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Determination of Thermodynamic Properties of Gibbsite from Its Solubility Data in NaOH Solutions[1)]

Byong-Tae CHANG

Department of Chemistry, Faculty of Science, Korea University, Kodaira, Tokyo 187

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A reasonable method for determination of thermodynamic properties of alumina hydrates from their solubility data in alkaline pH range was presented and applied to the solubility data of gibbsite in NaOH solutions with success. When $\log(K_s/a_w)$, where $K_s=m_H m_{Al}$ and a_w is the activity of water, was plotted against a Debye-Hückel function of the ionic strength I, $I^{1/2}/(1+B_t a_1 I^{1/2})$, a linear relationship to moderately high ionic strengths was found over the range of temperatures from 40 to 110 °C, having the theoretical Debye-Hückel limiting slope and the intercept of $\log K_s^\circ$ at $I=0$. Assuming the same ionic size parameters, $a_1=a_2$, the solubility product (K_s°) of gibbsite was found to depend upon temperature up to 110 °C as follows: $\log K_s^\circ=-4064/T-1.54$ or $-4023/T-1.65$. At high ionic strengths above 1.0, $\log(K_s/a_w)$ showed positive deviations from the straight line, which may be attributed to the formation of complex ions, *e.g.*, $Al_2O(OH)_6{}^{2-}$, or the dehydration of $Al(OH)_4{}^-$ to $AlO(OH)_2{}^-$ and $AlO_2{}^-$ ions.

The solubility of alumina hydrates such as gibbsite, boehmite, and diaspore in aqueous solutions is very important not only for alumina production by the alkaline or acid process, but also for quantitative understanding of aqueous geochemistry of aluminous minerals.[2–15)] Furthermore, the thermodynamics of Al–H_2O system is much useful in considering the corrosion and passivation of aluminium in water.[16)] A number of solubility data of gibbsite in alkaline solutions have been reported by many investigators.[2–13)] A purpose of most previous solubility studies is to determine precisely the standard thermodynamic properties of gibbsite and hydroxy-aluminium ions in aqueous solubtions. Unfortunately, these results do not agree well with each other; for example, as the ionic solubility product of gibbsite at 25 °C, Kittrick[6)] and May[10)] reported the values of 5.01×10^{-16} and 8.94×10^{-15}, respectively.

Russell, Edward and Taylor[2)] calculated an equilibrium constant (K_1) and its temperature dependancy from their solubility data of gibbsite in NaOH solutions from 40 to 170 °C, assuming that activity coefficients of OH^- and $AlO_2{}^-$ ions are equal to each other, *i.e.*, $\gamma_{OH^-}=\gamma_{AlO_2^-}$;

$$Al(OH)_3(s) + OH^-(l) = AlO_2{}^-(l) + 2H_2O(l), \tag{1}$$

$$K_1 = C_{Al}a_w^2/C_{OH}, \tag{2}$$

$$\log K_1^\circ = -1605/T + 4.11, \tag{3}$$

where C_{Al} and C_{OH} are the equivalents per liter of aluminate and hydroxide ions, a_w is the activity of the water in the molar fraction unit, and K_1° is the value derived by extraporating K_1 to zero NaOH concentration at a given temperature. There are some doubtful problems in the Russell's method for determining K_1°; firstly, the differences in the ion size and interactions between the ions and water were neglected, assuming that the activity coefficients of AlO_2^- and OH^- ions are the same. Secondly, the values of a_w for NaOH solutions at 25 °C were used for sodium aluminate and hydroxide solutions at higher temperatures up to 170 °C without any correction. Finally the aluminate ion was expressed in the form of $AlO_2{}^-$.

The purpose of this work is to determine the thermodynamic properties of gibbsite in NaOH solution from its solubility data by a more reasonable method according to the Debye-Hückel theory.

Theoretical

According to various studies on the sodium aluminate and hydroxide solutions, the most probable structure of the aluminate ion is tetrahedral $Al(OH)_4{}^-$ ion at low aluminium concentrations, which, at higher concentrations, becomes dehydrated $AlO_2{}^-$ ion.[17–19)] Therefore, it is reasonable to express the dissolution process of gibbsite as follows;

$$Al(OH)_3(s) + H_2O(l) = H^+(l) + Al(OH)_4{}^-, \tag{4}$$

$$K_s^\circ = a_H a_{Al}/a_w = K_s\cdot\gamma_1{}^2/a_w, \tag{5}$$

where $K_s=m_H m_{Al}$, $\gamma_1^2=\gamma_H\gamma_{Al}$, and m_i is the molality of species i. On the other hand, for the dissociation of water,

$$H_2O(l) = H^+(l) + OH^-(l), \tag{6}$$

$$K_w^\circ = a_H a_{OH}/a_w = K_w\gamma_2{}^2/a_w, \tag{7}$$

where $K_w=m_H m_{OH}$ and $\gamma_2^2=\gamma_H\gamma_{OH}$. From Eqs. 5 and 7 a general equation (8) for alumina trihydrates can be derived, introducing a new function, $f(I)$, of ionic strength (I).

