Thermodynamic Properties of $\text{Ga}_2(\text{SO}_4)_3-\text{H}_2\text{SO}_4-\text{H}_2\text{O}$ Solution System*

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The mean ionic activity coefficients of Ga$_2$(SO$_4$)$_3$ for the binary system Ga$_2$(SO$_4$)$_3$-$\text{H}_2\text{O}$ and the activities of water both for the binary system Ga$_2$(SO$_4$)$_3$-$\text{H}_2\text{O}$ and for the ternary system Ga$_2$(SO$_4$)$_3$-$\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ were determined by using the electrochemical and isopiestic methods, respectively, at 298 K. The water activities satisfactorily obey Zdanovskii's empirical rule. From the results obtained, the mean ionic activity coefficients of the solutes for the ternary system were calculated by applying the Mckay-Perring method. Furthermore, the applicability of Meissner's empirical procedure to estimate the mean ionic activity coefficients of Ga$_2$(SO$_4$)$_3$ and H$_2$SO$_4$ in the ternary system Ga$_2$(SO$_4$)$_3$-$\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ and that of the Robinson-Bower equation to evaluate its water activity were also discussed.

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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 back-ground for the precipitation operation, one commonly refers to the ion activity-pH diagrams of simple metal-$\text{H}_2\text{O}$ 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 made by the authors on the pH-dependence of the solubility of hydroxysalts of IIIb-metals$^{(1)-(3)}$ which are, in recent years, of great value as electronic materials. However, in order to analyze the experimental results obtained, some thermodynamic information about the systems M$_2$(SO$_4$)$_3$-$\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$ (M: In, Ga) at 298 K was required, and has been presented recently for the system In$_2$(SO$_4$)$_3$-$\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$$^{(4)}$. The objective of this paper is, therefore, to present hitherto unavailable information on the water and solute activities in the system Ga$_2$(SO$_4$)$_3$-$\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$.

II. Experimental

1. Measurement of the mean ionic activity coefficient of Ga$_2$(SO$_4$)$_3$ for the binary system Ga$_2$(SO$_4$)$_3$-$\text{H}_2\text{O}$

(I) Cell construction and principle of the measurement

The mean ionic activity coefficient of Ga$_2$(SO$_4$)$_3$ for the binary system Ga$_2$(SO$_4$)$_3$-$\text{H}_2\text{O}$ is first required for determining that of Ga$_2$(SO$_4$)$_3$ for the ternary system Ga$_2$(SO$_4$)$_3$-$\text{H}_2\text{SO}_4$-$\text{H}_2\text{O}$. Therefore, this value was measured electrochemically. The cell used for this purpose is represented as

$$\text{Pt, Hg, Hg}_2\text{SO}_4|\text{Ga}_2(\text{SO}_4)_3(m)|\text{Ga, Pt, } (C-1)$$

where $m$ is the stoichiometric molality of the solute, Ga$_2$(SO$_4$)$_3$. The Hg, Hg$_2$SO$_4$ electrode

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$^\dagger$ 1 $m$=1 mole of Ga$_2$(SO$_4$)$_3$/unit mass (kg) of the solvent.
served as the reference one. The electromotive force, $\varepsilon$, of the cell is given by

$$\varepsilon = \varepsilon^o + \frac{RT}{6F} \ln a$$  \hspace{1cm} (1)

where $\varepsilon^o$ is the standard electromotive force, $a$ is the activity of the solute, and $R$, $F$, and $T$ indicate the gas constant, Faraday’s constant, and the absolute temperature, respectively. As Ga$_2$(SO$_4$)$_3$ is a 3:2 electrolyte, then the following relation,

$$a = 10^{8.5 \cdot m^5}$$  \hspace{1cm} (2)

can be seen to hold between its activity $a$ and mean ionic activity coefficient, $\Gamma^\pm$, for the binary system. Substituting eq. (2) in eq. (1) and rearranging leads to

