

Kinetics and Mechanism of the Heterogeneous Reactions of γ -, κ -, and α -Aluminas with Aqueous Sodium Hydroxide Solutions

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γ -, κ -, and α -Alumina powders, prepared from gibbsite ($S_0 = 0.4 \text{ m}^2/\text{g.}$), react with excess of well stirred hydroxide solutions (1–16M) according to a second-order reaction with respect to powder weight (that is, third order in powder surface area).

The rate constants vary with $(a_{\pm})^{\frac{1}{2}}$ according to a Langmuir-type adsorption isotherm and also with a_w . For α -alumina, $k_{w,1} = ca. 0.001 \text{ g.}^{-1} \text{ hr.}^{-1}$ at 115° . For κ -alumina, $k_{w,1} = 0.018 \text{ g.}^{-1} \text{ hr.}^{-1}$ at 85° , 0.053 at 100° , and 0.180 at 115° . For γ -alumina $k_{w,1} 0.05 \text{ g.}^{-1} \text{ hr.}^{-1}$ at 85° , 0.20 at 100° , and 0.46 at 115° . The energy of activation for the reactions is for γ -alumina, 20,200; for κ -alumina, 22,000; and for α -alumina *ca.* 27,000 cal./mole. The kinetics suggest that the rate-determining step for dissolution of aluminas is a reaction between a hydrated defect region on the alumina surface and two hydroxyl ions, simultaneously weakly chemisorbed (near this region): additional water molecules may also participate in the reaction. Reaction mechanisms are discussed.

HETEROGENEOUS reactions between inorganic solids and aqueous hydroxide solutions are of theoretical and practical importance. The kinetics of dissolution of silica powders by sodium and calcium hydroxide solutions has been studied¹⁻⁶ but few quantitative studies

have been reported on the reactions of alumina with aqueous alkali solutions.^{7,8} This paper presents a study of the kinetics of the reactions of γ -, κ -, and α -alumina powders (prepared from gibbsite) with a large excess of sodium hydroxide solutions at 85 – 115° under

¹ D. W. Clelland, *J. Appl. Chem.*, 1952, **2**, 182.

² G. O. Assarsson, *J. Phys. Chem.*, 1956, **60**, 197, 1559; 1957, **61**, 473.

³ P. E. Halstead, N.B.S. Monograph, 1960, **43**, 321.

⁴ I. Bergman, *J. Appl. Chem.*, 1961, **11**, 369.

⁵ S. A. Greenberg, *J. Phys. Chem.*, 1961, **65**, 12.

⁶ J. G. Hooley, *Canad. J. Chem.*, 1961, **37**, 1221.

⁷ A. Bielanski, *Roczniki Chem.*, 1956, **30**, 995.

⁸ R. Schrader, *Z. anorg. Chem.*, 1967, **350**, 120, 130, 137.

conditions where the reactions are chemically rate-controlled.

EXPERIMENTAL

Gibbsite (4–50 μm . crystals prepared by the Bayer process) was supplied by Aluminium Company, America (Alcoa), and contained $\text{Al}(\text{OH})_3$, 99.83; SiO_2 , 0.008; Fe_2O_3 , 0.002; Na_2O , 0.16%. A 3–10 μm . fraction was obtained by sedimentation, washed, and dried to constant weight at 100°; overall surface area was 0.4 m^2/g . γ -Alumina (low surface area), κ -alumina, and α -alumina were prepared by heating the Gibbsite powder in air to constant weight (6 hr.) at 800°, 1000°, and 1200°. The samples were transferred to desiccators over freshly activated silica. Surface area per hydroxyl ion adsorption were 200, 80, and 12 m^2/g .

Solutions.—Sodium hydroxide solutions (0.5–16M) were prepared from AnalaR material in double-distilled CO_2 -free water. Concentrations were determined by titration against standard hydrochloric acid.

Mean Ionic Activity.— a_{\pm} Values at temperatures up to 70° are available from Åckerlof's work.¹¹ We noted that $\log a_{\pm}$ values decreased linearly with temperature (cf. ref. 12): a_{\pm} values at higher temperature were then estimated by extrapolation from plots of $\log a_{\pm}$ against temperature.

Water Activity.— a_w values at temperatures up to 70° are also available.¹¹ At higher temperatures they were similarly estimated by extrapolation from plots of $\log a_w$ against temperature.

