Determination of Thermodynamic Properties of Boehmite from its Solubility Data in NaOH Solutions[1)]

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Thermodynamic properties of boehmite in alkaline pH range are determined by applying the extended Debye-Hückel theory to its solubility data in NaOH solutions. When $\log(K_s/a_w^2)$, where $K_s=m_H m_{Al}$ and a_w is the activity of the water in NaOH solutions, is plotted against a Debye-Hückel function of ionic strength(I), $I^{1/2}/(1+B_t a_i I^{1/2})$, at a given temperature, the curve approaches gradually the theoretical Debye-Hückel limiting slope($2A_t$) with decrease in the ionic strength, and at high ionic strength it deviates positively from the straight line. Under the assumption of the same ionic size parameters for OH^- and $Al(OH)_4^-$ ions, the ionic solubility product, $K_s^\circ=a_H a_{Al}/a_w^2$, for boehmite is given by following equations in the temperature range from 80 to 250 °C: $\log K_s^\circ=-2663/T-5.71$ (Case 1) or $\log K_s^\circ=-2764/T-5.45$ (Case 2). From a comparison of the temperature dependences of K_s° for boehmite and gibbsite, a transition temperature between the two alumina hydrates was calculated to be 60±3 °C.

Thermodynamics of Al_2O_3–Na_2O–H_2O system is very important not only for alumina production by the Bayer process, but also for understanding corrosion and passivation of aluminium in water and aqueous geochemistry of aluminous minerals.[2–8)] In the previous paper,[1)] based on the Debye-Hückel theory, a more reasonable method was presented in order to determine thermodynamic properties of alumina hydrates from their solubility data, and was applied to the solubility data of gibbsite, one of alumina trihydrates, in NaOH solutions with success.

The purpose of this paper is to evaluate several thermodynamic properties of boehmite, one of alumina monohydrates, by applying the similar procedure to solubility data of boehmite in NaOH solutions at temperatures up to 300 °C.[2,9)] This problem may be also interesting as a study on the thermodynamics and the Debye-Hückel theory of high temperature aqueous solutions.[10,11)]

Theoretical

One can express a dissolution process of alumina monohydrate and the dissociation of water as follows:

$$AlOOH(s) + 2H_2O(1) = Al(OH)_4^-(1) + H^+(1), \quad (1)$$

$$K_s^\circ = a_{Al}a_H/a_w^2 = K_s\gamma_1^2/a_w^2, \quad (2)$$

$$H_2O(1) = H^+(1) + OH^-(1), \quad (3)$$

$$K_w^\circ = a_H a_{OH}/a_w = K_w\gamma_2^2/a_w, \quad (4)$$

where $K_s=m_{Al}m_H$, $K_w=m_H m_{OH}$, m_i the molality of species i, $\gamma_1^2=\gamma_{Al}\gamma_H$, $\gamma_2^2=\gamma_H\gamma_{OH}$, and a_w the activity of the water in the molar fraction unit. From Eqs. 2 and 4 we can derive a general equation for the alumina monohydrate, introducing a new function, $f(I)$, of ionic strength (I):

$$f(I) = \log(m_{Al}/m_{OH}) + \log(K_w^\circ/a_w)$$
$$= \log K_s^\circ + 2\log(\gamma_2/\gamma_1). \quad (5)$$

It should be noted that, in the case of the monohydrate, $f(I)$ involves a term of a_w, differing from the case of the trihydrate. Evaluation of the a_w values at a given temperature and pressure of sodium aluminate and hydroxide solutions, therefore, become much important together with the solubility data. Russell *et al.* have used the a_w values of corresponding NaOH solutions at 25 °C for the sodium aluminate and hydroxide solutions up to 170 °C without any correction.[2)] Dibrov *et al.* studied in detail the saturated vapor pressure exerted by the sodium aluminate and hydroxide solutions in the wide range of temperatures and concentrations.[12)] In this paper, the a_w values at a given temperature and concentration were calculated by using the vapor pressure data by Dibrov and virial coefficients, B′ and C′ of H_2O(g) by Kell,[13)] that is,

$$a_w = f_i/f_o = \gamma_i^\gamma P_i/\gamma_o^\gamma P_o, \quad (6)$$

$$RT\ln(f_i/P_i) = RT\ln\gamma_i^\gamma = B'P_i + C'P_i^2, \quad (7)$$

where f_i and γ_i^γ are the fugacity and activity coefficient of H_2O(g), respectively, and a subscript "o" means the pure water.

