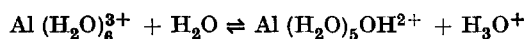


## On the Reactions of the Aluminium Ion with Water

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The system Al-OH has attracted the interest of many scientists; especially the solid aluminium hydroxide phases and conversion from one to another, and colloid-chemical and technical questions connected with them. On the other hand, the equilibrium in the system Al-OH has been very little dealt with. The most important of the few works dealing with it is Brönsted and Volqvartz's<sup>1</sup> classical paper on acid dissociation of aquo ions. By measuring the hydrogen ion concentration by reaction kinetic methods in aluminium perchlorate solutions with different amounts of perchloric acid, they come to the conclusion that at 15° C the first stage of protolysis of the hexaquo-aluminium ion follows the formula:



and that the equilibrium is determined by the formula:

$$\frac{[\text{H}^+] \cdot [\text{AlOH}^{2+}]}{[\text{Al}^{3+}]} = 5.5 \cdot 10^{-6}$$

Nevertheless, the writers point out that the change in the equilibrium constant with the total concentration of aluminium was not found to take place as would be expected from the changes in the ionic strength.

Faucherre<sup>2</sup> thought he was able to show that the protolysis suggested by Brönsted and Volqvartz explained conditions in solutions where the total concentration of aluminium was less than  $5 \cdot 10^{-3}$ . For higher concentrations he proposed the following formula:

$$\frac{[(\text{AlOH})_2^{4+}] \cdot [\text{H}^+]^2}{[\text{Al}^{3+}]^2} = k_1$$

Faucherre determined both  $k_1$  and Brönsted's constant ( $k_2$ ) at 20° C and at two different ionic strengths ( $I$ ) with the following results:

$I$	$k_1$	$k_2$
0.60	$5.82 \cdot 10^{-9}$	$1.07 \cdot 10^{-6}$
0.12	$8.72 \cdot 10^{-9}$	$1.83 \cdot 10^{-6}$

The precipitation of aluminium hydroxide gel and its re-dissolution by the addition of alkali to aluminium salt solutions have been studied qualitatively by many writers. Semiquantitative measurements have been made by Treadwell and Bonn<sup>3</sup>. These workers titrated  $\text{AlCl}_3$  solutions potentiometrically with  $\text{NaOH}$ , determining the pH with a hydrogen electrode. The opalescence and viscosity of the solutions were also investigated. The measurements show that the viscosity has a sharp maximum and the opalescence a flatter one near the point of equivalence. On the basis of their observations they suggested a possible mechanism for the reactions in question.

Finally, it should be mentioned that several determinations have been made of the solubility of different forms of aluminium hydroxide. The varying results indicate that the values obtained depend to a high degree on the experimental conditions.

Since, therefore, very little appears to be known of the equilibrium conditions in the system  $\text{Al-OH}$ , it would seem of interest to examine it more closely, particularly as the system is important both scientifically and technically.

#### EXPERIMENTAL METHODS

An examination of equilibria in complex systems is highly facilitated if it is possible to determine the concentrations both of the central group and the ligand. In the system  $\text{Al-OH}$  this is unfortunately impossible, as so far no satisfactory method has been found for determining  $[\text{Al}^{3+}]$ . (See, for instance, Berestneva and Kargin<sup>4</sup>.) In several cases, however, relatively much data has been obtained on the equilibrium conditions in complex systems even when only ligand concentration measurements have been available. The present investigation which is based mainly on pH measurements, shows that this is also true of the system  $\text{Al-OH}$ .

The measurements and results given below were preceded by a preliminary investigation carried out at 25° C. The results of the latter indicated that some of the equilibria studied are established very slowly at this temperature. This occurs more rapidly at higher temperatures. For this reason, and bearing

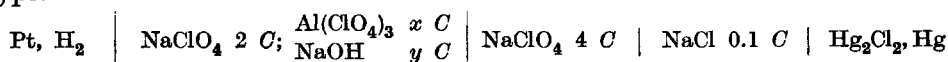
in mind that some technical processes based on the equilibrium conditions in the system Al-OH take place at 40° C it seemed best to carry out the main part of the investigation at the latter temperature.

The measurements consist of determinations of the hydrogen ion concentration in solutions containing aluminium perchlorate, sodium hydroxide, and sodium perchlorate as ionic medium. These measurements are divided into three series and comprise the following concentration levels\*:

		1	2	3
Total concentration of aluminium	= [Al <sub>t</sub> ]	0.002209	0.01107	0.05541 C
Total concentration of sodium hydroxide	= [NaOH <sub>t</sub> ]	0-14 · 10 <sup>-3</sup>	0-5 · 10 <sup>-2</sup>	0-2 · 10 <sup>-1</sup> C

The ionic strength of all the solutions was kept at 2.02 C by addition of NaClO<sub>4</sub>.

Within each series the hydrogen ion concentration was determined for different contents of [NaOH<sub>t</sub>] by measuring the EMF in cells of the following type:



For this a Jensen potentiometer, type 10 A, was used with a Multiflex galvanometer, type MG 3, as the zero instrument. The error in values for the potential was less than ± 0.1 mV. The temperature, which was regulated by a paraffin oil thermostat enclosed in an air thermostat, always lay within the limits 40.0° ± 0.1° C. Hydrogen from cylinders was purified in the usual manner over copper at 455° C. It was then passed successively through an alkaline solution, sulphuric acid, a solution of 2.02 C NaClO<sub>4</sub> at 40° C, a vessel containing the test solution, and finally through another vessel containing test solution into which a platinized platinum electrode was inserted. The EMF values obtained were corrected in the usual manner for changes in the atmospheric pressure. The hydrogen ion concentration was calculated from the formula

$$[\text{H}^+] = [\text{H}_s^+] \cdot 10^{-16.094(E-E_s)}$$

where  $E$  is the EMF of the cell for the solution in question and  $E_s$  its EMF when the aluminium salt solution is replaced by a "standard acid", *i.e.* a

\* All concentrations are given in C, *i.e.* mole per liter, at 40° C unless otherwise stated. When the ionic strength is defined by 2 C NaClO<sub>4</sub>, measurements have shown the following relation to exist:  $C_{40^\circ} = C_{20^\circ} \cdot 0.9888$ .

solution of perchloric acid of known concentration together with  $\text{NaClO}_4$  as ionic medium.

The concentrations of free and aluminium-bound hydroxyl ions were calculated from the expressions

$$[\text{OH}_{\text{free}}^-] = \frac{k_w}{[\text{H}_s^+]} \cdot 10^{+16.094(E-E_s)}$$

$$\text{and } [\text{NaOH}_t] - [\text{H}^+] - [\text{H}_a^+] = [\text{OH}_{\text{free}}^-] + [\text{OH}_{\text{bound}}^-]$$

where  $[\text{H}_a^+]$  is the possible concentration of free acid in the aluminium salt solution to which we added sodium hydroxide,  $k_w$  is the ion product of water at 40° C and at the ionic strength in question. The  $k_w$  was determined by measuring the hydrogen ion concentration in solutions of NaOH of known strength. The results are given in Table 1.

Table 1. Determination of  $k_w$  at 40° C.

[NaOH] + [NaClO <sub>4</sub> ] = 2.02 C		
[NaOH]	$k_w \cdot 10^{14}$	$\text{p}k_w$
0.009848	3.034	13.518
.01970	3.049	13.516
.02954	3.049	13.516
.03939	3.046	13.516

In the following we shall use the value 13.52 for  $\text{p}k_w$ .

#### PREPARATIONS

The following preparations have been used:

1.  $\text{NaClO}_4$ . Various Swedish and foreign preparations of different qualities were purified by a suitable number (2–5) of recrystallizations from 70 % alcohol. The purified products contained < 0.01 % chloride and chlorate and approximately 0.0014 mole per cent alkali (probably bicarbonate). The solutions were standardized by running samples through a  $\text{H}^+$ -saturated ion exchange column and titrating the hydrogen ions set free in the filtrate.

2.  $\text{HClO}_4$  solutions. These were prepared from perchloric acid (density 1.67) Merck pro analysi, and their concentrations were ascertained by the oxalate method.