$$\log \Gamma^\pm = 20.28(\varepsilon - \varepsilon^o) - \log m - 0.4067$$  \hspace{1cm} (3)

at 298 K. Equation (3) means that if the standard electromotive force, $\varepsilon^o$, is known, then the mean ionic activity coefficient of Ga$_2$(SO$_4$)$_3$, $\Gamma^\pm$, can be calculated from the measurement of the electromotive force, $\varepsilon$. The value of $\varepsilon^o$ can be obtained as follows: substituting the following equation,

$$\log \Gamma^\pm = -6 \times 0.5092 \sqrt{I + BI}$$  \hspace{1cm} (4)

which can be obtained by adding to the Debye-Hückel limiting law a term linear in ionic strength, $I$, as well as the relation of $I=15$ m in eq. (3) and rearranging, we get

$$\varepsilon' = \varepsilon - 0.04930(\log m + 0.4067) + 0.5834 \sqrt{m}$$

$$= \varepsilon^o + 0.7395Bm$$  \hspace{1cm} (5)

where $B$ is a constant. The value of $\varepsilon^o$ was determined on the basis of eq. (5), which indicates that $\varepsilon'$ can ultimately approach $\varepsilon^o$ by extrapolating $m$ to zero.

(2) Measurement of the electromotive force

The assembly of the cell, (C-1), is shown schematically in Fig. 1. Mercury was placed at the bottom of the pyrex cell having a side arm, and was then covered with a thin layer of dry mercurous sulfate. 50 cm$^3$ of Ga$_2$(SO$_4$)$_3$ aqueous solution was then poured down the side arm. Subsequently, a platinum electrode was dipped into the mercury, while a gallium electrode prepared by electroplating gallium on a platinum wire was located in the solution in the side arm. The pyrex vessel was completely immersed in a water bath thermostated at 298±0.05 K. The electromotive forces of the cell were measured on a pH-meter (Toa Electronics Ltd., HM-50AT) with an input impedance >10$^{10}$ $\Omega$, and the change of the electromotive forces with time was recorded. The value which remained constant over a period of more than 10.8 ks (3 h) was adopted as the equilibrium electromotive force in each experiment.

In order to verify proper functioning of the cell, (C-1), prior to the system Ga$_2$(SO$_4$)$_3$-H$_2$O, the electromotive forces were measured for the system In$_2$(SO$_4$)$_3$-H$_2$O, in which values of the mean ionic activity coefficient of In$_2$(SO$_4$)$_3$ were known($^5$)$^6$).

The gallium sulfate or indium sulfate solutions were prepared by weighing from the respective hydrous salts of the reagent grade, the gallium or indium content of which was determined in advance by atomic absorption spectrometry. The water used for making the solutions was prepared by single distillation at a temperature below the boiling point of the ordinary laboratory double distilled water.

By using commercially available Hg$_2$SO$_4$ (>99%) or Hg$_2$SO$_4$ prepared in the laboratory according to the method described by Ives and Janz($^7$) as reference electrodes, the electromotive forces were measured and compared.
Table 1 Comparison of the electromotive force of the cell, (C-1), obtained by using commercially available Hg$_2$SO$_4$ and Hg$_2$SO$_4$ prepared in the laboratory as the reference electrodes.

| $m_{\text{In}_2(\text{SO}_4)_3}$ | Commercially available Hg$_2$SO$_4$ | Hg$_2$SO$_4$ prepared in the laboratory |
|-------------------------------|-----------------------------------|----------------------------------------|
| 0.098                         | -1.0498                           | -1.0491                                |
| 0.226                         | -1.0422                           | -1.0407                                |

for the system In$_2$(SO$_4$)$_3$–H$_2$O with two different concentrations of In$_2$(SO$_4$)$_3$. As seen in Table 1, the difference of the electromotive forces between commercially available Hg$_2$SO$_4$ and Hg$_2$SO$_4$ prepared in the laboratory was, in both concentrations, within 0.0015 V. Consequently, commercial Hg$_2$SO$_4$ was used in all the measurements for the system Ga$_2$(SO$_4$)$_3$–H$_2$O.