Figure 1 gives the relationships between $f(I)$ and I obtained from Eq. 5, using the solubility data of boehmite reported by Russell (80—170 °C)[2)] and Bernshtein (250 and 300 °C),[9)] and the a_w values calculated by Eqs. 6 and 7. The K_w° values were quoted from Refs. 14 and 15.

On the other hand, using the following extended

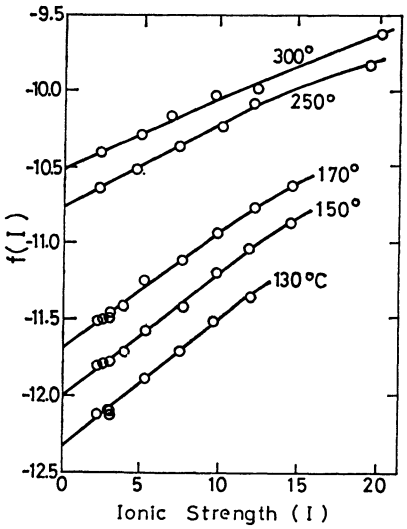

Fig. 1. Relationships between $f(I)$ and ionic strength (I) according to Eq. 5 at temperatures from 130 to 300 °C.

Debye-Hückel equation,

$$\log \gamma_i = -A_t I^{1/2}/(1+B_t a_i I^{1/2}) - c_i I - d_i I^2, \quad (8)$$

the function, $f(I)$, can be expressed by

$$f(I) = \log K_s^\circ + 2A_t I^{1/2}[1/(1+B_t a_1 I^{1/2}) - 1/(1+B_t a_2 I^{1/2})] + CI + DI^2, \quad (9)$$

where A_t is the theoretical Debye-Hückel limiting slope, and B_t, a_i, c_i, d_i, $C=2(c_1-c_2)$ and $D=2(d_1-d_2)$ are adjustable parameters. The problem is to decide the five parameters in Eq. 9 to get the best fit for the data given in Fig. 1.

Results and Discussion

The Case of the Same Ionic Size Parameters. Setting up the same ionic size parameters, that is, $a_1=a_2$, as did May[8] and Smith,[16] Eq. 9 can be simplified into a following equation;

$$f(I) = \log K_s^\circ + CI + DI^2. \quad (10)$$

Table 1 gives the values of $\log K_s^\circ$, C, and D obtained by the least squares method for Eq. 10 in the whole range of ionic strengths (Case 1). Moreover, as being obvious from Fig. 1, there are good linear relationships between $f(I)$ and the ionic strength in the range of low ionic strengths below *ca.* 10, *i.e.*,

$$f(I) = \log K_s^\circ + CI. \quad (11)$$

Table 1 also gives the values of $\log K_s^\circ$ and C for Eq. 11 (Case 2).

Figures 2 and 3 show variations of $\log K_s^\circ$ with the temperature in the case of 1 and 2, respectively. We can observe linear relationships between $\log K_s^\circ$ and $1/T$ in the range of temperature from 80 to 250 °C, which are given by following equations:

$$\log K_s^\circ = -2663/T - 5.71 \text{ (Case 1)}, \quad (12)$$

$$\log K_s^\circ = -2764/T - 5.45 \text{ (Case 2)}. \quad (13)$$

According to Eq. 12 or 13, the value of $\log K_s^\circ$ at 25 °C becomes −14.65 or −14.73, being a little larger than that for gibbsite, −15.18.[1] From the values of $\log K_s^\circ$ at 25 °C for gibbsite and boehmite, the standard Gibbs free energy of following reactions can be calculated as follows:

$$Al(OH)_3 + H_2O = Al(OH)_4^- + H^+, \quad \Delta G_{298}^\circ = 86.61 \text{ kJ}, \quad (14)$$

$$AlOOH + 2H_2O = Al(OH)_4^- + H^+, \quad \Delta G_{298}^\circ = 83.82 \pm 0.23 \text{ kJ}. \quad (15)$$

From the above two equations,

$$Al(OH)_3 = AlOOH + H_2O, \quad \Delta G_{298}^\circ = 2.79 \pm 0.23 \text{ kJ}. \quad (16)$$

This means that gibbsite is more thermodynamically

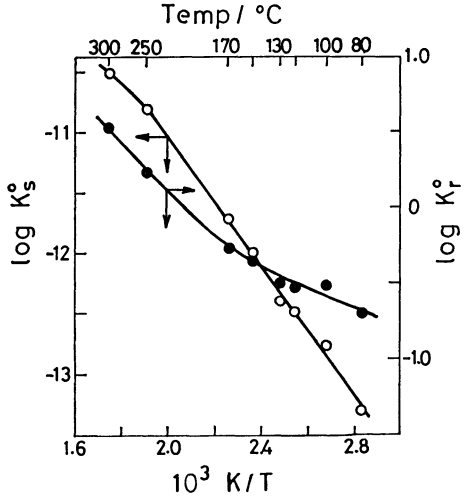

Fig. 2. Temperature dependences of $\log K_s^\circ$ and $\log K_r^\circ$ from 80 to 300 °C for the Case 1.