Solutions of Al Analysis.—EDTA solution (0.01M), zinc sulphate solution (0.01M), and acetic acid-ammonium acetate buffer solution (1M) were prepared from AnalaR materials in double glass-distilled water. Dithizone solution (0.001M) was made by dissolving 0.025 g. of B.D.H. reagent in 100 ml. of 95% ethanol.

Kinetics.—Alumina powder (0.51 g.) was dispersed in a large excess (100 ml.) of aqueous hydroxide solutions in a Quickfit flask, fitted with an air-condenser. The flask was heated in air at 85–115° ($\pm 1^\circ$) over an electrically heated hot-plate. The solution was stirred magnetically at 200 rev./min., that is, sufficiently rapidly to eliminate any modification of the 'chemical' reaction rate by slow diffusion processes.¹³ Solution (1 ml.) was withdrawn for analysis after various reaction times. In several runs, a series of separate flasks (each containing the same suspension) was used and successive flasks were removed from the air-bath. The unchanged powder from each flask was washed with distilled water and dried to constant weight (w_t) at 100°.

Chemical Analysis of the Reaction Solution.—Aliquot volumes of reaction solution were diluted to 10 ml. and centrifuged at 1000 rev./min. for 5 min. to remove any suspended finely divided powder that would react slowly with EDTA. 5 ml. of solution were then withdrawn and analysed by Waenninen's method¹⁴ modified for determination of aluminate and low molecular-weight polyoxoanions.¹⁵ 0.01M-EDTA solution (5 ml.) and 1M-acetic acid-ammonium acetate buffer solution (10 ml.) were added and the solution was heated to 80° for 2 min. to convert all

'aluminate' into complexed aquoaluminium cation at pH 4.5; the solution was cooled, and 95% ethanol (10 ml.) and 0.001M-dithizone solution (2 ml.) were added. The excess of EDTA was back-titrated against 0.01M-zinc sulphate from a microburette. Then 1 ml. of EDTA solution used $\equiv 0.2698$ mg. Al $\equiv 0.5100$ mg. Al_2O_3 dissolved as aluminate. The accuracy was $\pm 0.5\%$. Aluminate concentrations $(w_{\text{sol}})_t$ were corrected for volume change during the run.

RESULTS AND DISCUSSION

We have studied the dissolution of γ -, κ -, and α -alumina powders (overall surface area $S_0 = 0.4 \text{ m}^2/\text{g}$.) in aqueous sodium hydroxide solutions (concentrations 0.5–16M) at 85–115°. Solid and reaction solution were analysed during reaction.

Kinetics.—The kinetics of heterogeneous reactions are generally studied by measurement of solid weight (w_t) after different reaction times. The 'aluminate' concentration $(w_{\text{sol}})_t$ in any reaction solution as determined by the modified Waenninen's method (preheating with EDTA and buffer solution at 80°) was found equivalent to the weight loss (Δw_t) of the alumina powder. Low results for aluminate concentration were obtained unless the preheating procedure was followed: errors were greatest with solutions from concentrated hydroxide solution ($> ca. 4\text{M}$) at high temperature ($> 50^\circ$). That is, aluminas react with hydroxide solution to form hydrated 'aluminate' anion $[\text{Al}(\text{OH})_4(\text{H}_2\text{O})_2]^-$, with some low molecular-weight polyoxoanion at high pH and temperature.^{15,16} Values of w_t were generally determined by analysis of solution for $(w_{\text{sol}})_t$; then, $w_t = (w_0 - \Delta w_t) = [w_0 - (w_{\text{sol}})_t]$.

Reaction Order and Rate Constants.— α -Alumina. At 100°, with 16M-NaOH, 25% of the solid reacts in ≥ 30 hr. At 115°, with 12M-NaOH, 25% of solid reacts in > 30 hr., but with 16M-NaOH in 15 hr. Dissolution is even slower at lower hydroxide concentrations, while solutions boil at higher temperatures: exact reaction orders and rate constants could not be determined.

