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Solubilities and Rates of Dissolution of Diaspore in NaOH Aqueous Solutions

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The solubility of diaspore(α-$Al_2O_3 \cdot H_2O$ or α-AlOOH) has been measured in NaOH aqueous solutions from 523.15 K to 598.15 K, and at concentrations of Na_2O up to 150.7 g/l. In order to evaluate the equilibrium constant, $K_2^\circ = (a_{AlO_2^-} \cdot a_{H_2O})/a_{OH^-}$, for the dissolution equilibrium of diaspore $AlOOH(s) + OH^-(l) = AlO_2(l) + H_2O(l)$, two methods have been applied to the solubility data. In the first method, analogous to the method previously applied to the dissolution equilibria of gibbsite, bayerite and beohmite, the values of K_2 at relatively low concentrations of NaOH were extrapolated to zero NaOH concentrations. The temperature dependence of K_2° was expressed as $\log K_2^\circ = -(2500/T) + 4.45$. The second method was based on the extended Debye-Hückel theory for the variation in the activity coefficients of AlO_2^-, OH^-, and H^+ ions with ionic strength at any temperature, that is, the value of the solubility product, $K_1^\circ = a_{H^+} \cdot a_{AlO_2^-}$, was obtained at a given temperature by extrapolating values of K_1, equal to $(m_{H^+} m_{AlO_2^-})$, to zero ionic strength. According to the second method, K_2° was expressed as a function of the temperature: $\log K_2^\circ = -(1600/T) + 2.52$ when $A = 2.0$ or $\log K_2^\circ = -(1550/T) + 2.48$ when $A = 1.5$, where A is a parameter. From kinetic analysis of the dissolution rate of diaspore in NaOH solution, the rate constants per unit surface area of diaspore were found to be 0.31, 0.45, and 0.68 $m^{-2}\,h^{-1}$ at 548.15, 573.15, and 598.15 K, respectively.

The dissolution of alumina hydrates in aqueous NaOH solutions is well known, and serves as a key step in the extractive metallurgy of aluminium (the Bayer process). The solubilities of alumina hydrates in NaOH solutions have been measured by Russell, Edward and Taylor.[1] The solubilities of gibbsite, bayerite and boehmite in NaOH solutions from 313.15 K to 473.15 K were reported, and equilibrium constants for the reaction in which alumina hydrates react with OH^- ion to form AlO_2^- ion were presented. The solubility of gibbsite was precisely determined in order to calculate the free energy of formation and to clarify the structures of the aluminate ions in solution at high pH.[2-5] Bernshtein and Matsenok reported the solubilities of boehmite[6] and diaspore[7] at high temperatures between 532.15 and 573.15 K. The data on the solubilities of diaspore, however, appear to be insufficient for discussion of the thermodynamic properties of diaspore in NaOH solutions.

The purpose of this work is to determine the solubilities of diaspore in NaOH solutions and to clarify the thermodynamic and kinetic properties of the dissolution process.

Experimental

Diaspore samples were prepared by the hydrothermal treatment of boehmite in 0.5 M NaOH solution, to which 10 wt % of natural diaspore was added as seed crystals (623 K, 170 atm for two weeks).[8,9] In order to increase the purity of the diaspore samples, the hydrothermal treatment was repeated several times, using the synthesized diaspore as seed crystals. The results of chemical analysis of the samples are listed in Table 1. X-Ray diffraction analysis showed the presence of only diaspore. Furthermore, DTA analysis indicated an endothermic peak from 623 K to 873 K, corresponding to the transformation of diaspore into α-alumina. The above results confirmed the purity of the diaspore to be higher than 99%.

Table 1. Chemical compositions of diaspore samples (wt %)

Sample	Al_2O_3	SiO_2	Fe_2O_3	TiO_2	Ignition loss
Natural	76.86	4.04	0.43	3.75	15.16
No. 1	83.73	0.00	0.36	0.57	15.49
No. 2	85.22	0.00	0.04	0.10	14.57
Calcd	85.00	—	—	—	15.00

Measurements of the solubility of diaspore were as follows: a sample (0.40 g) and NaOH solution (5 ml) were laid in a Morey-type reactor which was made of Hastelloy with Ag packing. Heat was supplied and the temperature was kept constant in an electric furnace for the attainment of equilibrium. Quenching to room temperature, treatment with hot hydrochloric acid removed the aluminium hydroxide precipitated. Experimentally it was confirmed that the amounts of diaspore dissolved in the hot HCl solution were negligible. The concentrations of alumina dissolved in the NaOH solution, $m_{AlO_2^-}$, were calculated from the differences in the weights of the diaspore before and after dissolution. The concentrations of the OH^- ion at equilibrium, m_{OH^-}, were calculated from the differences between the initial concentration of NaOH, $(m_{OH^-})_0$, and that of $m_{AlO_2^-}$, *i.e.*, $m_{OH^-} = (m_{OH^-})_0 - m_{AlO_2^-}$.