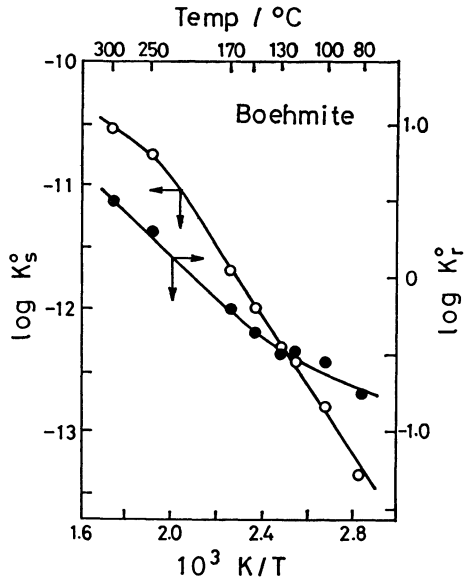

Fig. 3. Temperature dependences of $\log K_s^\circ$ and $\log K_r^\circ$ from 80 to 300 °C for the Case 2.

TABLE 1. TEMPERATURE DEPENDENCES OF K_s°, K_r°, C, AND D

No.	Temp °C	Case 1				Case 2		
		$\log K_s^\circ$	$C\times10^2$	$D\times10^3$	$\log K_r^\circ$	$\log K_s^\circ$	$C\times10^2$	$\log K_r^\circ$
1	80	−13.30	1.32	5.61	−0.71	−13.35	4.78	−0.76
2	100	−12.76	1.43	3.24	−0.52	−12.79	3.35	−0.54
3	120	−12.49	8.34	−5.35	−0.53	−12.44	4.99	−0.48
4	130	−12.34	8.41	−0.05	−0.50	−12.34	8.47	−0.50
5	150	−11.99	7.81	0.00	−0.36	−11.99	7.82	−0.36
6	170	−11.73	9.23	−1.19	−0.27	−11.68	7.27	−0.22
7	250	−10.80	6.50	−0.81	0.24	−10.75	4.95	0.30
8	300	−10.51	4.53	−0.12	0.53	−10.53	4.98	0.51

stable than boehmite at 25 °C and 1 atm. From a comparison of the temperature dependences of K_s° for gibbsite and boehmite, a transition temperature between the two alumina hydrates was found to be 60±3 °C. Based on the ΔG_f° value of −915.0 kJ/mol selected as a standard Gibbs free energy of formation for boehmite by Parks,[5] ΔG_f° value for $Al(OH)^-_4$ ion was obtained to be −1305.6 kJ/mol, which agrees well with the value of −1302.5 kJ/mol obtained in the case of gibbsite. A heat of Reaction 1 is equal to be 51.9±0.8 kJ between 80 and 250 °C, using Eqs. 12 and 13.

For a reaction of boehmite with OH^- ion,

$$AlOOH(s) + OH^-(1) + H_2O(1) = Al(OH)^-_4(1) \quad (17$$

$$K_r^\circ = a_{Al}/a_{OH}a_w \quad (18)$$

using Eqs. 2 and 4, K_r° is given by

$$K_r^\circ = K_s^\circ/K_w^\circ. \quad (19)$$

Table 1, and Figs. 2 and 3 also show the values of $\log K_r^\circ$ at various temperatures. They can be expressed approximately as a function of the temperature as follows;

$$\log K_r^\circ = 2217/T + 17.32 \log T - 51.10 \quad \text{(Case 1)}, \quad (20)$$

$$\log K_r^\circ = 1066/T + 11.58 \log T - 33.24 \quad \text{(Case 2)}. \quad (21)$$

It should be noted that the values of C, which usually reflect interactions between ions and solvent, have the magnitude of nearly 0.05 commonly for boehmite and gibbsite[1] in a wide temperature range.