κ -Alumina. This reacts with hydroxide solutions *ca.* 20 times more rapidly than α -alumina and according to a second-order mechanism with respect to powder weight: the function $(1/\alpha_t - 1)$ where $\alpha_t = w_t/w_0$ varies linearly with time (t) of reaction (see Figure 1). We thus obtain equation (1) where k_w is the rate constant with respect to powder weight ($\text{g}^{-1} \text{ hr}^{-1}$).

$$dw/dt = -k_w w_t^2 \quad (1)$$

γ -Alumina. This reacts with hydroxide solutions about four times more rapidly than κ -alumina. The function $(1/\alpha_t - 1)$ varies linearly with time for 78–80% of the reaction (Figure 2): the rate of dissolution then decreases somewhat.

⁹ H. C. Stumpf, *Ind. Eng. Chem.*, 1950, **42**, 1398.

¹⁰ G. W. Brindley and J. O. Choe, *Amer. Mineralogist*, 1961, **46**, 771.

¹¹ G. Åckerlof, *J. Amer. Chem. Soc.*, 1937, **59**, 1855.

¹² D. G. Ives, *Discuss. Faraday Soc.*, 1957, **24**, 147.

¹³ A. Packter and H. S. Dhillon, *J. Chem. Soc.*, (A), 1969, 2588.

¹⁴ E. Waenninen, *Analyt. Chem. Acta*, 1955, **12**, 308.

¹⁵ T. G. Pearson, R.I.C. Monograph, 1955, No. 3.

¹⁶ R. C. Plumb, *J. Phys. Chem.*, 1964, **68**, 2057.

Now, if the overall surface area is A_t at any reaction time t , as given by equation (2), we obtain equation (3)

$$A_t = \frac{6}{\rho^{\frac{2}{3}}} w_t^{\frac{2}{3}} = \bar{A} w_t^{\frac{2}{3}} \quad (2)$$

$$dw/dt = \frac{-k_w}{\bar{A}^3} A_t^3 = -k_A A_t^3 \quad (3)$$

where $k_A = k_w/\bar{A}^3$ is the rate constant with respect to overall surface area, in units of $\text{g.}^{-1} (\text{m.}^2/\text{g.})^{-3} \text{hr.}^{-1}$.

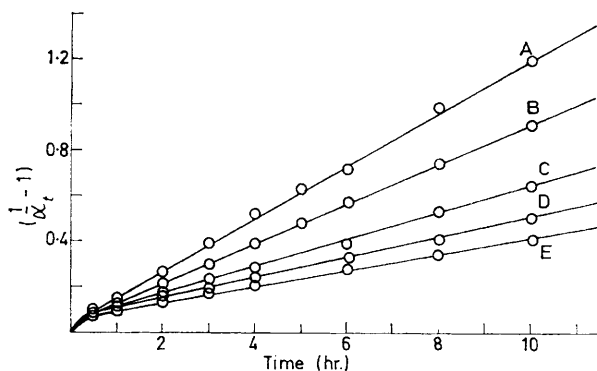


FIGURE 1 Reaction of κ -alumina with sodium hydroxide solutions at 100°; A, 14M; B, 10M; C, 6M; D, 4M; E, 2M

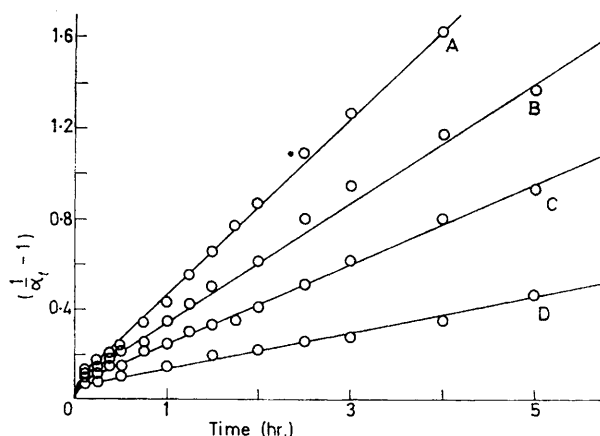


FIGURE 2 Reaction of γ -alumina with sodium hydroxide solutions at 100°; A, 10M; B, 6M; C, 2M; D, 1M

Also $\bar{A} = A_0/w_0^{\frac{2}{3}}$ where A_0 and w_0 are initial values of A_t and w_t , while initial overall surface area $A_0 = S_0 w_0$, where S_0 is initial specific surface area. Equation (4) follows, and these reactions are of the third order in

$$k_A = \frac{k_w}{(A_0/w_0^{\frac{2}{3}})^3} = \frac{k_w w_0^2}{A_0^3} = \frac{k_w}{S_0^3 w_0} \quad (4)$$

surface area and k_w is determined by k_A .