2. Activity of water for the ternary system Ga$_2$(SO$_4$)$_3$–H$_2$SO$_4$–H$_2$O

The apparatus and the experimental procedures used have been described elsewhere$^{(4)}$. All measurements were performed at 298 K.

III. Experimental Results

1. Mean ionic activity coefficients of In$_2$(SO$_4$)$_3$ for the binary system In$_2$(SO$_4$)$_3$–H$_2$O

Figure 2 shows that there is a linear relationship between $\varepsilon'$ and $m$ in eq. (5). Extrapolating $m$ to zero gives $-0.9474$ V as the value of $\varepsilon^0$. Using this value, the mean ionic activity coefficients of In$_2$(SO$_4$)$_3$ were calculated from eqs. (1) and (2) for various molalities. The results are listed in Table 2 and compared in Fig. 3 with those obtained by Hattox et al.$^{(5)}$. Both values are in good agreement. From this fact, it is seen that the cell, (C-1), operates correctly.
2. Mean ionic activity coefficients of Ga$_2$(SO$_4$)$_3$ for the binary system Ga$_2$(SO$_4$)$_3$–H$_2$O

When using the gallium electrode prepared in the same way as the indium one which was prepared at a temperature just above 293 K, molten gallium deposited and fell off from the platinum wire, the electromotive force fluctuated greatly and no stable value was obtained. For this reason, the gallium electrode was prepared in the present work at a temperature below 283 K to deposit solid gallium on the platinum wire, which resulted in a stable value of electromotive force even at the experimental temperature of 298 K. The linear relationship between $\varepsilon'$ and $m$ is shown in Fig. 4. The scatter of data is somewhat greater than that for the system In$_2$(SO$_4$)$_3$–H$_2$O, but each value of the electromotive force was very stable. By extrapolating $m$ to zero, $-1.1547$ V was obtained for $\varepsilon^0$. This value enables us to calculate the mean ionic activity coefficients of Ga$_2$(SO$_4$)$_3$ for various molalities, which are listed in Table 3 and shown in Fig. 5 in comparison with those of the solutes for the binary systems In$_2$(SO$_4$)$_3$–H$_2$O and Al$_2$(SO$_4$)$_3$–H$_2$O. For the concentration range from 0.2 to 0.5 mol·kg$^{-1}$, the mean ionic activity coefficient of three solutes is of nearly the same magnitude, while in the range below 0.1 mol·kg$^{-1}$ the value of Ga$_2$(SO$_4$)$_3$ is considerably lower than that of In$_2$(SO$_4$)$_3$ or Al$_2$(SO$_4$)$_3$.

3. Activity of water for the ternary system Ga$_2$(SO$_4$)$_3$–H$_2$SO$_4$–H$_2$O

Figure 6 shows the iso-activity lines of water for the ternary system Ga$_2$(SO$_4$)$_3$–H$_2$SO$_4$–H$_2$O, with the molality of Ga$_2$(SO$_4$)$_3$ for the binary system Ga$_2$(SO$_4$)$_3$–H$_2$O on the ordinate and that of H$_2$SO$_4$ for the binary system H$_2$SO$_4$–H$_2$O on the abscissa. In this case, the water activities for the present ternary system were determined on the basis of those for the binary systems H$_2$SO$_4$–H$_2$O and Ga$_2$(SO$_4$)$_3$–H$_2$O systems are equivalent is termed Zdanovskii’s rule and represented mathematically as

$$\frac{m_1}{M_1} + \frac{m_2}{M_2} = 1.$$ (6)