Results and Discussion

Solubility of Diaspore.　In Table 2 are shown the results of solubility measurements for diaspore (No. 1) in NaOH solution up to 4.83 M from 523.15 K to 598.15 K. The dissolution process for diaspore in NaOH solution may be expressed as follows;

$$Al_2O_3 \cdot H_2O(s) + 2OH^-(l) = 2AlO_2^-(l) + 2H_2O(l) \quad (1)$$

or

$$AlOOH(s) + OH^-(l) = AlO_2^-(l) + H_2O(l). \quad (2)$$

The equivalent ratio of the AlO_2^- ion to the OH^- ion, α, may be used as a measure of the solubility of diaspore, *i.e.*, as the solubility increases, α approaches unity. As shown in Fig. 1, the values of α shifted to unity not only with increase in the dissolution temperature but also with the initial concentrations of NaOH solution. Bernshtein and Matsenok[7] also observed

Table 2. Solubility and equilibrium constant of diaspore in NaOH solutions

Run	T (K)	Initial concentration of Na_2O (g/l)	Time (h)	Equilibrium concentration		H_2O activity (mole fraction)	Equilibrium constant K_2
				$m_{AlO_2^-}$ (equiv./l)	m_{OH^-} (equiv./l)		
1	523.15	6.8	116	0.08	0.14	0.996	0.57
2	523.15	13.6	116	0.15	0.30	0.99	0.50
3	523.15	22.3	95	0.22	0.51	0.985	0.43
4	523.15	31.6	97	0.33	0.70	0.98	0.56
5	523.15	63.6	94	0.51	1.55	0.94	0.31
6	523.15	91.5	100	0.77	2.18	0.89	0.31
7	553.15	6.2	72	0.10	0.10	0.996	1.00
8	553.15	13.6	72	0.23	0.21	0.99	1.08
9	553.15	22.3	71	0.34	0.38	0.985	0.88
10	553.15	31.6	71	0.48	0.54	0.98	0.87
11	553.15	63.6	72	1.08	0.97	0.94	1.05
12	553.15	119.0	70	2.29	1.55	0.84	1.24
13	573.15	4.9	82	0.09	0.07	0.997	1.28
14	573.15	9.9	74	0.17	0.15	0.994	1.13
15	573.15	22.3	74	0.39	0.32	0.985	1.20
16	573.15	31.6	48	0.57	0.45	0.98	1.24
17	573.15	45.6	70	0.83	0.64	0.96	1.25
18	573.15	63.6	69	1.16	0.88	0.94	1.24
19	573.15	91.1	7.	1.81	1.13	0.89	1.43
20	573.15	150.7	70	3.73	1.13	0.79	2.61
21	598.15	6.2	56	0.13	0.07	0.996	1.85
22	598.15	13.6	65	0.21	0.11	0.994	1.90
23	598.15	22.3	47	0.46	0.25	0.985	1.81
24	598.15	32.5	48	0.71	0.34	0.98	2.05
25	598.15	63.6	48	1.41	0.63	0.94	2.10
26	598.15	119.0	45	2.80	1.05	0.84	2.24
27	598.15	150.7	45	4.34	0.52	0.79	6.59

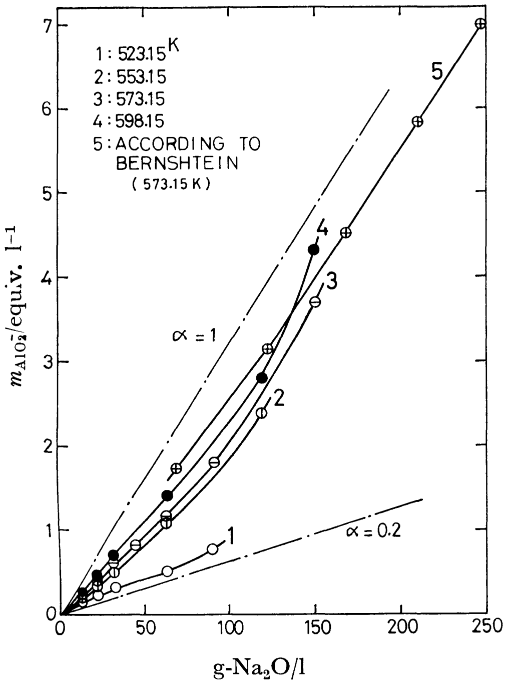

Fig. 1. Solubilities of diaspore in NaOH solutions from 523.15 K to 598.15 K.