3. NaOH solutions were prepared and kept in the usual way. The content of carbonate never exceeded 0.2 %.

4.  $\text{Al}(\text{ClO}_4)_3$ . For the preparation of this substance aluminium hydroxide was precipitated with NaOH from a hot water solution of  $\text{AlCl}_3 \cdot 6 \text{H}_2\text{O}$  (Merck pro analysi). The

precipitate was washed and then dissolved in perchloric acid. By repeated reprecipitation, washing and re-dissolution the last traces of chloride ion could be removed. The exceedingly hygroscopic substance was finally washed with chloroform to remove most of the free perchloric acid present. The preparation thus obtained was extremely pure. A very little sodium and some perchloric acid were the only impurities found. It would probably be very difficult to produce an absolutely neutral aluminium perchlorate and this is by no means necessary if we can determine the contents of the free acid in the preparation. Brönsted, for example, used an alkaline preparation which he obtained by letting  $\text{AlCl}_3$  react with  $\text{AgClO}_4$ ; the  $\text{AlCl}_3$  contained as usual somewhat less than 3 Cl per Al. He could then calculate the "base" content from his pH measurements.

In the present case a stock solution was made from the preparation obtained. The Al concentration of this solution was found to be  $0.449 \pm 0.001$  C. Determinations of the total content of cation equivalents by means of the ion exchange method showed that the preparation contained 11–12 mole-%  $\text{HClO}_4$ . More exact values could be obtained by EMF measurements.

If we determine the hydrogen ion concentration  $[\text{H}^+]$  in a series of solutions where  $[\text{Al}_t]$  is kept constant and where the amount of free acid is gradually increased by additions of  $[\text{H}_t^+]$  and if we plot

$\frac{[\text{H}^+] - [\text{H}_t^+]}{[\text{Al}_t]}$  against  $\frac{1}{[\text{H}^+]}$  and extrapolate to  $\frac{1}{[\text{H}^+]} = 0$ , i.e. an infinitely acid solution

where all kinds of protolyses are suppressed, a value is obtained which should represent the number of moles free acid per mole  $\text{Al}(\text{ClO}_4)_3$  in the stock solution. The results of such measurements are given in Table 2.

Table 2. Determination of free acid in the stock solution of  $\text{Al}(\text{ClO}_4)_3$ .

$$[\text{Al}_t] = 0.01116 \text{ C}; t = 25^\circ \text{C}$$

$[\text{H}^+]$  determined with a quinhydrone electrode

$[\text{H}_t^+] \text{ C} \cdot 10^3$	$[\text{H}^+] \text{ C} \cdot 10^3$	$\frac{1}{[\text{H}^+]} \text{ C}^{-1} \cdot 10^{-3}$	$\frac{[\text{H}^+] - [\text{H}_t^+]}{[\text{Al}_t]}$
0.150	1.464	0.6831	0.1180
0.473	1.780	0.5618	0.1171
1.224	2.519	0.3970	0.1160
2.483	3.772	0.2651	0.1155
3.725	5.012	0.1995	0.1153

The extrapolation gives the value 0.115, i.e. 11.5 mole-%, which agrees well with the analytical result.

#### EXPERIMENTAL RESULTS

The experimental determination of the complexity curve for the system Al-OH was performed as follows: two solutions — one containing aluminium perchlorate and ionic medium, the other sodium hydroxide and ionic medium

— were pre-heated to approximately 40° C and well mixed, after which the electrode vessel was filled as quickly as possible with the mixture and the hydrogen gas current turned on. The EMF of the cell was then read at suitable time intervals until equilibrium was reached. When mixing we poured the alkali into the aluminium salt solution, when the complex formation number  $\bar{n}$ , *i.e.* in this case the average number of bound OH<sup>-</sup>-groups per aluminium atom, was less than 3. In the cases where  $\bar{n}$  was greater than 3 the aluminium salt solution was poured into the alkali. In the range near  $\bar{n} = 3$  two experiments were made, one in each way.

Table 3. Series 1. [Al] =  $2.209 \cdot 10^{-3}$  mole/l. Temp. 40° C.

No.	(NaOH) <sub>t</sub> · 10 <sup>3</sup> mole/l	First value			Final value		
		<i>t</i> hours	pOH	$\bar{n}$	<i>t</i> hours	pOH	$\bar{n}$
1.1		0.50	10.016	0.033	1.33	10.015	0.033
2.1	0.277	0.58	9.686	0.082	1.55	9.685	0.082
3.1	0.366	0.45	9.632	0.115	18.03	9.648	0.117
4.1	0.554	0.53	9.543	0.189	20.22	9.615	0.198
5.1	0.752	0.37	9.493	0.273	21.70	9.600	0.285
6.1	1.088	0.47	9.467	0.423	19.30	9.573	0.434
7.1	1.978	0.62	9.433	0.823	20.25	9.498	0.829
8.1	2.472	0.75	9.367	1.041	20.27	9.467	1.049
9.1	3.589	0.41	9.262	1.540	20.33	9.384	1.548
10.1	4.687	0.40	9.031	2.027	20.30	9.250	2.036
11.1	5.310	0.37	8.918	2.305	19.95	9.066	2.310
12.1	5.781	0.41	8.782	2.515	19.40	8.845	2.517
13.1	6.427	0.35	6.502	2.799	19.60	7.995	2.801
14.1	6.650	0.37	6.056	2.900	20.77	6.887	2.900
15.1	6.758	0.32	5.708	2.948	9.80	5.842	2.948
16.1	6.872	0.35	5.470	2.999	45.76	4.895	2.995
17.1	6.872	0.40	5.576	3.000	43.92	5.228	2.998
18.1	6.981	0.45	5.345	3.048	21.12	4.610	3.039
19.1	7.189	0.47	5.104	3.141	19.87	4.364	3.125
20.1	7.812	0.23	4.942	3.421	96.23	3.888	3.368
21.1	8.453	0.27	4.477	3.702	40.10	3.606	3.605
22.1	8.658	0.40	4.313	3.787	44.88	3.511	3.670
23.1	8.905	0.55	4.183	3.892	84.42	3.371	3.729
24.1	10.18	0.28	3.017	4.063	2.65	3.016	4.061
25.1	10.96	0.36	2.766	4.076	2.56	2.766	4.077
26.1	13.81	0.40	2.333	4.042	5.15	2.328	4.020
27.1	14.04	0.40	2.313	4.047	1.74	2.311	4.039

Table 4. Series 2.  $[Al_t] = 1.107 \cdot 10^{-2}$  mole/l. Temp. 40° C.

No.	$[NaOH_t] \cdot 10^2$ mole/l	First value			Final value		
		$t$ hours	pOH	$\bar{n}$	$t$ hours	pOH	$\bar{n}$
1.2	0.1379	0.21	10.125	0.051	2.45	10.125	0.051
2.2	0.1822	0.24	10.018	0.083	2.17	10.016	0.083
3.2	0.2019	0.30	9.981	0.099	21.63	9.990	0.099
4.2	0.2265	0.30	9.942	0.119	21.38	9.969	0.120
5.2	0.2758	0.60	9.892	0.161	22.12	9.916	0.162
6.2	0.3742	0.35	9.799	0.245	21.85	9.858	0.248
7.2	0.5417	0.22	9.722	0.394	21.92	9.834	0.398
8.2	0.9848	0.45	9.669	0.792	21.60	9.776	0.796
9.2	1.231	0.35	9.587	1.013	19.98	9.756	1.018
10.2	1.231	0.48	9.591	1.013	19.43	9.747	1.017
11.2	1.792	0.34	9.527	1.519	20.14	9.699	1.523
12.2	2.340	0.31	9.360	2.010	10.76	9.532	2.013
13.2	2.344	0.37	9.366	2.014	45.00	9.558	2.017
14.2	2.620	0.57	9.209	2.261	43.63	9.384	2.253
15.2	2.890	0.38	8.908	2.502	22.00	9.135	2.504
16.2	2.895	0.20	8.864	2.508	93.58	9.229	2.510
17.2	3.166	0.47	7.663	2.750	47.55	8.607	2.751
18.2	3.209	0.37	6.972	2.789	71.64	8.379	2.789
19.2	3.320	0.30	5.971	2.889	53.10	7.798	2.889
20.2	3.333	0.74	6.073	2.901	25.50	6.909	2.901
21.2	3.375	0.47	5.332	2.938	70.37	6.392	2.939
22.2	3.403	0.33	5.103	2.963	49.67	5.978	2.964
23.2	3.431	0.28	4.941	2.988	67.76	4.588	2.987
24.2	3.431	0.24	4.989	2.988	68.65	4.925	2.988
25.2	3.442	0.30	4.929	2.893	69.20	4.505	2.997
26.2	3.442	0.30	4.907	2.998	68.57	4.559	2.997
27.2	3.486	0.27	4.739	3.037	90.42	4.297	3.034
28.2	3.699	0.38	4.063	3.223	19.50	3.302	3.186
29.2	3.955	0.30	3.869	3.451	65.62	2.807	3.322
30.2	4.029	0.38	3.985	3.521	22.13	2.716	3.355
31.2	4.473	0.87	3.326	3.888	23.40	2.448	3.609
32.2	4.826	0.33	2.630	4.038	22.03	2.558	4.000
33.2	4.911	0.34	2.545	4.070	23.44	2.491	4.035
34.2	4.944	0.22	2.437	4.026	19.70	2.440	4.028

The EMF was found to change in all cases in the course of time, quickly at the beginning of the experiments and then more slowly. In very acid and alkaline solutions the equilibrium was reached scarcely half an hour after the solution had been mixed ( $t = 0$ ), or in as short time as when measurements

Table 5. Series 3.  $[Al_t] = 5.541 \cdot 10^{-2}$  mole/l. Temp. 40° C.

