$- \left[ \frac{5 + x}{3} + \frac{2}{3[1 + \exp \{2.303(pH - 2.42)\}]} \right] \cdot \text{pH},$$

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

According to Stability Constants, gallium exists in the form of two ionic species; i.e. Ga$^{3+}$ and GaSO$_4^+$ in sulfate aqueous solutions. The following relationship holds between their molarities at 298 K.

$$\text{Ga}^{3+} + \text{SO}_4^{2-} = \text{GaSO}_4^+,$$  \hspace{1cm} \frac{C_{\text{GaSO}_4^+}}{C_{\text{Ga}^{3+}} \cdot C_{\text{SO}_4^{2-}}} = 977 \hspace{1cm} (9)$$

Since the temperature dependence of eq. (9) is unknown, assuming the validity of eq. (9) at 333 K also, the total concentration, $C_{\text{Ga}}^T$, of gallium dissolved in sulfate aqueous solution may be represented as

$$C_{\text{Ga}}^T = C_{\text{Ga}^{3+}} + C_{\text{GaSO}_4^+} = (1 + 977C_{\text{SO}_4^{2-}})C_{\text{Ga}^{3+}}.$$

Taking logarithm of eq. (10) and substituting eq. (8) into it gives
Furthermore, assuming the sum of the terms not including pH in eq. (11) to be constant, one finally obtains

$$\log C_{Ga}^\alpha = \text{const.} - \left[ \frac{5 + x}{3} \left( \frac{2}{3[1 + \exp \{2.303(pH - 2.42)\}] \right) \right] \cdot pH. \tag{12}$$

Introducing a parameter, $\varepsilon$, defined by

$$\varepsilon = \log (1 + 977C_{SO_4}^-) - \left\{ \log y_{Ga}^\alpha + \frac{1}{3} (x \log a_{Na^+} + \alpha \log a_{SO_4^-} + \beta \log a_{HSO_4^-}) \right\}, \tag{13}$$

the term "const." can be expressed as

$$\text{const.} = \varepsilon - \frac{1}{3} \log K_1 \tag{14}$$

which is a constant adjustable to fit the experimental data.

The relations between $\log C_{Ga}^\alpha$ and pH-value at equilibrium of the first step hydrolysis reaction are shown by the symbols, ○ (Run 2), ⊗ (Run 3), ● (Run 4), and ■ (Run 1) in Figs. 4–7 for four kinds of Ga(III)-hydroxysalts with different Na(I)-content. By fitting eq. (12) most closely on all data points in each figure, the values of const. were determined to be 2.49 (standard deviation $\sigma = 0.05$), 2.75 ($\sigma = 0.07$), 2.96 ($\sigma = 0.09$) and 2.81 ($\sigma = 0.14$) for $x = 0.13, 0.22, 0.38$ and 0.66, respectively. Such small values of the standard deviation demonstrate the validity of the assumption made above that the sum of the terms not including pH in eq. (11) is constant. Using const. = 2.49, 2.75, 2.96 and 2.81, the relationships of eq. (12) are shown by each heavy solid line in Figs. 4–7. Since the values of const. had been determined in this way, if it is possible to estimate the value of $\varepsilon$, one can obtain the values of the equilibrium constant, $K_1$, for the first step hydrolysis reaction of eq. (1). In order to estimate the value of $\varepsilon$, the molalities and activity coefficients of $Na^+$, $SO_4^{2-}$, and $HSO_4^-$ ions, activity coefficient of $Ga^{3+}$ ion, and ionic strength of the solution are required to be known.

2. Ionic strength of the solution and molalities of $Na^+$, $SO_4^{2-}$ and $HSO_4^-$ ions

Strictly speaking, $H_2SO_4$, $NaOH$, $Na_2SO_4$ and $Ga_2(SO_4)_3$ exist in the solution. However, the first step hydrolysis proceeds in a region so acidic that the existence of $OH^-$ ion is negligible. In this case, ions existing in the solution may be considered to be $H^+$, $HSO_4^-$, $SO_4^{2-}$,
Na$^+$, NaSO$_4^-$, Ga$^{3+}$ and GaSO$_4^+$, Their molalities can be calculated from a combination of the relations (A)–(H).