Rate Constants.—Integration of equation (1) leads to

¹⁷ S. J. Gregg, 'The Surface Chemistry of Solids,' Chapman and Hall, London, 1961, chap. 4A.

¹⁸ K. J. Laidler, 'Catalysis,' Reinhold, New York, 1954, vol. 1, chap. 4.

¹⁹ F. A. Long, *Chem. Rev.*, 1957, 935.

equations (5) and (6), and k_w was determined from the slopes of plots of α_t^{-1} against time.

$$\left(\frac{1}{\alpha_t} - 1\right) = w_0 \left(\frac{1}{w_t} - \frac{1}{w_0}\right) = k_w w_0 t \quad (5)$$

$$\therefore k_w = \frac{(\text{Gradient of plot of } \alpha_t^{-1} \text{ against time})}{w_0} \text{ g.}^{-1} \text{hr.}^{-1} \quad (6)$$

Hydroxide Concentration.—For a three-dimensional dissolution of a crystal, dw/dt should vary⁵ as A_t or $w_t^{\frac{2}{3}}$. The results indicate that the rate of alumina dissolution by aqueous hydroxide solution is controlled by a reaction between a reactive Al_2O_3 site on the solid surface and two hydroxyl ions adsorbed near this reactive site (*cf.* ref. 13). The activity of adsorbed hydroxyl ion would depend on both bulk solution activity and on solid surface area A_t : then dw/dt would depend on $A_t \cdot A_t^2$ *i.e.*, on A_t^3 . The rate of dissolution of aluminas increases with hydroxide concentration. Typical results for κ - and γ -alumina (k_w values at 100°) are in the Table 1, together with the mean ionic activities

Rate constants ($\text{g.}^{-1} \text{hr.}^{-1}$) at 100° for the reaction of aluminas with hydroxide solutions

| NaOH (M) | a_{\pm} (M) | k_w | NaOH (M) | a_{\pm} (M) | k_w |
|-------------------|---------------|-------|-------------------|---------------|-------|
| κ -Alumina | | | γ -Alumina | | |
| 1 | 0.68 | 0.038 | 1 | 0.68 | 0.138 |
| 2 | 1.18 | 0.078 | 2 | 1.18 | 0.290 |
| 4 | 2.82 | 0.094 | 4 | 2.82 | 0.380 |
| 6 | 5.28 | 0.126 | 6 | 5.28 | 0.478 |
| 8 | 8.90 | 0.153 | 8 | 8.90 | 0.600 |
| 10 | 11.3 | 0.174 | 10 | 11.3 | 0.735 |
| 12 | 16.2 | 0.198 | 12 | 16.2 | 0.833 |
| 14 | 25.5 | 0.235 | 14 | 25.5 | 0.882 |
| 16 | 37.6 | 0.280 | 16 | 37.6 | 0.902 |

(a_{\pm}) of the hydroxide solutions. $k_w(k_w)^{\frac{1}{2}}$ values increase linearly with $a_{\pm}(a_{\pm})^{\frac{1}{2}}$ only up to $a_{\pm} \approx 2$ M, and then fall off rapidly [see Figures 3(a) and (b)]. The curves of k_w against a_{\pm} can be expressed¹⁷ by adsorption isotherms [Figure 3(a)] (7) or (8)

$$k_w = k_{w,1} F_{\alpha}(a_{\pm}) \quad (7)$$

$$\text{or} \quad k_w = k_{w,1} [\phi_{\alpha}(a_{\pm})]^2 \quad (8)$$

where $k_w = k_{w,1}$ at $F_{\alpha}(a_{\pm}) = 1$ or $\phi_{\alpha}(a_{\pm}) = 1$. Alternatively, for simultaneous adsorption of two hydroxyl ions (from solution) on adjacent sites¹⁸ [Fig. 3(b)], we obtain isotherm (9) where $k_w = k_{w,1}$ at $f_{\alpha}(a_{\pm})^{\frac{1}{2}} = 1$.