similar results in the solubility of diaspore. The values of α for diaspore in this work, however, are lower.

In Fig. 2, the values of α for diaspore are compared with those of α-alumina for approx. equal concentrations of NaOH.[10] At 626 K the two curves intersected which agrees with the transformation temperature of diaspore into α-alumina under 100 atm in the phase diagram of Al_2O_3–H_2O system.[8,9] It is readily seen from Fig. 2 that the temperature dependancy of the solubility of diaspore was much larger

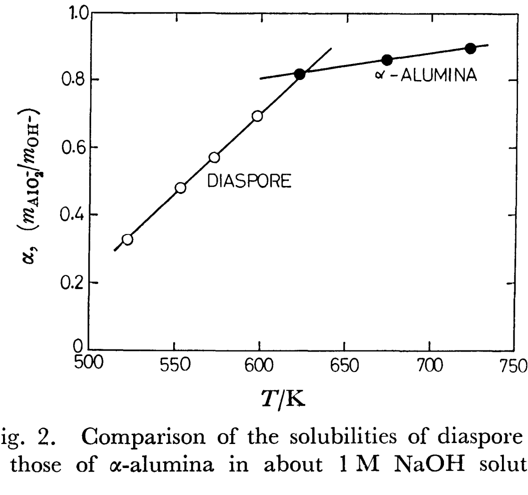

Fig. 2. Comparison of the solubilities of diaspore with those of α-alumina in about 1 M NaOH solution.

than that of α-alumina.

Equilibrium Constants of Dissolution. In order to discuss the dissolution process of diaspore, three equilibrium constants were used as follows:

$$AlOOH(s) = AlO_2^-(l) + H^+(l) \quad (3)$$

$$K_1^\circ = a_{AlO_2^-} \cdot a_{H^+} \quad (4)$$

$$AlOOH(s) + OH^-(l) = AlO_2^-(l) + H_2O(l) \quad (5)$$

$$K_2^\circ = a_{AlO_2^-} \cdot a_{H_2O}/a_{OH^-} \quad (6)$$

$$H_2O(l) = H^+(l) + OH^-(l) \quad (7)$$

$$K_w = a_{H^+} \cdot a_{OH^-}/a_{H_2O} \quad (8)$$

where

$$K_1^\circ = K_2^\circ \cdot K_w. \quad (9)$$

Russell *et al.*[1)] derived equilibrium constants, K_2°, at various temperatures by extrapolating $K_2 = m_{AlO_2^-} \cdot m_{H_2O}/m_{OH^-}$ to zero NaOH concentration, assuming that the activity coefficients of the OH^- and AlO_2^- ions are equal and using values of the activity of water in NaOH solutions at 298.15 K. The values of K_2° for diaspore obtained by Russell's method are given in Table 2 and Fig. 3 where the values of K_2° have been neglected at very low NaOH concentration because of large deviations. From the linear relationship between $\log K_2^\circ$ and $1/T$, K_2° was found to be a function of the temperature by the following equation:

$$\log K_2^\circ = -2500/T + 4.45. \quad (10)$$

In Table 3 the equilibrium constants and thermodynamic quantities for the dissolution equilibrium (5) obtained from K_2°, Eq. 10 and the thermodynamic relationships are given. The solubility product of $HAlO_2$, K_1°, was found to be 1.13×10^{-13} at 573.15 K, which was approx. six times greater than at 298.15 K(2×10^{-13}).[1)]

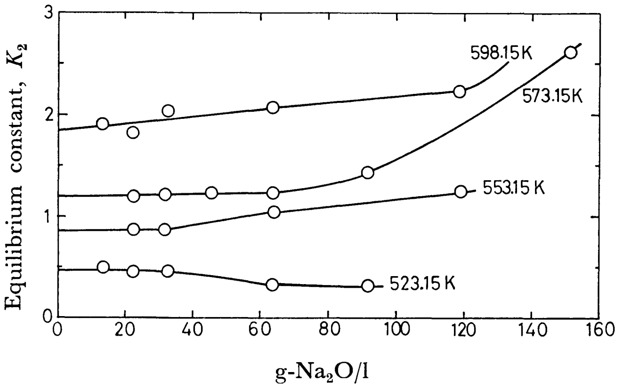

Fig. 3. Equilibrium constants (K_2) obtained by the Russel's method for the dissolution of diaspore in NaOH solutions.