A) Ionic strength, $I$

\[
I = \frac{1}{2} (m_{H^+} + m_{HSO_4^-} + 4m_{SO_4^{2-}} + m_{Na^+} + m_{NaSO_4} + 9m_{Ga^{3+}} + m_{GaSO_4^+}).
\]

B) Dissociation quotient $(m_{H^+} \cdot m_{SO_4^{2-}} / m_{HSO_4^-})$ of HSO$_4^-$ ion

\[
\log \left( \frac{m_{H^+} \cdot m_{SO_4^{2-}}}{m_{HSO_4^-}} \right)_{333K} = -2.420 + \frac{2.188}{1 + 0.41} \sqrt{I}.
\]

C) pH-value of the solution

\[
pH = - \log a_{H^+} = - \log \gamma_{H^+} - \log m_{H^+},
\]

\[
\log \gamma_{H^+} = -\frac{0.5471}{1 + \sqrt{I}} + bI + C,
\]

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

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

D) Mass balance of SO$_4^{2-}$

\[
m_{HSO_4^-} + m_{SO_4^{2-}} + m_{NaSO_4} + m_{GaSO_4^+} = m_{SO_4^{2-}}.
\]
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(E) Mass balance of Ga(III)
\[ m_{Ga^{3+}} + m_{GaSO_4} = m_{Ga^{3+}} \] (22)

(F) Mass balance of Na(I)
\[ m_{Na^{+}} + m_{NaSO_4} = m_{Na^{+}} \] (23)

(G) Stepwise formation constant of Na(I) sulfato-complex
Equation (9) is used by approximating C to be nearly equal to m.

(H) Stepwise formation constant of Ga(III) sulfato-complex

Equation (9) is used by approximating C to be nearly equal to m.

3. Activity coefficients of HSO\textsuperscript{4} and SO\textsubscript{4}\textsuperscript{2-} ions for the ternary system Na\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O at 298 K

Awakura et al.\textsuperscript{(6)} have reported the activities of H\textsuperscript{+}, HSO\textsuperscript{4}, and SO\textsubscript{4}\textsuperscript{2-} ions for the ternary system Na\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O at 298 K. The molalities of those ions can be obtained by solving the following simultaneous equations:

\[ I = \frac{1}{2} (m_{H^{+}} + m_{HSO_{4}^{-}} + 4m_{SO_{4}^{2-}} + m_{Na^{+}} + m_{NaSO_{4}^{-}}), \] (25)

\[ \log \left( \frac{m_{H^{+}} \cdot m_{SO_{4}^{2-}}}{m_{HSO_{4}^{-}}} \right)_{298K} = -1.991 + \frac{2.036 \sqrt{I}}{1 + 0.4 \sqrt{I}}, \] (26)

\[ m_{H^{+}} + m_{HSO_{4}^{-}} = 2m_{H_{2}SO_{4}}, \] (27)

\[ m_{Na^{+}} + m_{NaSO_{4}^{-}} = 2m_{Na_{2}SO_{4}}, \] (28)

\[ m_{HSO_{4}^{-}} + m_{SO_{4}^{2-}} = m_{H_{2}SO_{4}} + m_{Na_{2}SO_{4}}. \] (29)

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

The authors have analysed the activity coefficients of HSO\textsuperscript{4} and SO\textsubscript{4}\textsuperscript{2-} ions obtained in this way as a function of ionic strength by using \( m_{H_{2}SO_{4}} \) as a parameter on the basis of the following equation\textsuperscript{(3)}:

\[ \log \gamma_i = -A z_i^2 \sqrt{I} + b I + c, \] (30)

where \( z_i \) is the electric charge on ions, \( i \), and \( A \) is equal to 0.5092\textsuperscript{(7)} at 298 K. The results obtained are summarized as follows.

1. Activity coefficient of HSO\textsuperscript{4} ion
\[ m_{H_{2}SO_{4}} = 0.1 - 0.2: \]
\[ b = 0.276, \quad c = -0.0823. \] (31)

2. Activity coefficient of SO\textsubscript{4}\textsuperscript{2-} ion
\[ m_{H_{2}SO_{4}} = 0.1 - 2.0: \]
\[ b = 0.288 \quad c = 0.285m_{H_{2}SO_{4}}^{1.04} - 0.737 \] (32).

