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Determination of Thermodynamic Properties of Diaspore from Its Solubility Data in NaOH Solutions

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Synopsis. Thermodynamic properties of diaspore in the alkaline pH range were determined from its solubility data in NaOH solutions by a method presented earlier by the author. The ionic solubility product, $K_S^\circ = a_{Al}a_H/a_w^2$, of diaspore was found to depend upon temperature between 280 and 325 °C as follows: $\log K_S^\circ = -1367/T - 8.67$.

In the previous paper,[1)] the following general equations were derived in order to determine thermodynamic properties of alumina monohydrate from its solubility data in NaOH solutions, they were applied successfully to a dissolution process of boehmite in NaOH solutions:

$$\mathrm{AlOOH(s)} + 2\mathrm{H_2O\,(l)} = \mathrm{Al(OH)_4^-(l)} + \mathrm{H^+(l)}, \tag{1}$$

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

$$\left.\begin{aligned} f(I) &= \log(m_{Al}/m_{OH}) + \log(K_w^\circ/a_w) \\ &= \log K_s^\circ + 2\log(\gamma_2/\gamma_1) \end{aligned}\right\}, \tag{3}$$

where $K_S = m_{Al}m_H$, m_i the molality of species i, $\gamma_1^2 = \gamma_{Al}\gamma_H$, $\gamma_2^2 = \gamma_H\gamma_{OH}$, $K_w^\circ = a_H a_{OH}/a_w$, and a_w the activity of water in a given sodium aluminate and hydroxide. The authors reported solubility data of diaspore in NaOH solutions and discussed its thermodynamic properties by applying an extended Debye-Hückel equation to the solubility data.[2)] An essential question arose because the slopes of the straight lines of $\log K_S$ *vs.* $I^{1/2}/(1+1.5I^{1/2})$ or $I^{1/2}/(1+2.0I^{1/2})$ were only about half of the theoretical Debye-Hückel limiting slopes. The purpose of this paper is to revaluate the solubility data according to Eqs. 1—3.

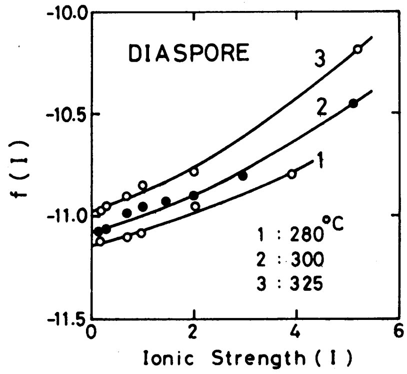

Fig. 1. Relationships between f(I) and ionic strength, I, according to Eq. 3.

TABLE 1. TEMPERATURE DEPENDENCES OF $\log K_S^\circ$, C, D, AND $\log K_r^\circ$ FOR DIASPORE

No.	Temp/°C	$\log K_S^\circ$	$C\times10^2$	$D\times10^3$	$\log K_r^\circ$
1	280	−11.15	8.56	0.80	−0.13
2	300	−11.06	6.95	8.77	−0.02
3	325	−10.96	6.43	16.46	0.19

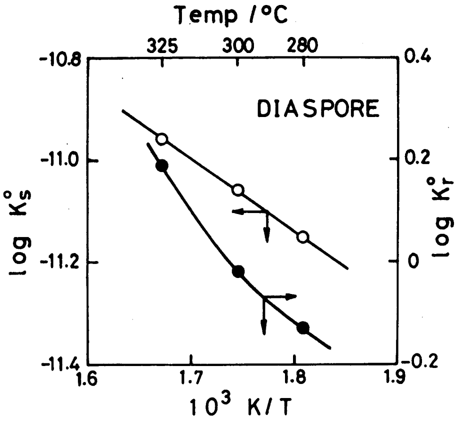

Fig. 2. Temperature dependences of $\log K_s^\circ$ and $\log K_r^\circ$.

Figure 1 gives relationships between f(I) and ionic strength, I, obtained from the solubility data and Eq. 3.[3)] Under an assumption of the same ionic size parameters, Eq. 3 can be rewritten as

$$f(I) = \log K_s^\circ + CI + DI^2, \tag{4}$$

where C and D are adjustable parameters. Table 1 gives the values of $\log K_s^\circ$, C, and D determined from the data in Fig. 1 by a method of least squares. Figure 2 shows a temperature dependence of $\log K_s^\circ$ together with that of $\log K_r^\circ$ calculated by following relations:

$$\mathrm{AlOOH(s)} + \mathrm{OH^-(l)} + \mathrm{H_2O(l)} = \mathrm{Al(OH)_4^-(l)}, \tag{5}$$

$$K_r^\circ = a_{Al}/a_{OH}a_W = K_s^\circ/K_w^\circ. \tag{6}$$

These values are expressed as functions of temperature as follows:

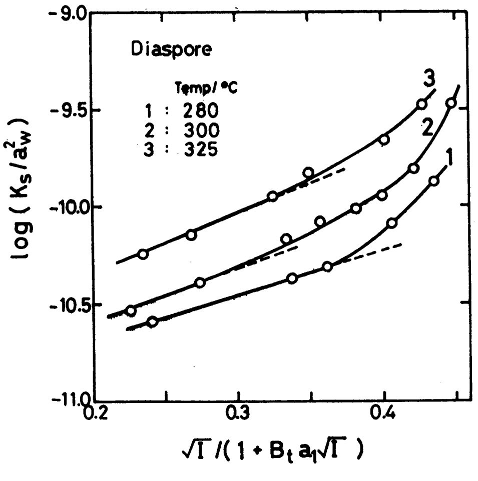

Fig. 3. Plots of $\log(K_s/a_w^2)$ *vs.* $I^{1/2}/(1+B_t a_1 I^{1/2})$ at 280, 300, and 325 °C in the case of $a_1 = 4.5$ Å and $a_2 = 5.0$ Å. Values of $B_t a_1$ are equal to 1.75, 1.79, and 1.87 for curves 1, 2, and 3, respectively.

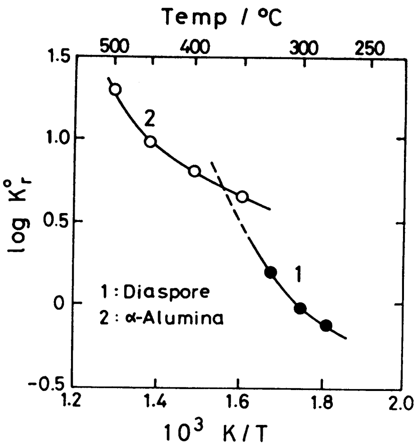

Fig. 4. Temperature dependences of equilibrium constant, K_r°, for diaspore and α-alumina.

$$\log K_s^\circ = -1367/T - 8.67, \tag{7}$$

$$\log K_r^\circ = 2907 - 3.11 \times 10^4/T + 8.27 \times 10^6/T^2, \tag{8}$$

and the heat of Reaction 1 is estimated to be 26.15 kJ.

In the case of different ionic size parameters, the following equations are derived for the dissolution process of alumina monohydrate in NaOH solutions under some assumptions.[1)]

$$\log(K_s/a_w^2) = \log(K_w^\circ/a_w) + \log(m_{Al}/m_{OH}) + 2A_tI^{1/2}/(1 + B_ta_2I^{1/2}), \tag{9}$$

$$\log(K_s/a_w^2) = \log K_s^\circ + 2A_tI^{1/2}/(1 + B_ta_1I^{1/2}), + 2c_1I + 2d_1I^2, \tag{10}$$

Figure 3 gives plots of log (K_s/a_w^2) *vs.* $I^{1/2}/(1+B_ta_1I^{1/2})$ at 280, 300, and 325 °C in the case of $a_1=4.5$ Å and $a_2=5.0$ Å. All the curve consist commonly of a straight line in the range of low ionic strength and a positive deviation from it in the range of high ionic strength. Slopes of the straightline are nearly equal to the theoretical Debye-Hückel limiting slopes, $2A_t$. This means that the essential question about the limiting slope described above could be solved by applying more reasonably the extended Debye-Hückel equation. Furthermore, such behaviors of the curves in Fig. 3 are quite consistentwith those of gibbsite[4)] and boehmite.[1)]

Comparison of the temperature dependence of K_s° for diaspore with that of boehmite suggested that the transition temperature between diaspore and boehmite was 170 °C. On the other hand, the transition temperature between diaspore and α-alumina become 368 °C as shown in Fig. 4,[5)] which agrees well with the Al_2O_3-H_2O phase diagram presented by Neuhaus[7)] and Yamaguchi.[8)]

References

1) Thermodynamics of Al_2O_3–Na_2O–H_2O System, Part 4. Part 3: B.-T. Chang, *Bull. Chem. Soc. Jpn.*, **54**, 2579 (1981).

2) B.-T. Chang, L.-H. Pak, and Y.-S. Li, *Bull. Chem. Soc. Jpn.*, **52**, 1321 (1979).

3) The values of m_{Al} and m_{OH} in Ref. 2 were partly corrected in Fig. 1, considering the weight loss of sample in repeated blank tests in pure water, under the same conditions otherwise.

4) B.-T. Chang, *Bull. Chem. Soc. Jpn.*, **54**, 1960 (1981).

5) Values of K_r° for α-alumina were calculated from its solubility data in NaOH solutions[6)] by using $K_r^\circ = a_{Al}/a_{OH}a_w^{3/2}$ and a value of $a_w = 0.97$ at 350 °C.

6) G. Yamaguchi, H. Yanagida, and S. Soejima, *Bull. Chem. Soc. Jpn.*, **35**, 1789 (1962).

7) H. Neuhaus and H. Heide, *Ber. Dtsch. Keram. Ges.*, **42**, 167 (1965).

8) H. Yanagida and G. Yamaguchi, *J. Ceram. Assoc. Jpn.*, **74**, 94 (1966).