Several assumptions are made in the detremination of equilibrium constants by Russell's method. Firstly, the activity coefficients of AlO_2^- and OH^- ions are assumed to be equal, neglecting the difference in ion size. Secondly, the values of a_{H_2O} at 298.15 K were used at high temperatures without any correction (up to 598.15 K). Thirdly, it is not appropriate to mix units in an equilibrium constants expression by multiplying the activity of water on the mole fraction scale together with the activities of AlO_2^- and OH^- ions on the normality scale.

As described above, generally the value of α at a given temperature becomes larger with increase in the concentration of NaOH solution. The addition of salts such as NaCl, Na_2SO_4, and $NaNO_3$ to the NaOH solution increased the solubility of the alumina hydrates.[4)] In the case of diaspore, it was experimentally confirmed that the solubility in a mixed solution containing 1 M NaOH and 1 M NaCl was one and a half times larger than in 1 M NaOH solution at 573.15 K. This indicates that the increase in NaOH concentration raises the solubility of diaspore not only through an increase in the OH^- ion concentration but also through an increase in the ionic strength of the solution. Marshall *et al.* discussed the effect of ionic strength on the solubilities of $CaSO_4$ and its hydrates, and $Ca(OH)_2$ by applying the extended Debye-Hückel theory to high temperature aqueous solution sup to the critical temperature of water.[12,13)]

According to Marshall's method, the solubility products are given as follows:

$$K_1^\circ = m_{H^+} \cdot m_{AlO_2^-} \cdot \gamma_{H^+} \cdot \gamma_{AlO_2^-} \quad (11)$$

$$= K_1 \cdot \gamma_\pm^2 \quad (12)$$

where

$$K_1 = m_{H^+} m_{AlO_2^-}. \quad (13)$$

According to the extended Debye-Hückel theory,

$$\log \gamma_\pm = -S_T I^{1/2}/(1+baI^{1/2})$$
$$= -S_T I^{1/2}/(1+AI^{1/2}) \quad (14)$$

where S_T is the limiting Debye-Hückel slope, b is a function of temperature and dielectric constant, a is an "ion size parameter," and $A = ba$. From Eqs. 12 and 14,

$$\log K_1^\circ = \log K_1 + 2S_T I^{1/2}/(1+AI^{1/2}). \quad (15)$$

The ionic strengths, I, are equal to the initial concentrations of NaOH solution expressed as molality, *i.e.*,

TABLE 3. EQUILIBRIUM CONSTANTS OBTAINED BY RUSSEL'S METHOD AND THERMODYNAMIC QUANTITIES FOR THE DISSOLUTION EQUILIBRIUM

T (K)	Equilibrium constants K_1°	K_2	K_w[a)]	ΔG (kJ)	ΔH (kJ)	ΔS (J/deg)
523.15	4.01×10^{-12}	0.45	8.91×10^{-12}	3.4	47.8	85
553.15	8.70×10^{-12}	0.87	1.00×10^{-11}	0.63	47.8	85
573.15	1.13×10^{-11}	1.24	9.12×10^{-12}	−1.0	47.8	85
598.15	1.29×10^{-11}	1.82	7.08×10^{-12}	−3.0	47.8	85

a) From Ref. 11.