$$\begin{aligned} f(I) &= \log(m_{Al}/m_{OH}) + \log K_w^\circ \\ &= \log K_s^\circ + 2\log(\gamma_2/\gamma_1)\,. \end{aligned} \tag{8}$$

It should be noted that f(I) is independent on the activity of water. Figure 1 gives relationships between f(I) and I which were calculated from the solubility data of gibbsite reported by Russell *et al.*[2)] and K_w° values[20)] at a given temperature.

Using the extended Debye-Hückel equation with added terms, we can express the mean activity coefficient (γ_i) as follows;

$$\log\gamma_i = -A_t I^{1/2}/(1+B_t a_i I^{1/2}) - c_i I - d_i I^2, \tag{9}$$

where A_t is the theoretical limiting Debye-Hückel slope, B_t a parameter depending upon temperature and dielectric constant of solvent, a_i an ion size parameter, and c_i and d_i are adjustable parameters. Substituting Eq. 9 into Eq. 8,

$$\begin{aligned} f(I) = \log K_s^\circ &+ 2A_t I^{1/2}[1/(1+B_t a_1 I^{1/2}) \\ &-1/(1+B_t a_2 I^{1/2})] + CI + DI^2, \end{aligned} \tag{10}$$

where $C=2(c_1-c_2)$ and $D=2(d_1-d_2)$. The problem is to decide the five parameters, K_s°, a_1, a_2, C, and

TABLE 1. TEMPERATURE DEPENDENCY OF K°_s, K°_w, C, AND D

No.	t/°C	Case 1				Case 2		
		$\log K^\circ_s$	$C\times10^2$	$D\times10^3$	$\log K^\circ_r$	$\log K^\circ_s$	$C\times10^2$	$\log K^\circ_r$
1	40	−14.51	3.44	4.11	−0.97	−14.55	5.98	−1.01
2	60	−13.76	6.94	1.78	−0.74	−13.75	6.18	−0.74
3	70	−13.36	3.20	4.99	−0.57	−13.38	5.68	−0.59
4	80	−13.03	4.82	2.66	−0.44	−13.04	5.94	−0.45
5	90	−12.73	4.61	3.61	−0.32	−12.74	6.14	−0.33
6	100	−12.42	3.97	3.29	−0.18	−12.44	5.72	−0.19
7	110	−12.15	4.27	−0.57	−0.05	−12.22	6.80	−0.12
8	130	−11.77	5.24	5.68	0.08	−11.83	9.04	0.02
9	150	−11.54	11.18	−3.89	0.09	−11.51	9.24	0.12
10	170	−11.16	7.37	10.31	0.30	−11.26	13.71	0.20

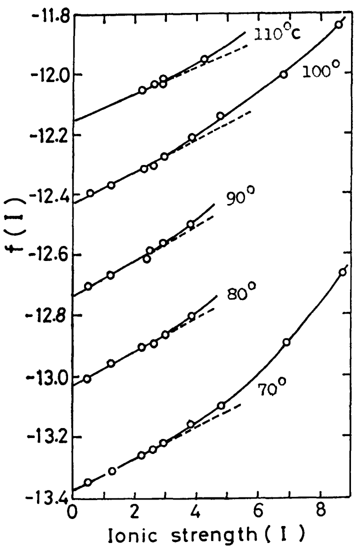

Fig. 1. Relationships between f(I) and ionic strength(I) according to Eq. 8.

D to get the best statistical fit for the data given in Fig. 1.

Results and Discussion

Most of solubility measurements of gibbsite in alkaline solutions presented up to date were carried out at 25 °C. Lyapunov reported interesting results showing an effect of NaCl addition on the solubility of gibbsite at 60 and 95 °C, but the range of conditions of solubility measurements was limited.[11)] The Russel's data seems to be the most useful solubility data of gibbsite in the range of higher temperature and NaOH concentrations. The method presented here, therefore, was applied mainly to the Russel's data.