The Case of Different Ionic Size Parameters. In order to evaluate an effect of difference in the ionic size parameters, a_1 and a_2, on magnitudes of K_s°, we assumed conveniently $c_2=0$ and $d_2=0$ for the dissociation of water as well as did in the previous paper.[1] Then, from Eqs. 4 and 8,

$$\log (K_w/a_w) = \log K_w^\circ + 2A_tI^{1/2}/(1+B_ta_2I^{1/2}) \quad (22)$$

using $K_s=m_Hm_{Al}=K_w(m_{Al}/m_{OH})$ and Eq. 22,

$$\log (K_s/a_w^2) = \log (K_w^\circ/a_w) + \log (m_{Al}/m_{OH}) + 2A_tI^{1/2}/(1+B_ta_2I^{1/2}). \quad (23)$$

At a given temperature, K_w°, A_t, and B_t are constant, and so the values of $\log (K_s/a_w^2)$ depend upon (m_{Al}/m_{OH}), a_w, a_2, and I. Figure 4 gives plots of $\log(K_s/a_w^2)$ and $I^{1/2}/(1+1.59I^{1/2})$ at 150 °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 the values of $\log (K_s/a_w^2)$ and $\log K_s^\circ$ increase with decrease in the a_2 value.

On the other hand, from Eqs. 2 and 8,

$$\log (K_s/a_w^2) = \log K_s^\circ + 2A_tI^{1/2}/(1+B_ta_1I^{1/2}) + 2c_1I + 2d_1I^2. \quad (24)$$

Figure 4 also shows that the curves approach gradually the theoretical slope, $2A_t$=1.38, as the ionic strength decreases, and deviate positively from the straight line in the range of high ionic strength owing to the last two terms in Eq. 24. The similar tendency was observed at different temperatures up to 300 °C, for example, as shown in Fig. 5. Furthermore, such behaviors are consistent with those of gibbsite in NaOH solutions. Therefore, plots of $\log (K_s/a_w^2)$ *vs.* $I^{1/2}/(1+B_ta_1I^{1/2})$ consist of the straight line in low I range and the positive deviation in high I range, and the latter may be attributed to the formation of complex ion(s) such as $Al_2O(OH)_6^{2-}$ and/or the dehydration of $Al(OH)_4^-$ to $AlO(OH)_2^-$ and AlO_2^- ions.[12] It should be noted that the sodium aluminate and hydroxide solutions show the same behavior according to the extended Debye-Hückel expression in the wide range of temperatures from 40 to 300 °C for the both solid phases of gibbsite and boehmite.

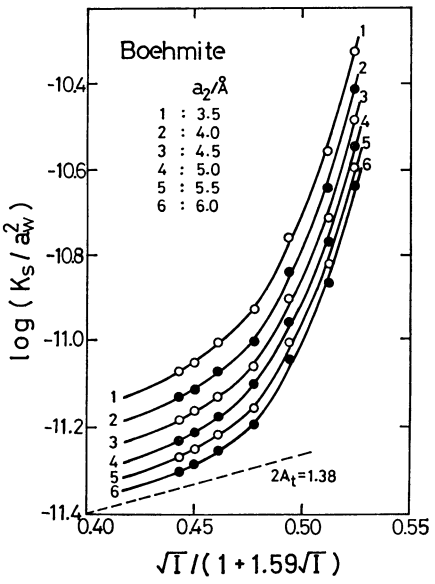

Fig. 4. Plots of $\log(K_s/a_w^2)$ *vs.* $I^{1/2}/(1+1.59I^{1/2})$ at various values of a_2 in the case of a_1=4.5 Å and 150 °C.

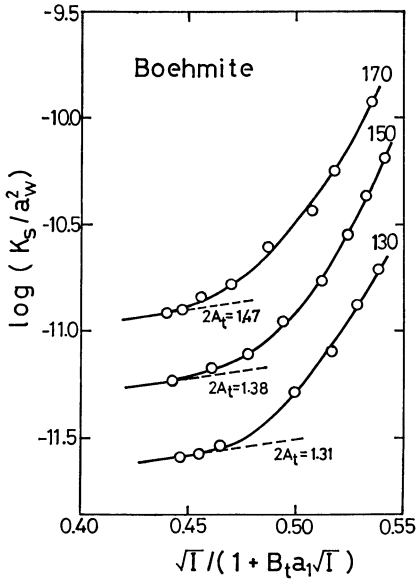

Fig. 5. Plots of $\log(K_s/a_w^2)$ *vs.* $I^{1/2}/(1+B_ta_1I^{1/2})$ at temperatures of 130, 150, and 170 °C in the case of a_1= 4.5 Å and a_2=5.0 Å. A value of B_ta_1 is equal to 1.57, 1.59, and 1.61 at 130, 150, and 170 °C, respectively.

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