4. Activity coefficients of HSO\textsuperscript{4} and SO\textsubscript{4}\textsuperscript{2-} ions in the solution at 333 K used in this investigation

In calculation, the following items were assumed.

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

(ii) The value of \( A \) of the Debye-Hückel expression depends only on temperature \( (A = 0.5471 \textsuperscript{(7)} \) at 333 K), while the values of \( b \) and \( c \) are independent of temperature.

Under these assumptions, the activity coefficients of HSO\textsuperscript{4} and SO\textsubscript{4}\textsuperscript{2-} ions in the solution at 333 K used in this investigation can be calculated from eqs. (30), (31) and (33).

5. Activity coefficients of the Ga\textsuperscript{3+} ion and activity of the Na\textsuperscript{+} ion

As mentioned in section IV. 2, the solution used in this investigation can be regarded as the Ga\textsubscript{2}(SO\textsubscript{4})\textsubscript{3}-Na\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}SO\textsubscript{4}-H\textsubscript{2}O system. By applying Meissner's empirical procedure\textsuperscript{(8)-(11)} to this system, the total mean activity coefficients\textsuperscript{†} of Ga\textsubscript{2}(SO\textsubscript{4})\textsubscript{3} and Na\textsubscript{2}SO\textsubscript{4}, and

† Terms proposed by R. M. Pytkowicz\textsuperscript{(12)}. A total mean activity coefficient of an electrolyte refers to its mean ionic activity coefficient calculated by assuming the complete dissociation of electrolytes in mixed solutions, and a free activity coefficient to the activity coefficient of a free ion which is not in the form of ion pairs\textsuperscript{(12)}.
hence their activities can be estimated\(^\dagger\). These activities, \(a_{Ga_2(SO_4)_3}\) and \(a_{Na_2SO_4}\), are related to the molalities, \(m_{Ga^{3+}}\), \(m_{Na^+}\) and \(m_{SO_4^{2-}}\), of free \(Ga^{3+}\), \(Na^+\) and \(SO_4^{2-}\) ions and their free activity coefficients, \(\gamma_{Ga^{3+}}\), \(\gamma_{Na^+}\) and \(\gamma_{SO_4^{2-}}\), by the equations,

\[
a_{Ga_2(SO_4)_3} = \gamma_{Ga^{3+}} \gamma_{SO_4^{2-}} m_{Ga^{3+}} m_{SO_4^{2-}}^3 \tag{34}
\]

and

\[
a_{Na_2SO_4} = \gamma_{Na^+} \gamma_{SO_4^{2-}} m_{Na^+} m_{SO_4^{2-}} \tag{35}
\]

from which the values of \(\gamma_{Ga^{3+}}\) and \(\gamma_{Na^+}\) can be determined by calculating the values of \(m_{Ga^{3+}}\), \(m_{Na^+}\) and \(m_{SO_4^{2-}}\) with the aid of the methods described in sections IV.2 and 4, respectively.

6. Standard free energies of formation of the Ga(III)-hydroxysalts and pH-dependence of their solubility in sulfate aqueous solution

The values of \(\alpha\), \(\beta\), \(\varepsilon\), and \(\log K_1\) can be calculated from the activity coefficients and/or molalities of \(H^+\), \(HSO_4^-\), \(SO_4^{2-}\), \(Ga^{3+}\), and \(Na^+\) estimated in section IV.2-5. By applying the values of \(\alpha\) and \(\beta\) to eq. (1), one can determine the standard free energies of formation of the Ga(III)-hydroxysalts with different Na(I)-content. The results obtained are listed in Table 3.