The Case of the Same Ion Size Parameters. Assuming the same ion size parameters, *i.e.*, $a_1=a_2$, as did May[10)] or Smith,[21)] Eq. 10 can be simplified into a following equation:

$$f(I) = \log K^\circ_s + CI + DI^2 \quad \text{(Case 1)}. \tag{11}$$

Table 1 gives $\log K^\circ_s$, C, and D obtained by the least square calculations for Eq. 11. Furthermore, Fig. 1 shows good straight line relationship between f(I) and I in the range of low ionic strengths, that is,

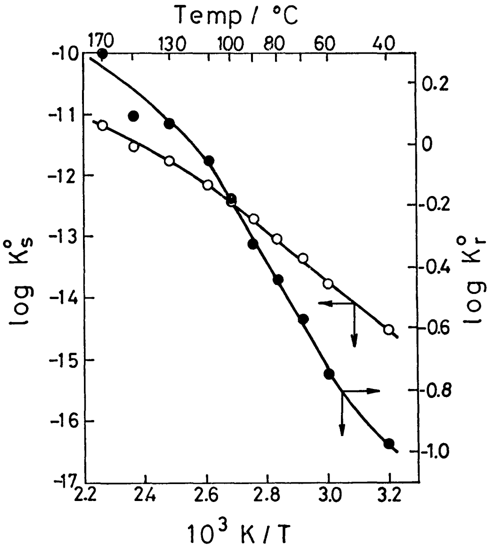

Fig. 2. Temperature dependencies of $\log K^\circ_s$ and $\log K^\circ_r$ from 40 to 170 °C for the case 1.

$$f(I) = \log K^\circ_s + CI \quad \text{(Case 2)}. \tag{12}$$

Table 1 also gives the values of $\log K^\circ_s$ and C for Eq. 12.

Figures 2 and 3 show temperature dependency of the ionic solubility product of gibbsite for the case 1 and 2, respectively. Good linear relationships between $\log K^\circ_s$ and $1/T$ can be observed in the range of 40—110 °C.

$$\log K^\circ_s = -4064/T - 1.54 \quad \text{(Case 1)}, \tag{13}$$

$$\log K^\circ_s = -4032/T - 1.65 \quad \text{(Case 2)}. \tag{14}$$

According to Eqs. 13 and 14, the values of $\log K^\circ_s$ at 25 °C become the same value of −15.18, which is very close to the value of −15.30 reported by Kittrick,[6)] being considerably lower than the value of −14.05 presented by May.[10)] Based on the ΔG°_f value of −1151.9 kJ/mol selected for gibbsite by Parks,[8)] the standard Gibbs free energy of formation (ΔG°_f) for $Al(OH)_4^-$ ion is calculated to be −1302.5 kJ/mol. The heat of reaction of Eq. 4 was found to be 77.4 −77.8 kJ between 40 and 110 °C, and to have a tendency to decrease at temperature above 110 °C.

For the following reaction of gibbsite with OH^- ion,

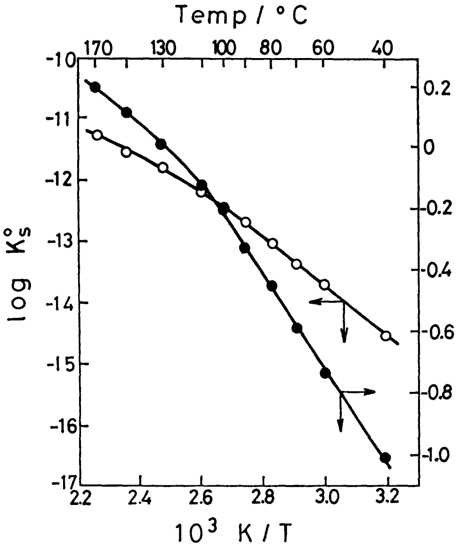

Fig. 3. Temperature dependencies of log $K_{\rm s}^\circ$ and log $K_{\rm r}^\circ$ from 40 to 170 °C for the case 2.

$$\mathrm{Al(OH)_3(s) + OH^-(l) = Al(OH)_4^-(l)}, \tag{15}$$

$$K_{\rm r}^\circ = a_{\rm Al}/a_{\rm OH}, \tag{16}$$

using Eqs. 5 and 7, $K_{\rm r}^\circ$ is given by

$$K_{\rm r}^\circ = K_{\rm s}^\circ/K_{\rm w}^\circ. \tag{17}$$

Table 1, Figs. 2 and 3 also show the values of log $K_{\rm r}^\circ$, and its temperature dependency in the range from 40 to 110 °C is given as follows;

$$\log K_{\rm r}^\circ = -1598/T + 4.10 \quad \text{(Case 1)}, \tag{18}$$

$$\log K_{\rm r}^\circ = -1567/T + 3.98 \quad \text{(Case 2)}. \tag{19}$$

According to Eq. 18 or 19, the heat of reaction of Eq. 15 is 30.1—30.5 kJ.