No.	[NaOH] <sub>t</sub> mole/l	First value			Final value		
		t hours	pOH	$\bar{n}$	t hours	pOH	$\bar{n}$
1.3	0.01681	0.28	10.213	0.202	20.98	10.225	0.203
2.3	0.03283	0.26	10.036	0.488	46.15	10.180	0.491
3.3	0.08683	0.20	9.767	1.457	44.75	9.973	1.462
4.3	0.1412	0.28	9.223	2.438	43.80	9.485	2.439
5.3	0.1569	0.31	8.315	2.722	259.40	9.346	2.722
6.3	0.1703	0.27	5.014	2.963	91.40	6.589	2.963
7.3	0.1719	0.25	4.659	2.991	1.63	4.870	2.991

were carried out on the reference acid. We can, therefore, conclude that in a very acid or alkaline solution containing aluminium ion, the hydrogen ion concentration quickly reaches its equilibrium value. In other cases slow reactions occur which cause successive changes in the hydrogen ion concentration of the system. The measurements carried out are given in Tables 3, 4, and 5. In these tables the first values for pH and  $\bar{n}$  indicate the state approximately half an hour after the preparation of the solution, *i.e.* at the moment when the hydrogen electrode might be supposed to give correct values; whereas the last pair of values will correspond, at least very nearly, to a state of equilibrium and has been calculated from the last read EMF, which did not appear to change with time. The data given in these tables are also to be found in Figs. 1, 2, and

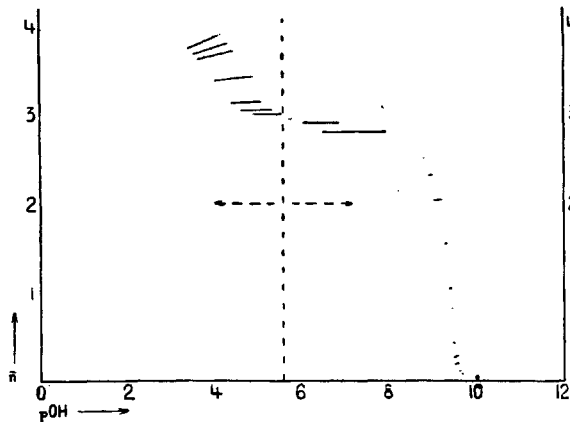


Fig. 1 (Table 3).



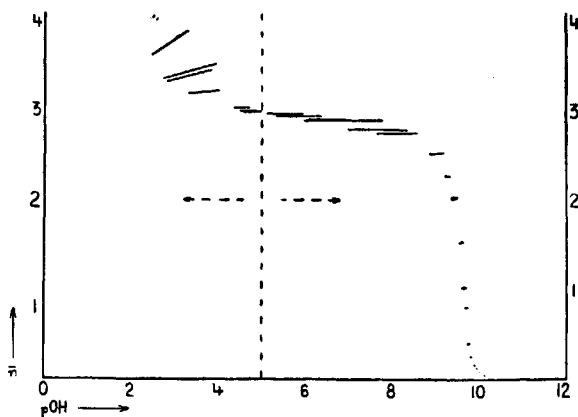


Fig. 2 (Table 4).

3. Here the first and last readings are joined by a line. The arrows mark the direction of the change. As will be seen this is reversed at  $\bar{n} \sim 3$ .

The way in which these changes take place in the hydrogen ion concentration was studied more closely. It was then found that for a given total concentration of aluminium salt the character of the process is mainly determined by the ratio  $[\text{NaOH}_t]/[\text{Al}_t]$ . The observations can be summarized in the following way:

1. If a small amount of alkali is added to an acid solution of aluminium perchlorate so that the solution still remains acid,  $[\text{OH}^-]$  is independent of time (Table 6 a, Fig. 4 a).

2. If more NaOH is added to an aluminium perchlorate solution so that  $[\text{NaOH}_t]/[\text{Al}_t]$  lies within 0.1–2.5, the system gets a higher  $\text{OH}^-$  ion concentration than the equilibrium value immediately after this addition. The

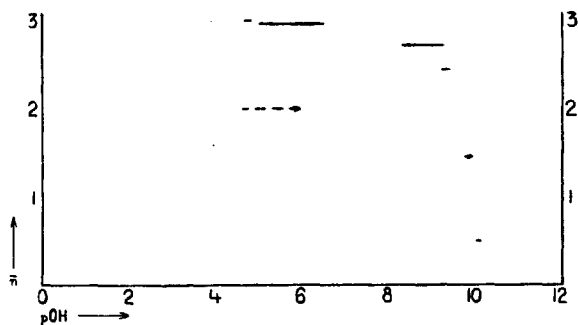


Fig. 3 (Table 5).

equilibrium is reached by a slow process during which  $[\text{OH}^-]$  falls to its limiting value. This effect becomes more and more accentuated as the ratio  $[\text{NaOH}_t]/[\text{Al}_t]$  is increased to  $\sim 2.5$ . (Table 6 b, Fig. 4 b.)

3. If NaOH is added to an aluminium perchlorate solution so that the ratio  $[\text{NaOH}_t]/[\text{Al}_t]$  lies between 2.5 and 3, the solution in this case, too, will become relatively alkaline immediately after the addition.  $[\text{OH}^-]$  falls, however, in a more complicated manner to its equilibrium value than in the earlier case, for after having decreased rather fast for a couple of hours it passes through a minimum and then through a maximum, before later continuing steadily to its limiting value. Such a process is illustrated by Table 6 c and Fig. 4 c. The minimum becomes more and more marked as the ratio  $[\text{NaOH}_t]/[\text{Al}_t]$  approaches 3.

4. For  $[\text{NaOH}_t]/[\text{Al}_t] \sim 3$  the change in the hydroxyl ion concentration is as shown in Tables 6 d and e and Figs. 4 d and e. In this case there is a very rapid fall in the concentration and then a slow rise. The tables and figures give two series of experiments. One when a NaOH solution was added to a solution of aluminium perchlorate (e), the other when an aluminium salt solution was added to the alkali (d). As will be seen the progress in this case is not appreciably affected by the way in which the solution was mixed.

5. In the range  $\bar{n}$  greater than 3 the change in  $\text{OH}^-$  ion concentration with time is very characteristic. If an aluminium perchlorate solution is added to a sodium hydroxide solution the  $\text{OH}^-$  ion concentration of the latter falls instantaneously to a relatively low value, and then rises quickly for an hour or so immediately afterwards. After this the speed of reaction diminishes suddenly and the  $\text{OH}^-$  ion concentration continues to rise slowly to what appears to be the equilibrium value. The process is shown in Table 6 f and Fig. 4 f.

6. When NaOH and the Al salt solution are mixed so that  $\bar{n}$  approaches 4 the  $\text{OH}^-$  ion concentration of the solution again becomes independent of time (Table 6 g and Fig. 4 g).