$$I = (m_{AlO_2^-} + m_{OH^-} + m_{Na^+})/2 \quad (16)$$

$$= (m_{NaOH})_0. \quad (17)$$

Figures 4 and 5 presnet the experimental data for the solubilities of diaspore plotted as $\log K_1$ against the Debye-Hückel function, $I^{1/2}/(1+AI^{1/2})$. The values of $A=1.5$ and 2.0 used correspond to $a=3.2$ and4.3 Å at 573.15 K, respectively. In the range of relatively low ionic strengths $\log K_1$ changed linearly with the Debye-Hückel function at three temperatures except 523.15 K. The slopes correspond to $2S_T$ in Eq. 15 with the extrapolated values at zero ionic strength corresponding to $\log K_1^\circ$. Figure 6 shows an almost linear relationship between $\log K_2^\circ$ and $1/T$, *i.e.*,

$$\log K_2^\circ = -1550/T + 2.48 \quad (A=1.5) \quad (18)$$

$$\log K_2^\circ = -1600/T + 2.52 \quad (A=2.0). \quad (19)$$

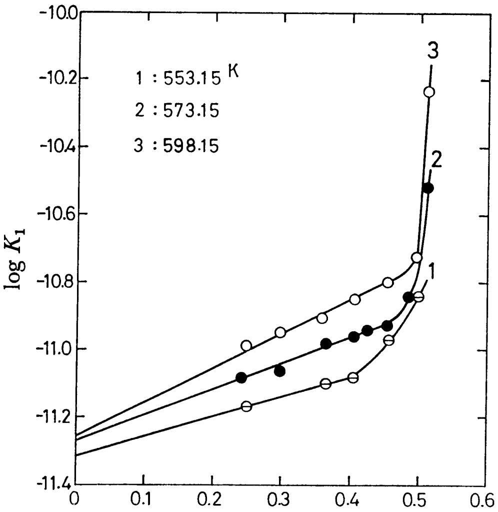

Fig. 4. Logarithm of solubility products (K_1) of diaspore in NaOH solutions *vs.* $I^{1/2}/(1+1.5I^{1/2})$.

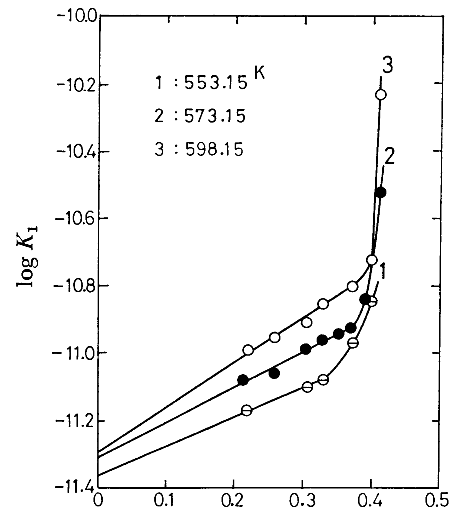

Fig. 5. Logarithm of solubility products(K_1) of diaspore in NaOH solutions *vs.* $I^{1/2}/(1+2I^{1/2})$.

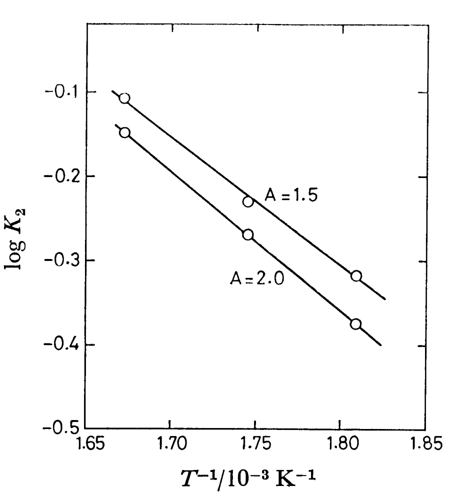

Fig. 6. Temperature dependencies of equilibrium constant K_2 obtained by the Marshall's method.

In Table 4 the equilibrium constants and the thermodynamic quantities are listed for Reaction 5 which have been calculated using Eqs. 18 and 19, and thermodynamic relationships. The magnitudes of K_2° were smaller than those obtained by Russell's method. Although the values of S_T were about half the calculated values according to the Debye-Hückel theory, the values of K_2° obtained by Marshall's method may be more reasonable due to the improved extrapolation. As shown in Figs. 4 and 5, $\log K_1^\circ$ deviated from linearity largely at high ionic strength, which may be a direct consequence of ion-solvent interactions[14] and/or the formation of a new solid phase(s) such as $Na_2O \cdot Al_2O_3 \cdot 2.5H_2O$, $3Na_2O \cdot Al_2O_3 \cdot 6H_2O$, *etc.*[15]

Rate of Dissolution of Diaspore. In Fig. 7, the amounts of dissolved diaspore (No. 2) have been plotted as $m_{AlO_2^-}$ against reaction time, t, at three temperatures (548.15, 573.15, and 598.15 K) with a constant initial NaOH concentration of 0.970 M. The times required for the dissolution equilibrium to be