Here, 1 and 2 symbolize H$_2$SO$_4$ and Ga$_2$(SO$_4$)$_3$, respectively. $m_1$ and $m_2$ are the molalities of the solutes for the ternary system Ga$_2$(SO$_4$)$_3$–H$_2$SO$_4$–H$_2$O (mixed solution), and $M_1$ and $M_2$ are those of the solutes for the binary systems H$_2$SO$_4$–H$_2$O and Ga$_2$(SO$_4$)$_3$–H$_2$O (single solu-
tion), respectively, having the same water activity as that for the ternary system. The relationships of eq. (6) are represented in Fig. 6 with dashed straight lines. The ternary system \( \text{Ga}_2(\text{SO}_4)_3-\text{H}_2\text{SO}_4-\text{H}_2\text{O} \) follows Zdanovskii's empirical rule very well as does the ternary system \( \text{In}_2(\text{SO}_4)_3-\text{H}_2\text{SO}_4-\text{H}_2\text{O} \).

In Fig. 7, the activities of water for the binary system \( \text{Ga}_2(\text{SO}_4)_3-\text{H}_2\text{O} \) are compared with those for three binary systems containing trivalent metal sulfates; i.e. \( \text{In}_2(\text{SO}_4)_3-\text{H}_2\text{O} \), \( \text{Al}_2(\text{SO}_4)_3-\text{H}_2\text{O} \), and \( \text{Fe}_2(\text{SO}_4)_3-\text{H}_2\text{O} \). The system \( \text{In}_2(\text{SO}_4)_3-\text{H}_2\text{O} \) has a strong resemblance to the system \( \text{Al}_2(\text{SO}_4)_3-\text{H}_2\text{O} \), while the system \( \text{Ga}_2(\text{SO}_4)_3-\text{H}_2\text{O} \) has water activities intermediate between the systems \( \text{Al}_2(\text{SO}_4)_3-\text{H}_2\text{O} \) and \( \text{Fe}_2(\text{SO}_4)_3-\text{H}_2\text{O} \).

### IV. Discussion

1. Mean ionic activity coefficients of \( \text{Ga}_2(\text{SO}_4)_3 \) for the binary system \( \text{Ga}_2(\text{SO}_4)_3-\text{H}_2\text{O} \)

As mentioned above, denoting \( \text{H}_2\text{SO}_4 \) and \( \text{Ga}_2(\text{SO}_4)_3 \) by suffixes 1 and 2, respectively, the solution of the Gibbs-Duhem equations for both binary systems \( \text{H}_2\text{SO}_4-\text{H}_2\text{O} \) and \( \text{Ga}_2(\text{SO}_4)_3-\text{H}_2\text{O} \) under isopiestic conditions can be represented as

\[
\ln \Gamma_{\pm,2} = \ln \Gamma_{\pm,1} + \ln R' + \int_{M_1=0}^{M_1=M_2} (R' - 1) \, d \ln \Gamma_{\pm,1} \cdot M_1 \tag{7}
\]

with

\[
R' = \frac{v_1M_1}{v_2M_2}, \tag{8}
\]

where \( \Gamma_{\pm} \) is the mean ionic activity coefficient of the solute of the binary aqueous solution and \( R' \) is called the isopiestic ratio, in which \( v \) denotes the total number of moles of ions produced by complete dissociation of one mole of electrolyte. Use of eq. (7) requires that the values of \( \Gamma_{\pm,1} \) and \( R' \) are known over the necessary concentration range.
Graphical integration of the third term on the right-hand side of eq. (7) in the vicinity of \( M_1 = 0 \) is difficult, since \( (R' - 1) \) approaches zero, while \( \ln \Gamma_{\pm,1} M_1 \) approaches minus infinity at \( M_1 = 0 \). However, if a single value \( \Gamma_{\pm,2} \) of \( \Gamma_{\pm,2} \) is available at \( M_2 = M_2^\circ \), then eq. (7) becomes

\[
\ln \Gamma_{\pm,2}^\circ = \ln \Gamma_{\pm,1}^\circ + \ln R'^\circ + \int_{M_1 = 0}^{M_1 = M_1^\circ} (R' - 1) \, d \ln \Gamma_{\pm,1} M_1 \tag{9}
\]

and, from eqs. (7) and (9), one obtains

\[
\ln \frac{\Gamma_{\pm,2}}{\Gamma_{\pm,2}^\circ} = \ln \frac{\Gamma_{\pm,1}}{\Gamma_{\pm,1}^\circ} + \ln \frac{R'}{R'^\circ} + \int_{M_1 = 0}^{M_1 = M_1^\circ} (R' - 1) \, d \ln \Gamma_{\pm,1} M_1. \tag{10}
\]