These isotherms are all far steeper than the Langmuir isotherm for adsorption from solution.¹⁸ The non-

$$k_w = k_{w,1} [f_{\alpha}(a_{\pm})^{\frac{1}{2}}]^2 \quad (9)$$

linearity of plots of k_w against a_{\pm} (or $k_w^{\frac{1}{2}}$ against $a_{\pm}^{\frac{1}{2}}$) plots suggest that k_w may depend both on the hydroxide ion and on the water activity (a_w) of the reaction solution.^{13,19} We have plotted k_w/a_w and $(k_w/a_w)^{\frac{1}{2}}$ against a_{\pm} and $a_{\pm}^{\frac{1}{2}}$ in Figures 4(a) and (b). k_w/a_w varies with a_{\pm} according to a Langmuir isotherm (10) [Fig. 4(a)], where $F_{\beta}(a_{\pm}) = Ba_{\pm}/(1 + Ba_{\pm})$ and

$k_w = k_{w,1}$ at $F_\beta(a_\pm) = 1$, and $a_w = 1$. In dilute

$$\frac{k_w}{a_w} = k_{w,1} F_\beta(a_\pm) \quad (10)$$

hydroxide solutions, equation (10) becomes (11).

$$k_w = k_{w,1} B a_\pm a_w \quad (11)$$

For reaction involving two separate adsorbed hydroxyl ions, however Figure 4(a) leads to equation (12) and

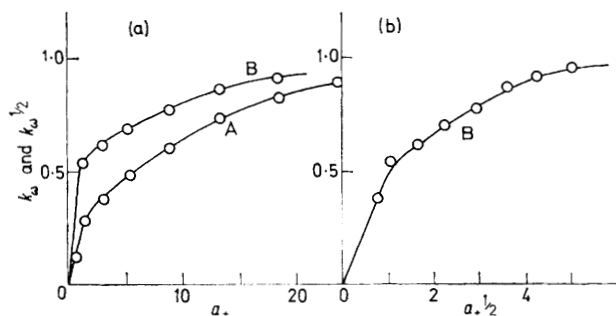


FIGURE 3 Reaction of γ -alumina with sodium hydroxide solutions at 100°; variation of rate constant (k_w) with sodium hydroxide activity (a_\pm); A, k_w ; B, $k_w/a_\pm^{1/2}$

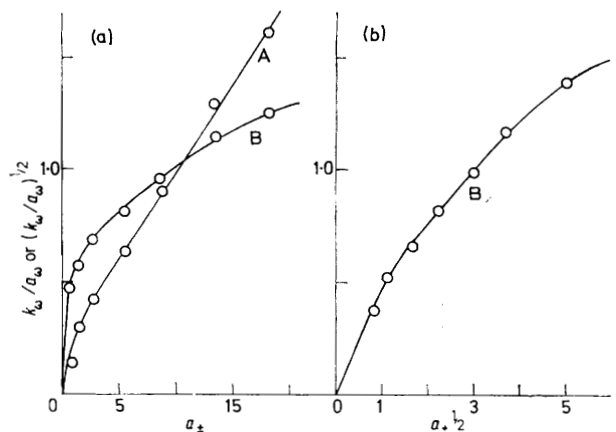


FIGURE 4 Reaction of γ -alumina with sodium hydroxide solutions at 100°; variation of rate constant (k_w) with sodium hydroxide activity (a_\pm) and water activity (a_w); A, k_w/a_w ; B, $(k_w/a_w)^{1/2}$

$\phi_\beta(a_\pm)$ is not a Langmuir isotherm. Alternatively, for

$$k_w/a_w = k_{w,1} [\phi_\beta(a_\pm)]^2 \quad (12)$$

simultaneous adsorption of two hydroxyl ions on adjacent sites, Figure 4(b) leads to isotherm (13) where

$$\frac{k_w}{a_w} = k_{w,1} [f_\beta(a_\pm)]^2 \quad (13)$$

$$k_w = k_{w,1} b^2 a_\pm a_w \quad (14)$$

$f_\beta(a_\pm)^{1/2} = b a_\pm^{1/2} / (1 + b a_\pm^{1/2})$, a Langmuir isotherm, and $k_w = k_{w,1}$ at $f_\beta(a_\pm)^{1/2} = 1$ and $a_w = 1$. In dilute hydroxyl solutions equation (13) becomes (14).

²⁰ J. H. de Boer and G. M. M. Houken, *Internat. Symposium Reactivity Solids*, 1952, **1**, 237.

²¹ F. Umland, *Z. anorg. Chem.*, 1962, **317**, 129.