#### ANALYSIS OF THE TIME FACTOR IN THE SLOW REACTIONS

The general impression we get when we study the slow reactions described in the former section is that they are caused by a relatively complicated mechanism, where several effects are superimposed or occur successively. We can, however, distinguish a few simpler relations:

1. In highly acid and alkaline solutions the equilibrium is established very quickly;

Table

a(No. 3.2)		b(No. 16.2)		c(No. 17.2)				d(No.	
<i>t</i> hours	pOH	<i>t</i> hours	pOH	<i>t</i> hours	pOH	<i>t</i> hours	pOH	<i>t</i> hours	pOH
0.30	9.981	0.20	8.864	0.47	7.658	6.00	7.911	0.30	4.929
0.38	9.981	0.30	8.872	0.48	7.748	6.25	7.914	0.33	4.897
0.50	9.975	0.42	8.885	0.52	7.844	6.50	7.916	0.40	4.887
0.63	9.974	0.47	8.889	0.53	7.924	6.75	7.921	0.43	4.886
0.71	9.975	0.62	8.900	0.58	8.005	6.78	7.925	0.47	4.897
0.80	9.975	0.92	8.924	0.62	8.037	7.33	7.937	0.50	4.911
1.11	9.975	1.17	8.939	0.70	8.069	10.03	8.037	0.52	4.920
1.25	9.975	1.67	8.963	0.80	8.070	10.25	8.045	0.53	4.926
1.63	9.975	2.17	8.977	0.82	8.069	26.22	8.452	0.55	4.944
2.05	9.976	2.83	8.992	0.83	8.067	26.42	8.454	0.57	4.960
2.28	9.976	3.17	8.996	0.88	8.064	26.60	8.455	0.58	4.977
2.46	9.977	19.51	9.107	0.92	8.060	26.63	8.456	0.60	4.993
2.68	9.977	19.75	9.108	0.95	8.056	26.75	8.458	0.62	5.008
2.85	9.980	20.33	9.110	0.98	8.054	28.25	8.473	0.63	5.024
3.23	9.980	21.03	9.111	1.02	8.050	30.00	8.489	0.65	5.041
6.13	9.981	22.20	9.114	1.07	8.047	30.50	8.493	0.67	5.057
6.38	9.982	23.25	9.118	1.08	8.044	31.00	8.499	0.68	5.073
6.61	9.984	23.50	9.121	1.13	8.040	31.08	8.497	0.70	5.089
19.66	9.987	25.17	9.124	1.18	8.037	31.13	8.496	0.72	5.105
19.96	9.990	26.20	9.126	1.22	8.037	31.18	8.496	0.75	5.137
20.30	9.991	26.75	9.126	1.23	8.033	31.20	8.496	0.78	5.170
20.76	9.991	43.42	9.159	1.33	8.030	31.22	8.496	0.83	5.202
21.00	9.990	44.25	9.159	1.40	8.025	31.23	8.496	0.90	5.285
21.30	9.990	45.30	9.161	1.47	8.021	31.25	8.496	1.03	5.267
21.63	9.990	46.43	9.164	1.53	8.012	31.28	8.496	1.10	5.270
		48.19	9.167	1.65	8.002	31.32	8.497	1.13	5.270
		91.50	9.226	1.73	7.998	31.50	8.529	1.23	5.269
		91.92	9.226	1.78	7.995	35.75	8.594	1.27	5.268
		92.08	9.227	1.83	7.992	47.20	8.593	1.30	5.267
		92.37	9.227	1.88	7.990	47.55	8.598	1.35	5.264
		92.97	9.227	1.93	7.986			1.40	5.263
		93.58	9.229	1.98	7.984			1.45	5.259
				2.25	7.970			1.50	5.256
				2.50	7.960			1.57	5.252
				2.75	7.952			1.65	5.247
				3.00	7.944			1.82	5.237
				3.25	7.935			1.98	5.224
				3.50	7.927			2.15	5.212
				3.75	7.924			2.32	5.199
				4.00	7.919			2.48	5.186
				4.25	7.915			2.65	5.176
				4.50	7.913			2.82	5.166
				4.75	7.911			2.98	5.156
				5.00	7.909			3.15	5.147
				5.25	7.907			3.32	5.136
				5.50	7.907			3.48	5.127
				5.75	7.909			3.53	5.126

## ALUMINIUM ION

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6.

25.2)		e(No. 26.2)				f(No. 29.2)		g(No. 33.2)	
<i>t</i> hours	pOH	<i>t</i> hours	pOH	<i>t</i> hours	pOH	<i>t</i> hours	pOH	<i>t</i> hours	pOH
5.48	5.034	0.30	4.907	5.25	5.081	0.30	3.869	0.34	2.545
5.65	5.028	0.32	4.892	5.50	5.072	0.35	3.761	0.47	2.514
5.82	5.022	0.34	4.876	5.75	5.064	0.44	3.537	0.92	2.490
5.98	5.015	0.37	4.871	6.00	5.056	0.52	3.422	3.09	2.494
6.15	5.013	0.39	4.871	6.50	5.041	0.69	3.301	3.17	2.491
6.32	5.013	0.44	4.876	7.00	5.027	0.77	3.270	3.34	2.493
6.65	5.011	0.47	4.883	7.50	5.015	1.09	3.182	3.45	2.491
6.82	5.009	0.49	4.891	8.72	4.986	1.24	3.161	3.67	2.493
7.15	5.006	0.54	4.891	10.10	4.956	4.10	3.032	3.84	2.491
9.65	4.977	0.57	4.926	10.54	4.818	17.80	2.813	4.04	2.493
9.82	4.970	0.60	4.939	18.80	4.817	18.35	2.813	4.22	2.491
9.98	4.964	0.64	4.956	18.99	4.814	18.87	2.803	4.59	2.493
19.65	4.887	0.65	4.973	19.50	4.808	19.20	2.803	4.84	2.491
19.82	4.886	0.67	4.987	20.00	4.800	19.49	2.801	5.04	2.493
20.15	4.883	0.70	5.004	20.50	4.794	19.87	2.798	5.20	2.491
20.57	4.879	0.72	5.021	21.00	4.788	20.52	2.794	5.59	2.492
20.90	4.875	0.74	5.036	21.50	4.782	21.24	2.793	5.97	2.491
21.15	4.863	0.75	5.052	22.00	4.776	22.44	2.781	6.09	2.492
21.50	4.858	0.77	5.068	22.50	4.768	64.77	2.806	22.50	2.490
21.82	4.848	0.80	5.100	23.02	4.765	65.10	2.806	22.67	2.490
22.15	4.838	0.82	5.117	23.57	4.757	65.62	2.807	22.87	2.490
22.48	4.827	0.84	5.133	24.00	4.754			23.09	2.490
22.82	4.818	0.87	5.148	24.50	4.747			23.30	2.491
23.15	4.808	0.90	5.181	25.24	4.738			23.44	2.491
23.48	4.799	0.94	5.197	25.50	4.736				
23.82	4.790	0.95	5.213	26.00	4.731				
24.23	4.780	1.00	5.246	26.50	4.724				
24.73	4.766	1.04	5.263	29.54	4.694				
25.87	4.740	1.09	5.277	30.00	4.690				
26.43	4.726	1.12	5.288	42.65	4.614				
27.40	4.707	1.19	5.295	43.00	4.612				
30.03	4.662	1.25	5.302	43.50	4.610				
32.27	4.629	1.32	5.306	44.00	4.607				
33.35	4.618	1.35	5.306	44.65	4.604				
45.30	4.545	1.39	5.303	45.00	4.602				
45.93	4.539	1.45	5.301	45.50	4.601				
46.43	4.539	1.49	5.299	46.00	4.598				
47.95	4.533	1.55	5.295	46.50	4.596				
50.40	4.527	1.69	5.295	47.50	4.593				
51.80	4.525	1.82	5.286	48.00	4.591				
67.65	4.511	2.00	5.275	50.00	4.585				
68.15	4.511	2.50	5.221	50.90	4.583				
68.50	4.510	3.07	5.182	66.79	4.557				
69.20	4.505	4.50	5.111	67.24	4.557				
		4.75	5.100	67.50	4.556				
		4.92	5.094	68.15	4.556				
		5.00	5.091	68.57	4.559				

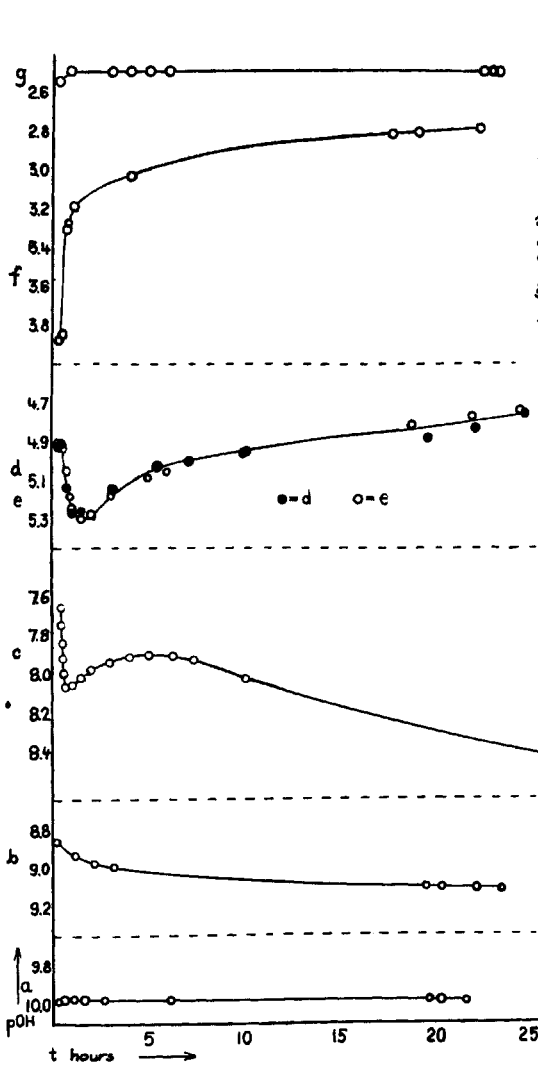


Fig. 4.