This equation enables us to graphically integrate the third term on the right-hand side, since both \( (R' - 1) \) and \( \ln \Gamma_{\pm,1} M_1 \) are finite at \( M_1 = M_1^\circ \). \( M_2^\circ \) and \( \Gamma_{\pm,1} \) are the molality of solute 1 and its mean ionic activity coefficient, respectively, in the binary 1-water solution, whose water activity is the same as that of the binary 2-water solution at \( M_2 = M_2^\circ \). \( R'^\circ \) is the isopiestic ratio at \( M_1 = M_1^\circ \) and \( M_2 = M_2^\circ \). Thus, for single aqueous solutions, when even a single value of \( \Gamma_{\pm,2} \) is known in addition to the water activities, the other values of \( \Gamma_{\pm,2} \) can be obtained by calculation using eq. (10). Such values of \( \Gamma_{\pm,2} \) calculated from eq. (10) by adopting 0.0241 as the value of \( \Gamma_{\pm,2}^\circ \) at \( M_2^\circ = 0.0991 \) mol·kg\(^{-1}\) (marked by an asterisk in Fig. 5), and 0.231\(^0\) as the value of \( \Gamma_{\pm,1}^\circ \) at \( M_2^\circ = 0.148 \) mol·kg\(^{-1}\), are given in the \( M_2 \)-concentration range above 0.0991 mol·kg\(^{-1}\) in Fig. 5 with the dashed line, which shows fairly good agreement with the values measured electrochemically.

2. Mean ionic activity coefficients of H\(_2\)SO\(_4\) and Ga\(_2\)(SO\(_4\))\(_3\) for the ternary system Ga\(_2\)(SO\(_4\))\(_3\)–H\(_2\)SO\(_4\)–H\(_2\)O

In the case where the activities of water for the ternary system Ga\(_2\)(SO\(_4\))\(_3\)–H\(_2\)SO\(_4\)–H\(_2\)O measured by the isopiestic method follow Zdanovskii’s empirical rule satisfactorily, the mean ionic activity coefficients of H\(_2\)SO\(_4\) and Ga\(_2\)(SO\(_4\))\(_3\); i.e., \( \gamma_{\pm,1} \) and \( \gamma_{\pm,2} \) can be calculated from the equations\(^{(4)}\),

\[
\gamma_{\pm,1} = \frac{\Gamma_{\pm,1}}{\Gamma_{\pm,1}^\circ} = \frac{v_1 M_1}{v_1 m_1 + v_2 m_2} \tag{11}
\]

and

\[
\gamma_{\pm,2} = \frac{\Gamma_{\pm,2}}{\Gamma_{\pm,2}^\circ} = \frac{v_2 M_2}{v_1 m_1 + v_2 m_2}, \tag{12}
\]

which are derived by using the method presented by McKay and Perring\(^{(11)}\). Figure 8 illustrates the effect of gallium sulfate addition on the mean ionic activity coefficients of H\(_2\)SO\(_4\) in the ternary system Ga\(_2\)(SO\(_4\))\(_3\)–H\(_2\)SO\(_4\)–H\(_2\)O. The values of \( \gamma_{\pm,1,H_2SO_4} \) for the H\(_2\)SO\(_4\) concentrations of 0.1 to 0.8 mol·kg\(^{-1}\) decrease initially, take the respective minima, and then continue to rise with increasing concentration of Ga\(_2\)(SO\(_4\))\(_3\). The molality of Ga\(_2\)(SO\(_4\))\(_3\) at the minimum of \( \gamma_{\pm,1,H_2SO_4} \) shifts to a lower concentration region of Ga\(_2\)(SO\(_4\))\(_3\) with an increase in H\(_2\)SO\(_4\) content. At \( m_{H_2SO_4} = 1.0 \) mol·kg\(^{-1}\), the value of \( \gamma_{\pm,1,H_2SO_4} \) tends to rise monotonously with increasing concentration of Ga\(_2\)(SO\(_4\))\(_3\).