Temperature.—Rates of dissolution of κ -alumina by hydroxide solutions increase 3–4 times for 15° temperature rise, and rates of dissolution of γ -alumina increases 3 times. Plots of $\log k_{w,1}$ against $1/T$ are in Figure 5. Energy of activation was determined from equation (15), and for α -alumina approximate E_{act} values were determined from equation (16) where $t_{0.1}$ is time for 10%

$$E_{act} = R \partial \ln k_{w,1} / \partial (1/T) \quad (15)$$

$$E_{act} = R \partial \ln \left(\frac{1}{t_{0.1}} \right) / \partial \left(\frac{1}{T} \right) \quad (16)$$

reaction. For temperatures in the range 85–115° the activation energies are *ca.* 27 kcal./mole for α -alumina, and 20.2 and 22.0 kcal./mole for γ - and κ -alumina respectively.

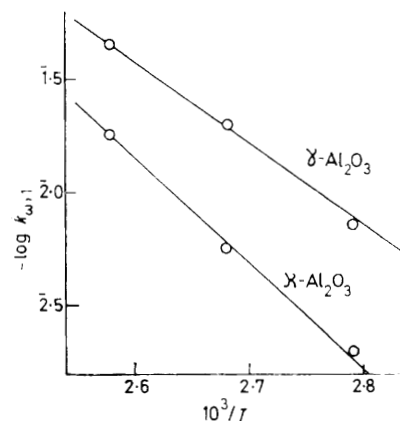
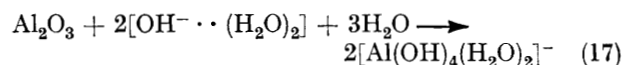


FIGURE 5 Variation of rate constant ($k_{w,1}$) with temperature in the reaction of aluminas with sodium hydroxide solutions

Mechanisms.— α - and κ -Alumina. The stoichiometric equation for the dissolution of α - and κ -alumina powders by aqueous hydroxide solution is (17). In fact (even in the



absence of hydroxyl ions) alumina surfaces are always hydrated with chemisorbed water molecules.^{20,21} The energies of activation for dissolution are also very much less than the energy required to break an Al–O bond.²² Most probably, then, the reaction occurs at regions containing adjacent (hydrated) electron acceptor defect sites $^+\text{AlO} \cdots (\text{H}_2\text{O})$ together with electron donor defect sites $^-\text{AlO}_2 \cdots (\text{H}_2\text{O})$.²³ The kinetics suggest that the rate of dissolution is controlled by a reaction between such regions on the alumina surface and hydroxyl ions simultaneously weakly chemisorbed nearby. Water molecules may also participate in this reaction. The rate-determining steps could then occur as in Scheme 1.

γ -Alumina. This has been assigned a defect spinel structure $\text{Al}_{64}\text{O}_{96}$ with eight defect sites per $\text{Al}_{72}\text{O}_{96}$

²² C. S. G. Phillips and R. J. G. Williams, 'Inorganic Chemistry,' Oxford Univ. Press, 1965, chap. 13.

²³ B. D. Flockhart, J. A. N. Scott, and R. C. Pink, *Trans. Faraday Soc.*, 1965, **61**, 730; B. D. Flockhart, I. R. Leith, and R. C. Pink, *ibid.*, 1968, **64**, 542.

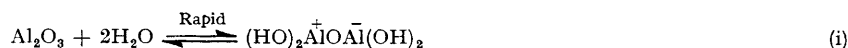
unit.^{24,25} However, after chemisorption of water molecules, the surface contains also (AlH) spinel sites of stoichiometric composition $\text{Al}_5\text{HO}_5(2\frac{1}{2}\text{Al}_2\text{O}_3, \frac{1}{2}\text{H}_2\text{O})$, that is $\text{Al}_2\text{HO}_4, \text{Al}_3\text{O}_4$. The reaction with hydroxide solution probably occurs between these sites and two hydroxyl ions, simultaneously weakly chemisorbed. The rate-determining steps could then occur as in Scheme 2. For the reactions in Scheme 2 we obtain equations (18) and (19) where k_s is the rate constant at unit overall

where $f(a_{\pm})^{\frac{1}{2}}$ is given by equation (21) and $a(\text{OH}^-)_{\text{ads}} = mf(a_{\pm})^{\frac{1}{2}}A_t$, and $(a_{\text{OH}^-})_{\text{ads}} = mf(a_{\pm})^{\frac{1}{2}}A_t$. We then obtain