TABLE 4. EQUILIBRIUM CONSTANTS OBTAINED BY MARSHALL'S METHOD AND THERMODYNAMIC QUANTITIES FOR THE DISSOLUTION EQUILIBRIUM

A	T (K)	Equilibrium constants K_1°	K_2	K_w	ΔG (kJ)	ΔH (kJ)	ΔS (J/deg)	Limiting slope S_T
1.5	553.15	4.8×10^{-12}	0.48	1.00×10^{-11}	3.3	29.6	48	0.34
	573.15	5.4×10^{-12}	0.59	9.12×10^{-12}	2.5	29.6	47	0.39
	598.15	5.5×10^{-12}	0.78	7.08×10^{-12}	1.2	29.6	47	0.50
2.0	553.15	4.2×10^{-12}	0.42	1.00×10^{-11}	3.9	30.6	48	0.44
	573.15	4.9×10^{-12}	0.54	9.12×10^{-12}	2.9	30.6	48	0.52
	598.15	5.0×10^{-12}	0.71	7.08×10^{-12}	1.7	30.6	48	0.67

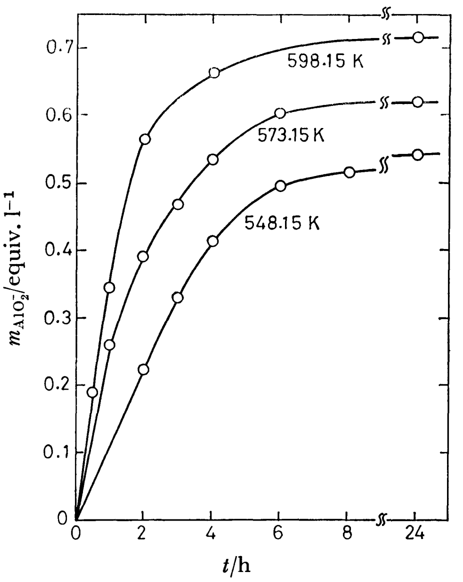

Fig. 7. Dissolution curves of diaspore in 0.970 M NaOH solution at three temperatures.

attained were 40 h(548.15 K), and 24 h(573.15 and 598.15 K). The diaspore sample of No. 2 had a special surface area of 3.40 m^2/g(BET).

Assuming that the chemical reaction of AlOOH with OH^- ions on the surface of the diaspore is the rate-determining step, the rate of dissolution may be expressed as follows:

$$d(m_{AlO_2^-}/m_{OH^-})/dt = kS[(m_{AlO_2^-}/m_{OH^-})_e - (m_{AlO_2^-}/m_{OH^-})] \tag{20}$$

where k is the rate constant per unit of surface area of the sample, S is the total surface area of undissolved diaspore at time t and $(m_{AlO_2^-}/m_{OH^-})$ is the concentration ratio of AlO_2^- to OH^- ions at equilibrium.

In terms of a new variable, x, Eq. 20 becomes

$$dx/dt = kS(x_e - x) \tag{21}$$

where

$$x = m_{AlO_2^-}/m_{OH^-}. \tag{22}$$

From the experimental data, x_e equals 0.59 at 548.15 K, 0.64 at 573.15 K, and 0.74 at 598.15 K, respectively.

The value of S is also a function of x. Introducing the mean size of the diaspore particles, r, S, and the weight of the undissolved diaspore, W, may be expressed as follows:

$$S(r) = a_1 r^2 \tag{23}$$

$$W(r) = a_2 r^3 \tag{24}$$

$$S(r)/S(r_0) = (r/r_0) = [W(r)/W(r_0)]^{2/3} \tag{25}$$

where a_1 and a_2 are proportionality constants and r_0 is the initial mean size. From the mass balance for the diaspore sample,

$$W(r_0) - W(r) = (m_{AlO_2^-} \cdot G \cdot V)/1000. \tag{26}$$

In this equation, G is the gram equivalent of diaspore equal to 60 and V is the volume of the solution. Substituting V=5 ml and G=60,

$$W(r_0) - W(r) = 0.030 m_{AlO_2^-}. \tag{27}$$

Furthermore, since $W(r_0)$=0.40 g and (m_{OH^-})=0.970 M, S may be expressed as a function of x as follows:

$$S(x)/S_0 = [(1+0.27x)/(1+x)]^{2/3} \tag{28}$$

where S_0 is the initial total surface area and equal to 1.36 m^2 when $W(r_0)$=0.40 g. Substituting Eq. 28 into Eq. 20:

$$dx/dt = kS_0[(1+0.27x)/(1+x)]^{2/3}(x_e - x). \tag{29}$$

This differencial equation may be solved as follows:

$$[f(1) - f(y)]/(BS_0) = kt \tag{30}$$

where

$$y = [(1+0.27x)/(1+x)]^{1/3} \tag{31}$$

$$\begin{aligned} f(y) = n^2\Big[\ln(y-m) - \frac{1}{2}\ln(y^2+my+m^2) \\ + 3^{1/2}\tan^{-1}\Big(\frac{2y+m}{\sqrt{3}}\Big)\Big] \\ - m^2\Big[\ln(y-n) - \frac{1}{2}\ln(y^2+ny+n^2) \\ + 3^{1/2}\tan^{-1}\Big(\frac{2y+n}{\sqrt{3}}\Big)\Big] \end{aligned} \tag{32}$$

$$B = 1.38m^2n^2(m^3-n^2)(1+x_e) \tag{33}$$

$$m = [(1+0.27x_e)/(1+x_e)]^{1/3} \tag{34}$$

$$n = (0.27)^{1/3} = 0.65. \tag{35}$$

Figure 8 shows the linear relationship between t and $[f(1) - f(y)]/(BS_0)$. From the slopes of the straight lines, the values of k were obtained as follows:

$$k = 0.31\ m^{-2} \cdot h^{-1} \quad (548.15\ K) \tag{36}$$

$$= 0.45 \quad (573.15\ K) \tag{37}$$

$$= 0.68. \quad (598.15\ K). \tag{38}$$

From the Arrhenius plot between $\log k$ and $(1/T)$, the activation energy for the dissolution of diaspore in NaOH solution was found to be 44 kJ.

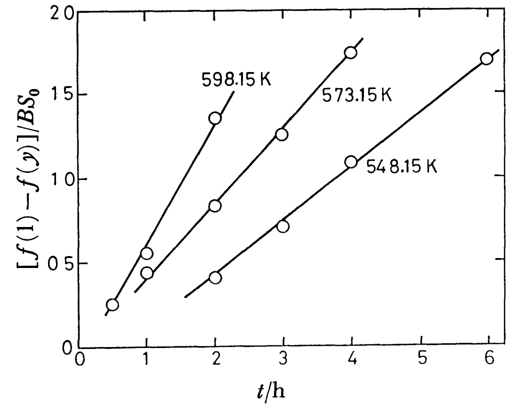

Fig. 8. $f(1) - f(y)/(BS_0)$ *vs.* dissolution time.

References

1) A. S. Russell, J. D. Edwards, and C. S. Taylor, *Trans. AIME J. Metals*, **7**, 1123 (1955).

2) K. Goto, *Nippon Kagaku Zasshi*, **81**, 349 (1960).

3) C. R. Frink and M. Peech, *Soil Sci. Soc. Am., Proc.*, **26**, 346 (1962).

4) A. N. Lypunov, A. G. Khodakova, and Z. G. Galkina, *Tsuvet. Met.*, **37**, 48 (1964).

5) J. A. Kittrick, *Soil Sci. Soc. Am., Proc.*, **30**, 595 (1966).

6) V. A. Bernshtein and E. A. Matsenok, *Zh. Prak.*

Khim., **34**, 982 (1961).

7) V. A. Bernshtein and E. A. Matsenok, *Zh. Prak. Khim.*, **38**, 1935 (1965).

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

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

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

11) J. R. Fisher and H. L. Barnes, *J. Phys. Chem.*, **76**, 90 (1972).

12) W. L. Marshall, R. Slusher, and E. V. Jones, *J. Chem. Eng. Data*, **9**, 187 (1964); W. L. Marshall and E. V. Jones, *J. Phys. Chem.*, **70**, 4028 (1966).

13) L. B. Yeatts and W. L. Marshall, *J. Phys. Chem.*, **71**, 2641 (1967).

14) J. O'M. Bockris and A. K. N. Reddy, "Modern Electrochemistry," Plenum Press, New York (1970), Vol. 1, p. 238.

15) S. I. Kuznechov, V. A. Tserevyankin, and P. Sh. Shklyan, *Zh. Prak. Khim.*, **35**, 2588 (1962).