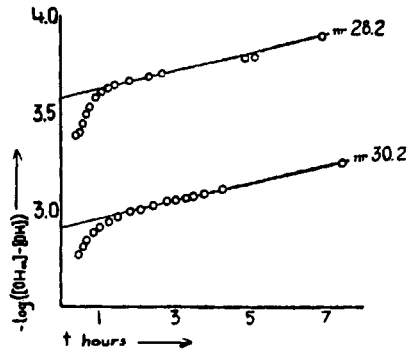


Fig. 5

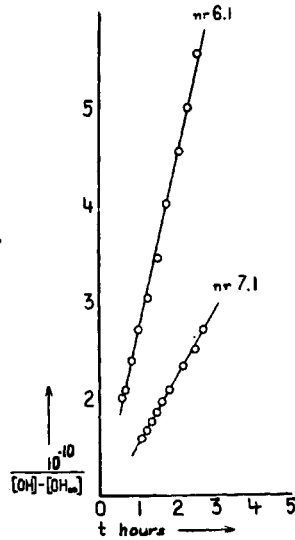


Fig. 6.

2. In moderately alkaline solutions ( $3 < \bar{n} < 4$ ) equilibrium is established by a number of different processes, of which the final one appears, at least, to be of the first order and satisfies the following expression:

$$\log ([OH_{\infty}] - [OH]) = k' \cdot t + C'$$

where  $[OH_{\infty}]$  is the final value, independent of time, of the OH ion concentration, and  $k'$  and  $C'$  are constants. An example of this relation is given in

Fig. 5, where both the curves appear to give the same value for the velocity constant. In other cases, however, different velocities have been found without obvious correlation with the experimental conditions (see Table 7).

Table 7.  $\log ([\text{OH}_\infty] - [\text{OH}]) = k' \cdot t + C'$ .

no.	$k'$ hours <sup>-1</sup>	no.	$k'$ hours <sup>-1</sup>
19.1	-0.034	27.2	-0.026
20.1	-0.009	28.2	-0.041
21.1	-0.047	29.2	-0.052
22.2	-0.035	30.2	-0.044
23.1	-0.014	31.2	-0.12

3. In solutions where  $\bar{n}$  remains between 0 and 1.5 the equilibrium appears to be established by a reaction (or at least a partial reaction) of the second order. Thus the expression

$$\frac{1}{[\text{OH}] - [\text{OH}_\infty]} = k'' \cdot t + C''$$

is satisfied, as is shown by Fig. 6. In this case too the velocity constant varies with the experimental conditions in an indeterminable manner.

It is well-known that the addition of alkali to an aluminium salt solution gradually results in the formation of an aluminium hydroxide gel, that re-dissolves on larger additions of alkali. The solid phases formed during such reaction have been the subject of numerous examinations, chiefly by R. Fricke and his collaborators. From these and other investigations (see for instance Geiling and Glocker<sup>5</sup>) it has been concluded that aluminium ion reacts at suitable pH forming primarily a so-called  $\alpha$ -gel with composition  $\text{Al}(\text{OH})_3$ . Geiling and Glocker showed that this gel has an amorphous liquid-structure.  $\alpha$ -gel ages rapidly, however, in a neutral or alkaline environment forming the ill-defined substance called  $\beta$ -gel. X-ray photographs of the latter (Geiling and Glocker<sup>5</sup>) show, however, both the liquid-interferences of the  $\alpha$ -gel and diffuse böhmite lines. We may thus consider  $\beta$ -gel to be a product in which the highly disordered structure of the  $\alpha$ -gel has begun to turn into the böhmite lattice. After some time, the length of time depending on the experimental conditions, the preparation changes into pure böhmite. In this case water is given off, as böhmite has the composition  $\text{AlOOH}$ . Böhmite is then very slowly through absorption of water turned into bayerite  $\text{Al}(\text{OH})_3$  and finally hydrargillite (also  $\text{Al}(\text{OH})_3$ ).

We were able to prove by means of X-ray powder photographs that solid crystalline phases appeared at an early stage in an alkaline environment. This was not the case, however, if the gel was kept in an acid solution, even if it were kept for as long as 2 months.

*From this we are tempted to conclude that the first order reaction occurring in an alkaline environment is a direct manifestation of the aging process whilst the second order reaction in an acid environment is associated with the formation of  $\alpha$ -gel or products which lead later to its formation.* Therefore, the final values of pH and pOH in acid solutions will correspond to the (transient) equilibrium value in a system where there are no crystalline phases, while corresponding values in an alkaline environment are equivalent to an equilibrium in a heterogeneous system where, at least, one phase possesses a well-defined lattice.

Thus, it would be possible to examine the entire system Al-OH under similar equilibrium conditions if, within the alkaline range, we disposed of values corresponding to the state of equilibrium that would be established if the process of aging did not exist. If, however, as already assumed, this process of aging influences the pH of the solutions in the first order reaction observed in the alkaline range, such values can naturally be obtained by extrapolation of the reaction to  $t = 0$ . A calculation of this kind was made and will be described in the next section.

#### REACTION MECHANISM AND EQUILIBRIUM CONDITIONS IN THE SYSTEM Al-OH

The experimental material on which the considerations in this section is based is given in Table 8. The values are also plotted in Fig. 7. In this material, which is assumed to correspond to the equilibrium conditions in the system Al-OH in the absence of crystalline phases, we took for  $\bar{n} < 3$  the final values from Tables 3, 4, and 5, while the pairs of values for  $\bar{n} > 3$  were calculated as follows:  $\log ([\text{OH}_\infty] - [\text{OH}])$  was plotted against  $t$ . As already mentioned this function becomes linear for higher values of  $t$  (Fig. 5), which thus makes a linear extrapolation to  $t = 0$  possible. In this way we obtain  $[\text{OH}_\infty] - [\text{OH}_0]$  and therefore  $[\text{OH}_0]$ , i.e. the hydroxyl ion concentration which the system would have reached in the different cases at equilibrium, had the process of aging not existed. It is these values  $[\text{OH}_0]$  which are used for the calculation of pOH and  $\bar{n}$  in Table 8 and Fig. 7 for the points where  $\bar{n} > 3$ .

Despite numerous different trials we have not succeeded in finding an explanation of the connection found experimentally between  $\bar{n}$  and pOH by using the usual expressions for homogeneous or heterogeneous complex functions. Furthermore, our measurements showed that aquo ion protolysis

Table 8.