![Fig. 8 Effect of gallium sulfate addition on the mean ionic activity coefficients of H\(_2\)SO\(_4\) for the ternary system Ga\(_2\)(SO\(_4\))\(_3\)–H\(_2\)SO\(_4\)–H\(_2\)O at 298 K.](image-url)
The curves illustrated in Fig. 9, which shows the effect of sulfuric acid addition on the mean ionic activity coefficients of Ga$_2$(SO$_4$)$_3$, have forms analogous to those in Fig. 8. The above behavior of the mean ionic activity coefficients may be understood as a superimposition of the increase of the Debye-Hückel interaction among ions on the decrease of the effective concentration of water with increasing concentration of the solutes.

3. Estimation of the mean ionic activity coefficients of H$_2$SO$_4$ and Ga$_2$(SO$_4$)$_3$ in their mixed aqueous solutions by Meissner's empirical procedure

Meissner et al.\(^{(13)-(20)}\) have presented a method to estimate the mean ionic activity coefficients of many types of electrolytes in both single and mixed aqueous solutions at any temperature between 298 and 393 K. This method is based on their initial finding\(^{(13)}\) that when the common logarithm of the reduced activity coefficient, $\Gamma_{ij}$, defined by

$$\Gamma_{ij} = \left[ 1 + B(1 + 0.1I_{ij}) - B \right] \mu_{ij}^*$$

where

$$B = 0.75 - 0.065q_{ij}^*$$

and

$$\log \mu_{ij}^* = \frac{-0.5107 \sqrt{I_{ij}}}{1 + c \sqrt{I_{ij}}}$$

with

$$c = 1 + 0.055q_{ij}^* \exp(-0.023I_{ij}^0)$$

$q_{ij}^*$ is a factor characterizing each electrolyte. According to these equations, the value of $q_{ij}^*$ is uniquely determined, if the total ionic strength, $I_{ij}^0$, and the corresponding value of $\Gamma_{ij}$ are given. For given values of $q_{ij}^*$ and $I_{ij}^0$, a corresponding value of $\Gamma_{ij}$ is also obtained.

It is found that eqs. (14)–(17) are also valid for mixed aqueous solutions. In this case, $\mu_{ij,mix}$, $\mu_{ij,mix}^*$, $q_{ij,mix}$, and $I_T$ (total ionic strength) must be used for $\mu_{ij}^*$, $\mu_{ij}^*$, $q_{ij}^*$, and $I_{ij}^0$, respectively. The value of $q_{ij,mix}$ in a mixed aqueous solution is not, in general, the same as that of $q_{ij}^*$ in a single aqueous solution, and is calculated by the following isothermal equation\(^{(20)}\):

$$q_{ij,mix} = \frac{I_1}{I_T} q_{ij}^* + \frac{I_2}{I_T} q_{ij}^* + \frac{I_3}{I_T} q_{ij}^* + \cdots + \frac{I_j}{I_T} q_{ij}^* + \cdots$$

$$+ \frac{I_1}{I_T} q_{ij}^* + \frac{I_2}{I_T} q_{ij}^* + \frac{I_3}{I_T} q_{ij}^* + \cdots$$