The Case of Different Ion Size Parameters. In order to evaluate effects of the ion size parameters, a_1 and a_2, on log $K_{\rm s}^\circ$, we assumed conveniently $c_2 = d_2 = 0$ for the dissociation of water. Then, from Eqs. 7 and 9.

$$\log (K_{\rm w}/a_{\rm w}) = \log K_{\rm w}^\circ + 2A_{\rm t}I^{1/2}/(1+B_{\rm t}a_2I^{1/2}). \tag{20}$$

Using $K_{\rm s} = m_{\rm H}m_{\rm Al} = K_{\rm w}(m_{\rm Al}/m_{\rm OH})$ and Eq. 20,

$$\log (K_{\rm s}/a_{\rm w}) = \log K_{\rm w}^\circ + \log (m_{\rm Al}/m_{\rm OH}) + 2A_{\rm t}I^{1/2}/(1+B_{\rm t}a_2I^{1/2}). \tag{21}$$

At a given temperature, the value of log $(K_{\rm s}/a_{\rm w})$ depends upon the concentration ratio, $(m_{\rm Al}/m_{\rm OH})$, at equilibrium and the ion size parameter, a_2, for $\mathrm{H^+}$ and $\mathrm{OH^-}$ ions. Figure 4 shows plots of log $(K_{\rm s}/a_{\rm w})$ and $I^{1/2}/(1+1.51I^{1/2})$ at 70 °C with $a_1 = 4.5$ Å and various values of a_2 from 3.5 to 6.0 Å. It is obvious from Fig. 4 that log $(K_{\rm s}/a_{\rm w})$ and slopes of curves increase with decrease in the a_2 value.

On the other hand, from Eqs. 5 and 9,

$$\log (K_{\rm s}/a_{\rm w}) = \log K_{\rm s}^\circ + 2A_{\rm t}I^{1/2}/(1+B_{\rm t}a_1I^{1/2}) + 2c_1I + 2d_1I^2. \tag{22}$$

According to the Debye-Hückel theory, generally a plot of log $(K_{\rm s}/a_{\rm w})$ *vs.* $I^{1/2}/(1+B_{\rm t}a_1I^{1/2})$ produces a straight line at low Ionic strengths with the theoretical limiting slope, $2A_{\rm t}$, and the intercept of log $K_{\rm s}^\circ$ at $I=0$, and the last two terms becomes important only at higher ionic strengths. Figure 5 shows a plot of log $(K_{\rm s}/a_{\rm w})$ *vs.* $I^{1/2}/(1+B_{\rm t}a_1I^{1/2})$ at 70, 80, 90, and 100 °C in the case of $a_1 = 4.5$ Å and $a_2 = 5.0$ Å.[24] Similarly, Fig. 6 shows a plot of log $(K_{\rm s}/a_{\rm w})$ *vs.* $I^{1/2}/(1+B_{\rm t}a_1I^{1/2})$ at 60 °C, which were calculated from the Russell's data in NaOH solutions and the Lyapunov's data in both NaOH and (NaOH+NaCl) solutions. It is obvious from Figs. 5 and 6 that the straight line relationships hold at ionic strengths as high as 1.0, and that these slopes are very close to the theoretical values, $2A_{\rm t}$, of 1.09, 1.11, 1.14, 1.16, and 1.19 at 60, 70, 80, 90, and 100 °C, respectively. The Lyapunov's data in NaOH and (NaOH+NaCl) solutions are able to be represented by the same curve as shown in Fig. 6, and gives log $K_{\rm s}^\circ = -13.60$ at $I=0$, which differs a little from a value of log $K_{\rm s}^\circ = -13.73$ for the Russell's data.

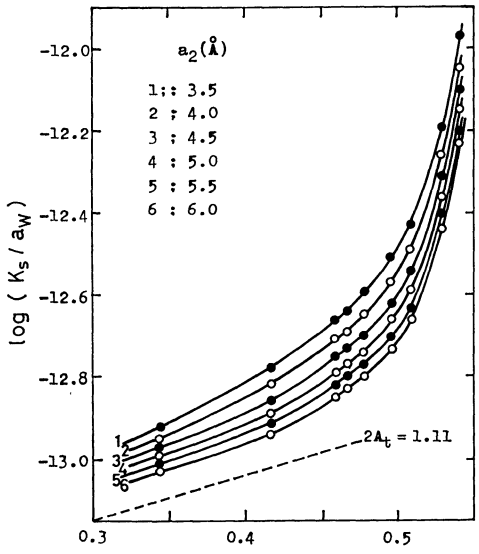

Fig. 4. Plots of $\log(K_{\rm s}/a_{\rm w})$ *vs.* $I^{1/2}/(1+1.51I^{1/2})$ at various values of a_2 in the case of $a_1 = 4.5$ Å and 70 °C.