[Al <sub>t</sub> ] = 2.209 · 10 <sup>-3</sup> mole/l			[Al <sub>t</sub> ] = 1.107 · 10 <sup>-2</sup> mole/l			[Al <sub>t</sub> ] = 5.541 · 10 <sup>-2</sup> mole/l		
No.	pOH	$\bar{n}$	No.	pOH	$\bar{n}$	No.	pOH	$\bar{n}$
1.1	10.015	0.033	1.2	10.125	0.051	1.3	10.225	0.203
2.1	9.685	0.082	2.2	10.016	0.083	2.3	10.180	0.491
3.1	9.648	0.117	3.2	9.990	0.099	3.3	9.973	1.462
4.1	9.615	0.198	4.2	9.969	0.120	4.3	9.485	2.439
5.1	9.600	0.285	5.2	9.916	0.162	5.3	9.346	2.722
6.1	9.573	0.434	6.2	9.858	0.248	6.3	6.589	2.963
7.1	9.498	0.829	7.2	9.834	0.398	7.3	4.870	2.991
8.1	9.467	1.049	8.2	9.776	0.796			
9.1	9.384	1.548	9.2	9.756	1.018			
10.1	9.250	2.036	10.2	9.747	1.017			
11.1	9.066	2.310	11.2	9.699	1.523			
12.1	8.845	2.517	12.2	9.532	2.013			
13.1	7.995	2.801	13.2	9.558	2.017			
14.1	6.887	2.900	14.2	9.384	2.253			
15.1	5.842	2.948	15.2	9.135	2.504			
16.1	4.895	2.995	16.2	9.229	2.510			
17.1	5.228	2.998	17.2	8.607	2.751			
18.1	4.979	3.05	18.2	8.379	2.789			
19.1	4.499	3.13	19.2	7.798	2.889			
20.1	4.226	3.40	20.2	6.909	2.901			
21.1	3.762	3.64	21.2	6.392	2.939			
22.1	3.733	3.73	22.2	5.978	2.964			
23.1	3.594	3.81	23.2	4.588	2.987			
24.1	3.016	4.061	24.2	4.925	2.988			
25.1	2.766	4.077	25.2	4.505	2.997			
26.1	2.328	4.020	26.2	4.559	2.997			
27.1	2.311	4.039	27.2	4.479	3.04			
			28.2	3.622	3.21			
			29.2	3.236	3.41			
			30.2	3.156	3.47			
			31.2	2.886	3.81			
			32.2	2.558	4.000			
			33.2	2.491	4.035			
			34.2	2.440	4.028			

cannot be the only existing reaction mechanism even in relatively acid solutions. These facts together with the observations described above on the kinetic conditions have finally led us to form certain hypotheses on the mechanism



for the reactions between aluminium ion and water. This reaction mechanism has been found, at least formally, to be somewhat different on the acid and the alkaline side of  $\bar{n} = 3$ . In the description below we thought it best to begin by explaining the conditions on the alkaline side, since these appear to be more perspicuous than is the case on the acid side.

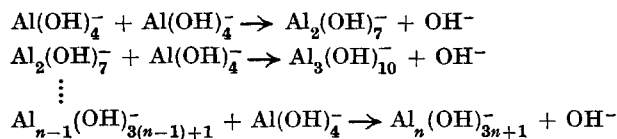
$$\bar{n} > 3$$

The observations on the alkaline side of  $\bar{n} = 3$  can be explained qualitatively if the following reaction mechanism is assumed:

1. In an alkaline environment, aluminium ion is protolysed instantaneously to  $\text{Al}(\text{OH})_4^-$ . This manifests itself in a very rapid decrease in the pH of a sodium hydroxide solution into which aluminium ions have been introduced.

2. If the alkali excess is sufficiently large a solution is immediately obtained where practically speaking all the aluminium occurs as  $\text{Al}(\text{OH})_4^-$  (limiting complex) and where equilibrium prevails. In this case therefore a constant pH value is very rapidly reached. The viscosity must be low under these conditions, which was also the case in the measurements made by Treadwell and Bonn<sup>3</sup>.

3. If a smaller excess of alkali is present ( $3 < \bar{n} < 4$ ) the above-mentioned protolysis and simultaneous decrease in alkalinity are succeeded by the following reactions:

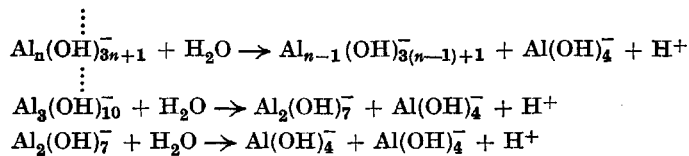


As is seen these reactions cause the formation of very large groups (ions) with the simultaneous increase of the pH of the solution. As  $n$  increases the probability for the ion in question to be neutralized by a cation ( $\text{Na}^+$ ) forming  $\alpha$ -gel presumably increases. This gel is, therefore, not to be considered as a definite solid phase.

4. The  $\alpha$ -gel ages slowly under the formation of a crystalline phase. But the formation of a *solid phase* with the composition  $\text{Al}(\text{OH})_3$  (or  $\text{AlOOH}$ ) in a system where  $\bar{n}$  lies between 3 and 4 would imply that the ratio  $[\text{NaOH}_t]/[\text{Al}_t]$  in the solution increased and thus the pH of the solution slowly rose.

The series of reactions given above under 3) are, at least formally, rather like the process of hydrolysis of  $\text{Bi}^{3+}$  ion examined by Granér and Sillén<sup>6</sup>. It would therefore seem probable that here, too, as in the case of bismuth hydrolysis, it would be possible to calculate the equilibrium from two equilibrium constants only. This calculation was performed in the following manner:

Instead of the reactions under 3) we will consider the reverse process, *i.e.* the transformation of  $\alpha$ -gel into aluminate ion:



For shortness we introduce the following symbols for concentrations:

$$\begin{aligned} [\text{Al}(\text{OH})_4^-] &= b & [\text{H}^+] &= h \\ [\text{Al}_2(\text{OH})_7^-] &= c_2'' \\ [\text{Al}_3(\text{OH})_{10}^-] &= c_3'' \\ &\vdots \\ [\text{Al}_n(\text{OH})_{3n+1}^-] &= c_n'' \\ &\vdots \end{aligned}$$

The following equilibrium equations are obtained:

$$\begin{aligned} \frac{c_{n-1}'' \cdot b \cdot h}{c_n''} &= k_{2, (n-1)} \\ &\vdots \\ \frac{c_2'' \cdot b \cdot h}{c_3''} &= k_{2,2} \\ \frac{b \cdot b \cdot h}{c_2''} &= k_{2,1} \end{aligned}$$

As in Granér and Sillén's <sup>6</sup> expressions we can approximately put  $k_{2,2} = k_{2,3} \dots = k_{2, (n-1)} = k_2$ .

Further, if we put

$$k_{2,1} = k_2', \quad \frac{b^2 \cdot h}{k_2'} = y \quad \text{and} \quad \frac{b \cdot h}{k_2} = x$$

we obtain

$$\begin{aligned} [\text{Al}(\text{OH})_4^-] &= b \\ [\text{Al}_2(\text{OH})_7^-] &= c_2'' = y \\ [\text{Al}_3(\text{OH})_{10}^-] &= c_3'' = y \cdot x \\ &\vdots \\ [\text{Al}_n(\text{OH})_{3n+1}^-] &= c_n'' = yx^{n-2} \end{aligned}$$

Using these expressions we now calculate  $[Al_t]$  and the total concentration of hydroxyl ion bound to the aluminium, *i.e.*  $\bar{n} \cdot [Al_t]$ . Denoting  $[Al_t]$  by  $a_t$  we get the following equations:

$$a_t = b + 2 y + 3 yx + 4 yx^2 + \dots + nyx^{n-2} + \dots$$

$$\bar{n} \cdot a_t = 4 b + 7 y + 10 yx + 13 yx^2 + \dots + (3 n + 1) yx^{n-2} + \dots$$

These give us:

$$a_t = b + y (2 + 3 x + 4 x^2 + \dots + nx^{n-2} + \dots)$$

$$\bar{n} \cdot a_t = 4 b + y \{7 + (7 + 1 \cdot 3)x^1 + (7 + 2 \cdot 3)x^2 + \dots + (7 + n \cdot 3)x^n + \dots\}$$

Summation of the infinite series finally gives:

$$\left. \begin{aligned} a_t &= b + y \frac{2-x}{(1-x)^2} \\ \bar{n} \cdot a_t &= 4 b + y \frac{7-4x}{(1-x)^2} \end{aligned} \right\} \quad (1)$$

where

$$a_t = [Al_t]; \quad b = [Al(OH)_4^-]; \quad y = \frac{b^2 \cdot h}{k'_2};$$

$$x = \frac{b \cdot h}{k_2}; \quad \text{och } h = [H^+]$$

From this system of equations we obtain:

$$[Al(OH)_4^-] = \frac{2\bar{n} - 7}{\frac{[H^+]}{k_2} (\bar{n} - 4) + \frac{1}{[Al_t]}} \quad (2)$$

and 
$$[H^+] \cdot [Al_t] = A_2^2 \left\{ B_2 + \frac{1}{A_2} \pm \sqrt{B_2 \left( \frac{2}{A_2} + B_2 \right)} \right\} \quad (3)$$

where 
$$A_2 = \frac{k_2}{\bar{n} - 3} \quad \text{and} \quad B_2 = \frac{2(\bar{n} - 3.5)^2}{k'_2(4 - \bar{n})}$$