$$+ \frac{I_1}{I_T} q_{ij}^* + \cdots$$

where

$$I_T = I_1 + I_2 + I_3 + \cdots + I_j + I_{j+1} + \cdots$$

with the odd integers including $i$ and the even ones including $j$ of the subscripts representing cations and anions, respectively. (It should be noted that, only in this section, integers do not represent electrolytes, but ions.) For a three ion aqueous solution containing the electrolytes 12 and 32, eq. (18) is simplified as
The mean ionic activity coefficients of Ga$_2$(SO$_4$)$_3$ and H$_2$SO$_4$ for the ternary system Ga$_2$(SO$_4$)$_3$-H$_2$SO$_4$-H$_2$O calculated by eqs. (13)-(21) are compared in Figs. 10 and 11 with those obtained by calculation using the Mckay-Perring method from the water activities determined experimentally. The former is represented by dashed lines and the latter by dark circles. For these calculations, our present data (Fig. 5) and those cited in a data book$^9$ were used as the values of the mean ionic activity coefficients of Ga$_2$(SO$_4$)$_3$ and H$_2$SO$_4$ at 298 K for the binary systems Ga$_2$(SO$_4$)$_3$-H$_2$O and H$_2$SO$_4$-H$_2$O, respectively. In these figures, it should be noted that the comparisons are made for the seven different constant water activities corresponding to Fig. 6, and hence higher ionic strength means higher concentration of Ga$_2$(SO$_4$)$_3$ for each constant water activity. For the mean ionic activity coefficients of Ga$_2$(SO$_4$)$_3$, when the concentration of the solutes is low and hence the water activity is high, the agreement between the values calculated by Meissner’s method and those obtained experimentally is relatively good. However, a gradually widening deviation becomes apparent with increasing concentration of the solutes at each constant water activity, particularly at lower ionic strength, that is, in the composition region close to the binary system H$_2$SO$_4$-H$_2$O. With regard to the mean ionic activity coefficients of H$_2$SO$_4$, the agreement is not as good as in the case of Ga$_2$(SO$_4$)$_3$, even when the concentration of the solutes is low. This may be attributed to the fact that sulfuric acid does not obey the generalized correlation to form the above curve family, as has been pointed out by Kusik et al.$^{19}$.
4. Calculation of the water activities for the ternary system Ga$_2$(SO$_4$)$_3$-H$_2$SO$_4$-H$_2$O from the Robinson-Bower empirical equation

The Robinson-Bower empirical equation\(^{(4),(12)}\) is expressed as

\[
1 - a_{H_2O} = (1 - a_{H_2O,1}) \frac{m_1}{M_1(I)} + (1 - a_{H_2O,2}) \frac{m_2}{M_2(I)},
\]

where \(a_{H_2O}\) is the water activity of the mixed aqueous solution containing solute 1 of \(m_1\) and solute 2 of \(m_2\), \(M_1(I)\) or \(M_2(I)\) is the molality of solute 1 or solute 2 in each single aqueous solution having the same ionic strength \(I\) as that of the mixed aqueous solution, and \(a_{H_2O,1}\) or \(a_{H_2O,2}\) is the water activity of the single aqueous solution of \(M_1(I)\) or \(M_2(I)\). Majima and Awakura have applied eq. (22) to various sulfate systems and reported that satisfactory agreement can be obtained between water activities determined experimentally and calculated by assuming complete dissociation of sulfuric acid and metal sulfate and also by considering the dissociation of sulfuric acid and the formation of sulfato-complexes\(^{(10)}\).

Accordingly, the applicability of the Robinson-Bower equation was examined for the ternary system Ga$_2$(SO$_4$)$_3$-H$_2$SO$_4$-H$_2$O as well. For these calculations, our present data and those cited in a data book\(^{(9)}\) were used as the values of the water activities for the binary systems Ga$_2$(SO$_4$)$_3$-H$_2$O and H$_2$SO$_4$-H$_2$O, respectively. In Fig. 12, the calculation results, which are represented by broken lines for the complete dissociation of Ga$_2$(SO$_4$)$_3$ and H$_2$SO$_4$ and by dotted lines for the dissociation of H$_2$SO$_4$ and the formation of Ga(III) sulfato-complex, are compared with the experimentally determined values. In the latter case, the ionic strengths were calculated by considering the existence of H$^+$, HSO$_4^-$, SO$_4^{2-}$, Ga$_3^+$, and GaSO$_4^+$ from the following relations (A)–(D).