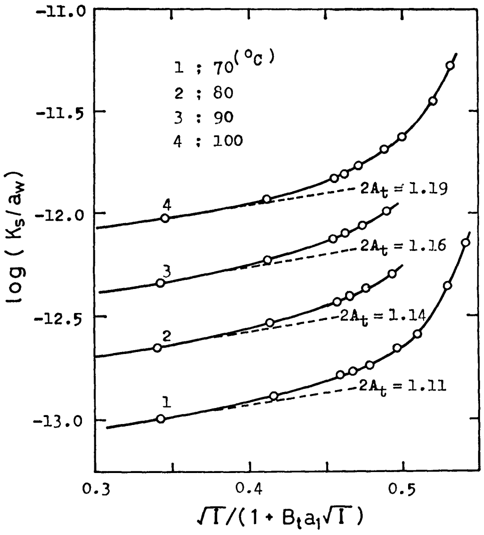

Fig. 5. Plots of $\log(K_{\rm s}/a_{\rm w})$ *vs.* $I^{1/2}/(1+B_{\rm t}a_1I^{1/2})$ at temperatures of 70, 80, 90, and 100 °C in the case of $a_1 =$ 4.5 Å and $a_2 = 5.0$ Å.

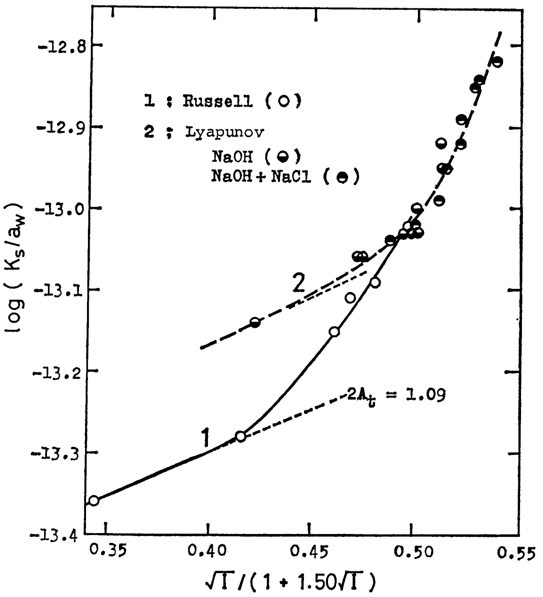

Fig. 6. Plots of $\log(K_s/a_w)$ *vs.* $I^{1/2}/(1+1.50I^{1/2})$ at 60 °C obtained from the Russell's data[2)] and the Lyapnov's data[11)] in the case of $a_1=4.5$ Å and $a_2=5.0$ Å.

At ionic strengths above 1.0, $\log(K_s/a_w)$ shows positive deviations from the straight line. Such positive deviation at high ionic strengths was also observed in $Ca(OH)_2$–$NaNO_3$–H_2O[22)] or $NiSO_4$–$CoSO_4$–$(NH_4)_2SO_4$–H_2O[23)] system, and was considered to be attributed to the formation of complexes. Moolnaar concluded from Infrared, Raman, and ^{23}Na and ^{27}Al NMR spectra of sodium aluminate solutions that at aluminium concentrations below 1.5 M, the tetrahedral $Al(OH)_4^-$ ions exist as the predominant aluminium-bearing species in the solution and that at aluminium concentrations of about 1.5 M and above, $Al(OH)_4^-$ condenses to form $Al_2O(OH)_6^{2-}$ ion.[19)] In a detailed study of the saturated vapour pressures exerted by sodium hydroxide and aluminate solutions, Dibrov advanced evidence for the aluminate ion undergoing dehydration to the meta-aluminate ion AlO_2^- at high concentrations of 15% Na_2O and above:

$$Al(OH)_4^- \longrightarrow AlO(OH)_2^- + H_2O \longrightarrow AlO_2^- + 2H_2O. \qquad (23)$$

From the above discussions it is reasonable to consider that the positive deviation from the straight line may be attributed to the formation of complex ion such as $Al_2O(OH)_6^{2-}$ and/or the dehydration of $Al(OH)_4^-$, leading to decrease in the activity coefficient of aluminate ion. This presents a striking contrast to increase in the activity coefficient designated by the salting-out effect.[20)] The similar application of the method presented in this paper to alumina monohydrates is currently performed with success.

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