The value of const., 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 one of the values of the standard free energies of formation of \{Na\(_x\), (H\(_2\)O\)\(_{1-x}\)\} Ga\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) listed in Table 3 (As far as the molar ratio of Na(I) to Ga(III) in the solution just before the beginning of the first step hydrolysis reaction is greater than 1.3, \(-3534\) kJ \cdot mol\(^{-1}\) (a mean value of \(\mu_{333K}\) for \(x=0.13\), 0.22 and 0.38) for the Ga(III)-concentration of less than 0.1 kmol \cdot m\(^{-3}\) and \(-3544\) kJ \cdot mol\(^{-1}\) for that of around 0.5 kmol \cdot m\(^{-3}\) should be used as the value of \(\mu_{333K}\)). Accordingly, from eqs. (12) and (14), one can determine the pH-dependence of the solubility of \{Na\(_x\), (H\(_2\)O\)\(_{1-x}\)\} Ga\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) with four different Na(I)-contents in sulfate aqueous solutions by using the value of const. as a parameter. The results obtained for various values of const. are shown with fine solid lines in Figs. 4-7. That is to say, if merely the composition of the solution immediately before the beginning of the first step hydrolysis reaction is known, it is possible to judge prior to the hydrolysis operation which solubility line should be used.

V. Conclusions

From the present investigation on the thermodynamic behavior of gallium during the hydrolysis operation of gallium sulfate aqueous solution containing Ga\(_3\)(SO\(_4\))\(_2\) of less than 0.24 kmol \cdot m\(^{-3}\) with sodium hydroxide solution, it was found that (i) the hydrolysis proceeds in two steps, (ii) Precipitates produced in the first and second step hydrolyses were \{Na\(_x\), (H\(_2\)O\)\(_{1-x}\)\} Ga\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) and GaOOH, respectively, (iii) \{Na\(_x\), (H\(_2\)O\)\(_{1-x}\)\} Ga\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) was thermodynamically stable, (iv) the first and second step hydrolysis reactions were represented by \(xNa^+ + 3Ga^{3+} + \alpha SO_4^{2-} + \beta HSO_4^- + (7-x)H_2O = \{Na\(_x\), (H\(_2\)O\)\(_{1-x}\)\} Ga\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) + (5 + x + \beta) H^+, where \(\alpha + \beta = 2\), and \{Na\(_x\), (H\(_2\)O\)\(_{1-x}\)\} Ga\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) + (x\(^{-1}\))H\(_2\)O = 3GaOOH + (x/2)Na\(_2\)SO\(_4\) + \((4-x)/2\)H\(_2\)SO\(_4\)\(_4\), respectively, and (v) the standard free energies of formation of \{Na\(_x\), (H\(_2\)O\)\(_{1-x}\)\} Ga\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) at 333 K

### Table 3

The standard free energies of formation, \(\mu_{333K}\), of \{Na\(_x\), (H\(_2\)O\)\(_{1-x}\)\} Ga\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) at 333 K.

| Sample | \(\mu_{333K}/kJ \cdot mol^{-1}\) |
|--------|----------------------------------|
| \{Na\(_{0.13}\), (H\(_2\)O\)\(_{0.87}\)\} Ga\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) | \(-3534\) ± 1 |
| \{Na\(_{0.22}\), (H\(_2\)O\)\(_{0.78}\)\} Ga\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) | \(-3532\) ± 3 |
| \{Na\(_{0.38}\), (H\(_2\)O\)\(_{0.62}\)\} Ga\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) | \(-3536\) ± 6 |
| \{Na\(_{0.66}\), (H\(_2\)O\)\(_{0.34}\)\} Ga\(_3\)(SO\(_4\))\(_2\)(OH)\(_6\) | \(-3544\) ± 10 |

\(\dagger\) Denoting the activity and the total mean activity coefficient of an electrolyte, \(i\), \(j\), as well as the molalities of a positive ion, \(i\), and a negative ion, \(j\), \(a_{i,j}, \gamma_{i,j}, m_i, m_j\), respectively, under the assumption of the complete dissociation of electrolytes in mixed solutions, the relation

\[a_{i,j} = \gamma_{i,j}^\nu m_i^m m_j^n\]

holds among them. The values of \(m_i\) and \(m_j\) can be determined by chemical analysis.
were $-3534 \pm 1$, $-3532 \pm 3$, $-3536 \pm 6$, and $-3544 \pm 10$ kJ mol$^{-1}$ for $x=0.13, 0.22, 0.38$, and 0.66 respectively. Furthermore, the pH-dependence of the solubility of $\{\text{Na}_x, (\text{H}_3\text{O})_{1-x}\}\text{Ga}_3(\text{SO}_4)_2(\text{OH})_6$ in gallium sulfate aqueous solution at 333 K was also determined.

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