In this way we have obtained a relation between  $[H^+]$  or  $[OH^-]$  and  $\bar{n}$ . For  $\bar{n} = 3.5$  we get immediately

$$[H^+]_{\bar{n}=3.5} \cdot [Al_t] = \left( \frac{k_2}{3.5 - 3} \right)^2 \cdot \frac{3.5 - 3}{k_2} = 2 k_2 \quad (4)$$

or 
$$p[\text{OH}^-]_{\bar{n}=3.5} = \log \frac{2k_2}{k_w} - \log [\text{Al}_t] \quad (5)$$

*i.e.* at  $\bar{n} = 3.5$  the hydroxyl ion concentration of the solutions is directly proportional to the total concentration of aluminium. The calculation of the constant  $k_2$  is, as is seen, very simple. For equation (4) gives us

$$k_2 = \frac{1}{2} [\text{H}^+]_{\bar{n}=3.5} \cdot [\text{Al}_t] \quad (6)$$

$k'_2$  can be calculated from equation (3), which we will now consider somewhat more closely. The following characteristics of the function are decisive here:

$\bar{n} \rightarrow$	symbol before the square root sign	$[\text{H}^+] \rightarrow$
4	+	$\infty$
4	-	0
3.5	$\pm$	independent of the sign
3	+	$\infty$
3	-	$k'_2$

In accordance with our assumption we apply, however (*vide infra*):

$$\lim_{\bar{n} \rightarrow 3} [\text{H}^+] = \infty$$

and 
$$\lim_{\bar{n} \rightarrow 4} [\text{H}^+] = 0$$

This implies the following choice of symbols before the square root sign

$$4 > \bar{n} > 3.5 : -$$

$$3.5 > \bar{n} > 3 : +$$

which leads to the function:

$$[\text{H}^+] \cdot [\text{Al}_t] = A_2^2 \left\{ \frac{1}{A_2} + B_2 + \frac{3.5 - \bar{n}}{|3.5 - \bar{n}|} \sqrt{\left(\frac{2}{A_2} + B_2\right) \cdot B_2} \right\} \quad (7)$$

where  $A_2 = \frac{k_2}{\bar{n} - 3}$  and  $B_2 = \frac{2(\bar{n} - 3.5)^2}{k'_2(4 - \bar{n})}$

In calculating  $k_2$  it is advantageous to use equation (6). In the present case we thereby obtain:

$$k_2 = 2.3_1 \cdot 10^{-13}$$

It is now necessary to find the value for  $k'_2$  which, when substituted in the equation (7), gives the best possible agreement with the experimental results. The values given in Table 9 have been calculated with  $k'_2 = 2 \cdot 10^{-11}$ .

Table 9.  $k'_2 = 2 \cdot 10^{-11}$ ;  $k_2 = 2.3_1 \cdot 10^{-13}$ .

$\bar{n}$	pOH	
	$[Al_t] = 1.107 \cdot 10^{-2}$	$[Al_t] = 2.209 \cdot 10^{-3}$
3.01	5.28	5.98
3.10	3.96	4.66
3.30	3.41	4.11
3.50	3.14	3.84
3.70	2.95	3.65
3.90	2.76	3.46
3.99	2.40	3.10

The two curves shown in the alkaline range in Fig. 7 are based on these values. As is seen the agreement between these theoretical curves and the results of measurement is good, especially for the higher aluminium concentrations.

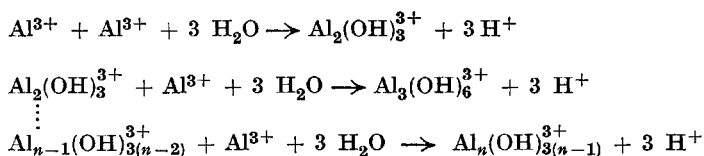
The reaction mechanism assumed in the foregoing paragraphs for the formation of  $\alpha$ -gel from aluminate ion or for the break-down of this gel into aluminate ions necessitates the hydrogen ion concentration for  $\bar{n} = 3$  being infinitely great. This, of course, is absurd and is due to the fact that no consideration has been paid to the break-down of the gel occurring in acid solution. In other words there are two processes, one of which manifests itself in the alkaline and the other in the acid range. At not too low total concentrations of aluminium, however, these processes assert themselves in pH ranges lying far from each other, which makes it possible to treat them separately. This implies a considerable simplification of the whole problem.

$$\bar{n} < 3$$

As already mentioned, the kinetic conditions in the range where  $\bar{n} < 3$  are more difficult to grasp. On the other hand, we do not seem in this case to have to consider the effects of aging. Bearing in mind that there exists experimental support for the assumption that a primary rapid protolysis and a subsequent "protolytic association" take place in the alkaline range, it is reasonable to try to interpret the conditions within the acid range too in a similar manner. In other words in this case also we should like to assume a

primary protolysis with subsequent "protolytic association". But while we might suppose that the protolysis in the alkaline range could lead direct to the limiting complex  $\text{Al}(\text{OH})_4^-$ , this is less likely in the acid range. Here, we could expect instead a primary formation of the ions  $\text{Al}(\text{OH})^{2+}$  and  $\text{Al}(\text{OH})_2^+$  with subsequent protolytic association in which these and  $\text{Al}^{3+}$  ions might take part. Since the adjustment of the equilibrium for the association is a slow process, it is conceivable that the primary protolysis in the range where  $\bar{n}$  approaches 3 at equilibrium, goes so far that  $\text{Al}(\text{OH})_4^-$  ions are formed to a considerable extent. Owing to this,  $\bar{n}$  can for a short time reach a value greater than 3, which must then cause a decided fall in the pH of the solution. As it approaches equilibrium, however,  $\bar{n}$  diminishes to approximately 3 or a value somewhat lower than 3. This successive decrease in  $\bar{n}$  must be followed by a corresponding increase in the pH of the solution. As already mentioned, such a change in pH (or pOH) with time has been observed. (See Figs. 4 c, d, and e.)

It might appear from the above that the reaction mechanism leading to the formation of  $\alpha$ -gel from aluminium ion and water probably consists of a complicated interaction between or succession of several partial processes. To try to find out the nature of these partial processes with the present experimental material seemed to be hazardous, especially as data on aluminium ion concentrations are not available. We can, however, limit ourselves to finding out whether there exists any total reaction mechanism, consistent with the experimental data, which is capable of explaining the process from the initial stage, the aluminium ion, to the final stage  $\alpha$ -gel, without giving the intermediate stages. The simplest possible total reaction mechanism fulfilling the conditions mentioned above seems to be the following:



We introduce the following symbols for concentrations:

$$\begin{aligned} [\text{Al}^{3+}] &= a & [\text{H}^+] &= h \\ [\text{Al}_2(\text{OH})_3^{3+}] &= c'_2 \\ [\text{Al}_3(\text{OH})_6^{3+}] &= c'_3 \\ \vdots & \\ [\text{Al}_n(\text{OH})_{3(n-1)}^{3+}] &= c'_n \end{aligned}$$

The following equilibrium equations are obtained:

$$\begin{aligned} \frac{c'_2 \cdot h^3}{a^2} &= k_{1,1} \\ \frac{c'_3 \cdot h^3}{c_2 \cdot a} &= k_{1,2} \\ \vdots \\ \frac{c'_n \cdot h^3}{c'_{n-1} \cdot a} &= k_{1,(n-1)} \end{aligned}$$

In the same way as before we put  $k_{1,2} = k_{1,3} = \dots = k_{1,(n-1)} = k_1$ . Further, we put  $k_{1,1} = k'_1$ ;  $\frac{k'_1 \cdot a^2}{h^3} = u$ ;  $\frac{k_1 \cdot a}{h^3} = z$ . Thus we get:

$$\begin{aligned} [\text{Al}^{3+}] &= a \\ [\text{Al}_2(\text{OH})_3^{3+}] &= u \\ [\text{Al}_3(\text{OH})_6^{3+}] &= uz \\ \vdots \\ [\text{Al}_n(\text{OH})_{3(n-1)}^{3+}] &= uz^{n-2} \end{aligned}$$

If  $[\text{Al}_t]$  is denoted by  $a_t$ , we obtain in the same way as before:

$$\begin{aligned} a_t &= a + 2u + 3uz + 4uz^2 + \dots + n \cdot uz^{n-2} + \dots \\ \bar{n} \cdot a_t &= 3u + 6uz + 9uz^2 + 12uz^3 + \dots + 3(n-1)uz^{n-2} + \dots \end{aligned}$$

Summation of the infinite series finally gives:

$$\left. \begin{aligned} a_t &= a + u \frac{2-z}{(1-z)^2} \\ \bar{n} \cdot a_t &= u \frac{3}{(1-z)^2} \end{aligned} \right\} \quad (8)$$

where  $a_t = [\text{Al}_t]$ ;  $a = [\text{Al}^{3+}]$ ;  $u = \frac{k'_1 \cdot a^2}{h^3}$ ;  $z = \frac{k_1 \cdot a}{h^3}$  and  $h = [\text{H}^+]$ .