(A) Ionic strength

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

(B) Dissociation equilibrium of HSO$_4^-$

\[
\log \frac{m_{H^+} \cdot m_{SO_4^{2-}}}{m_{HSO_4^-}} = -1.9914 + \frac{2.036 \sqrt{I}}{1 + 0.4 \sqrt{I}}.
\]

(C) Mass balance of H, Ga, and SO$_4$

\[
m_{H^+} + m_{HSO_4^-} = 2m_{H_2SO_4}.
\]

\[
m_{Ga^{3+}} + m_{GaSO_4^+} = 2m_{Ga_2(SO_4)_3}.
\]

\[
m_{HSO_4^-} + m_{SO_4^{2-}} + m_{GaSO_4^+} = m_{H_2SO_4} + 3m_{Ga_2(SO_4)_3}.
\]

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

\[
Ga^{3+} + SO_4^{2-} = GaSO_4^+ \quad \log \frac{m_{GaSO_4^+}}{m_{Ga^{3+}} \cdot m_{SO_4^{2-}}} = 1.5.
\]

Fig. 12 Comparison of measured water activities with those calculated by the Robinson-Bower empirical rule for the ternary system Ga$_2$(SO$_4$)$_3$-H$_2$SO$_4$-H$_2$O at 298 K.

---: calculated assuming the complete dissociation of Ga$_2$(SO$_4$)$_3$ and H$_2$SO$_4$

-----: calculated considering the dissociation of H$_2$SO$_4$ and the formation of Ga(III) sulfato-complexes

Here, the molarity is approximated by the molality. Good agreement was obtained between the experimentally determined and calculated values for the ternary system Ga$_2$(SO$_4$)$_3$-H$_2$SO$_4$-H$_2$O also, the deviation being less than 0.9% for the complete dissociation...
tion of Ga₂(SO₄)₃ and H₂SO₄ and less than 0.4% for the dissociation of H₂SO₄ and the formation of Ga(III) sulfato-complex.

V. Conclusion

Electrochemical measurement of the mean ionic activity coefficients of Ga₂(SO₄)₃ for the binary system Ga₂(SO₄)₃–H₂O and isopiestic determination of the water activities for both the binary system Ga₂(SO₄)₃–H₂O and the ternary system Ga₂(SO₄)₃–H₂SO₄–H₂O led to the following conclusions.

1. The mean ionic activity coefficient of Ga₂(SO₄)₃ for the binary system Ga₂(SO₄)₃–H₂O is of nearly the same magnitude as that of In₂(SO₄)₃ and Al₂(SO₄)₃ for the binary systems In₂(SO₄)₃–H₂O and Al₂(SO₄)₃–H₂O, respectively, in the concentration range from 0.2 to 0.5 mol·kg⁻¹. In the range below 0.1 mol·kg⁻¹, the value of Ga₂(SO₄)₃ is considerably lower than that of In₂(SO₄)₃ or Al₂(SO₄)₃.

Regarding the ternary system Ga₂(SO₄)₃–H₂SO₄–H₂O:

2. The water activities obey the Zdanovskii empirical rule satisfactorily.

3. The variation of the mean ionic activity coefficient of either Ga₂(SO₄)₃ or H₂SO₄ with increasing concentration of the other solute may be qualitatively explained as a superimposition of the increase of the Debye-Hückel interaction among ions on the decrease of the effective concentration of water with increasing concentration of the solutes.

4. Meissner's empirical method for estimating the mean ionic activity coefficients of the solutes is applicable only to Ga₂(SO₄)₃, and this too, on condition that the solution is dilute.

5. The water activities calculated by the Robinson-Bower equation are in satisfactory agreement with the experimentally determined values, both if the complete dissociation of sulfuric acid and gallium sulfate is assumed and if the dissociation of sulfuric acid and the formation of Ga(III) sulfato-complex are considered.

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