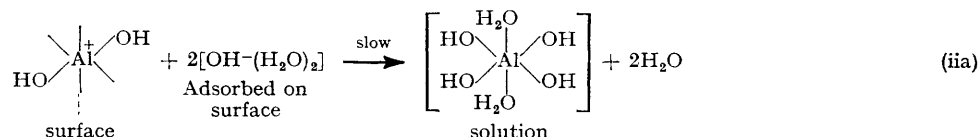
$$\theta = f(a_{\text{OH}^-})_{\text{bulk}}^{\frac{1}{2}} \approx f(a_{\pm})^{\frac{1}{2}} \quad (20)$$

$$f(a_{\pm})^{\frac{1}{2}} = \frac{ba_{\pm}^{\frac{1}{2}}}{1 + ba_{\pm}^{\frac{1}{2}}} \quad (21)$$

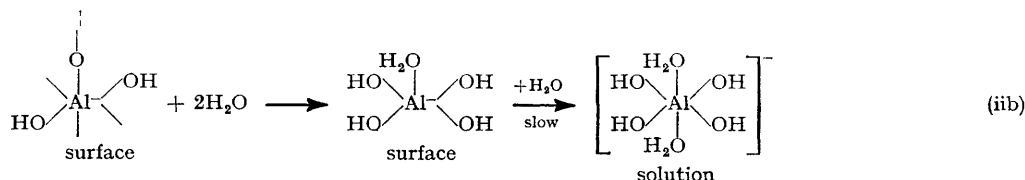
equations (22) and (23), which leads to equation (3) where $k_{A,1} = k_s m^2$ and $k_A = [f(a_{\pm})^{\frac{1}{2}}]^2 a_w k_A$. As we have indicated, $A_t = \bar{A}w_t^{\frac{1}{2}}$, we now obtain equation (1) when



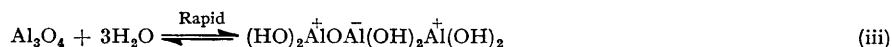
Then,



together with

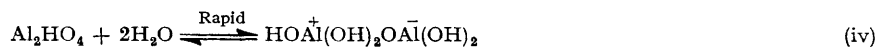


SCHEME 1

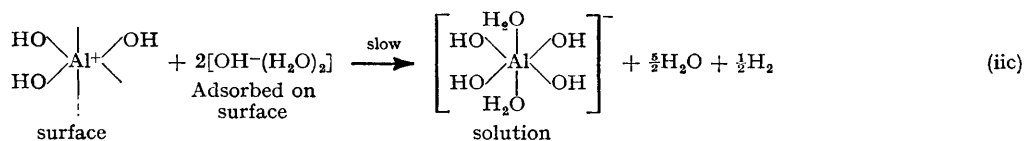


Then reactions (iia) and (iib) as above.

Also,



Then,



together with reaction (iib) as in Scheme 1.

SCHEME 2

surface area and unit adsorbed hydroxyl ion activity,

$$dw/dt = -k_s(a^\dagger)(a_{\text{OH}^-})_{\text{ads}}^2 \cdot a_w \quad (18)$$

$$= -k_s A_t (a_{\text{OH}^-})_{\text{ads}}^2 \cdot a_w \quad (19)$$

and a^\dagger refers to active sites. Now $(a_{\text{OH}^-})_{\text{ads}} = \theta m A_t$ where m is monolayer adsorption of hydroxyl ions in g.-ion/cm.² and θ is coverage. For simultaneous adsorption on two adjacent sites¹⁸ we obtain equation (20),

$k_w = k_A \bar{A}^3$ and $k_w = k_{w,1} [f(a_{\pm})^{\frac{1}{2}}]^2 a_w$, as observed experimentally.

$$dw/dt = -k_s m^2 [f(a_{\pm})^{\frac{1}{2}}]^2 a_w A_t^3 \quad (22)$$

$$= -k_{A,1} [f(a_{\pm})^{\frac{1}{2}}]^2 a_w A_t^3 \quad (23)$$

[9/1667 Received, October 1st, 1969]

²⁴ G. Hogg, *Z. phys. Chem.*, 1935, B, **29**, 88.

²⁵ A. F. Wells, 'Structural Inorganic Chemistry,' Oxford Univ. Press, 3rd edn., 1962, chap. 13.