From this system of equations we obtain:

$$[\text{Al}^{3+}] = \frac{2\bar{n} - 3}{\bar{n} \frac{k_1}{[\text{H}^+]^3} - \frac{3}{[\text{Al}_t]}} \quad (9)$$

and in the same way as before:

$$\frac{[\text{H}^+]^3}{[\text{Al}_t]} = A_1 + B_1 + \frac{1.5 - \bar{n}}{|1.5 - \bar{n}|} \sqrt{B_1 (2A_1 + B_1)} \quad (10)$$

where  $A_1 = \frac{k_1}{3} (3 - \bar{n})$  and  $B_1 = \frac{k'_1}{6\bar{n}} (2\bar{n} - 3)^2$

For  $2\bar{n} = 3$  we have  $B_1 = 0$  which gives:

$$\frac{([\text{H}^+]_{\bar{n}=\frac{3}{2}})^3}{[\text{Al}_t]} = \frac{k_1}{3} (3 - \frac{3}{2})$$

$$\therefore k_1 = \frac{2}{[\text{Al}_t]} \cdot ([\text{H}^+]_{\bar{n}=\frac{3}{2}})^3 \quad (11)$$

The following value for the equilibrium constant was obtained from (11)

$$k_1 = 6 \cdot 10^{-10}$$

It was then necessary to find the value of  $k'_1$  which, when substituted together with this value of  $k_1$  in equation (10), gives the best agreement with all the experimental data. Acceptable results were obtained for  $k'_1 = 5 \cdot 10^{-11}$ , and are given in Table 10.

Table 10.  $k'_1 = 5 \cdot 10^{-11}$ ;  $k_1 = 6 \cdot 10^{-10}$

$\bar{n}$	pOH		
	$[\text{Al}_t] = 55.41 \cdot 10^{-3}$	$[\text{Al}_t] = 11.07 \cdot 10^{-3}$	$[\text{Al}_t] = 2.209 \cdot 10^{-3}$
0.01	10.50	10.27	10.04
0.1	10.22	9.99	9.76
0.5	10.07	9.84	9.61
1.0	9.99	9.76	9.53
1.5	9.92	9.69	9.46
2.0	9.84	9.61	9.38
2.5	9.69	9.46	9.23
2.7	9.58	9.35	9.12
2.9	9.33	9.10	8.87
2.99	8.72	8.49	8.26



The values given in Table 10 are used for the three curves in the acid range in Fig. 7. As will be seen these curves lie slightly closer together than do the values obtained experimentally, which latter also approach  $\bar{n} = 3$  more slowly than is predicted by the theory. This latter deviation, which is apparent in the range  $2 < \bar{n} < 3$ , may have several causes, for instance:

1. that rather large approximations were made both in the reaction mechanism and in the equilibrium constants;
2. that real equilibrium was not attained in the experiments;
3. that no consideration was paid to possible participation of the perchlorate ion in the equilibrium.

Alternative (3) deserves special attention. Several experiments (see for instance, Marion and Thomas<sup>7</sup>) show that the course of the titration curve when aluminium ion is titrated with NaOH or KOH can be strongly influenced by different anions. For instance,  $\text{Cl}^-$  can undoubtedly replace in some way a bound  $\text{OH}^-$ , and  $\text{SO}_4^{2-}$  to some extent two bound  $\text{OH}^-$ .

We cannot, therefore, disregard the possibility of  $\text{ClO}_4^-$  ions replacing bound  $\text{OH}^-$  ions at low  $\text{OH}^-$  ion concentrations, at least to a slight extent. As the concentration of sodium perchlorate was the same (2.02 *C*) in all experiments this replacement will diminish with increasing  $\text{OH}^-$  ion concentration. At  $\text{pOH} \sim 6$  it does not seem to influence  $\bar{n}$  noticeably. On the other hand, at  $\text{pOH} \sim 10$  such an influence, even if great, would not make itself felt in the curves in Fig. 7 as  $\bar{n}$  varies very strongly here with  $\text{pOH}$ . Thus the influence of the perchlorate ion which might depress the number of  $\text{OH}^-$  ions bound by aluminium, *i.e.* diminish the observed value of  $\bar{n}$ , will manifest itself most markedly in the region where  $\text{pOH}$  is still sufficiently high but  $\bar{n}$  is not very sensitive to changes in  $\text{pOH}$ . In our case this region lies at  $\text{pOH} \sim 8-9$  and the discrepancy between the observed values and the theoretical curves is, as was to be expected, most pronounced here.

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It can be seen from the above analysis that if we consider the formation of  $\alpha$ -gel in acid and alkaline solutions as being independent phenomena each of the processes can be described by means of a pair of equilibrium constants. A quantity which does not appear in this connection is the solubility product of  $\text{Al}(\text{OH})_3$ . This is probably because the above system has been considered in the absence of crystalline phases. Furthermore the  $\alpha$ -gel contained in the system has been described as a series of macromolecules with varying numbers of aluminium atoms. It cannot possess a well-defined activity in this form and so *the concept of solubility product will not apply in this case.* The relatively

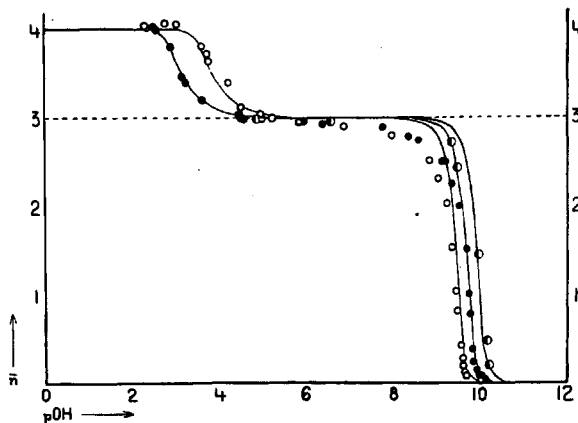


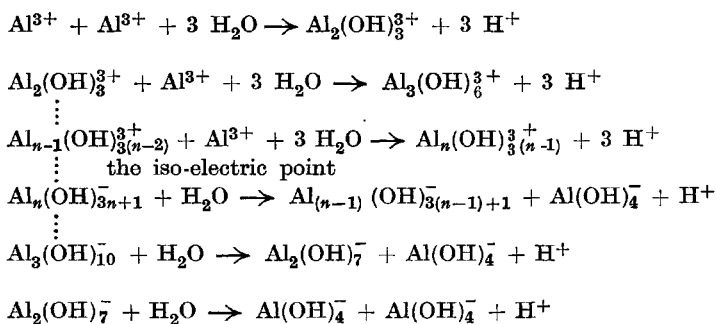
Fig. 7.

good agreement obtained between theory and experiment seems, at least to some extent, to support this view.

## SUMMARY

1. In the absence of solid crystalline phases, the equilibrium conditions in the system Al-OH were studied by means of pH measurements.

2. Certain observations on kinetic reaction conditions led to the following assumptions on the reactions between aluminium ion and water:



3. The equilibrium conditions in the system are expressed by the following equations:

$$\frac{[\text{Al}_2(\text{OH})_3^{3+}] \cdot [\text{H}^+]^3}{[\text{Al}^{3+}]^2} = k'_1$$

$$\frac{[\text{Al}_n(\text{OH})_{3(n-1)}^{3+}] \cdot [\text{H}^+]^3}{[\text{Al}_{(n-1)}(\text{OH})_{3(n-2)}^{3+}] \cdot [\text{Al}^{3+}]} = k_1$$

$$\frac{[\text{Al}_{(n-1)}(\text{OH})_{3(n-1)+1}^-] \cdot [\text{Al}(\text{OH})_4^-] \cdot [\text{H}^+]}{[\text{Al}_n(\text{OH})_{3n+1}^-]} = k_2$$

$$\frac{[\text{Al}(\text{OH})_4^-]^2 \cdot [\text{H}^+]}{[\text{Al}_2(\text{OH})_7^-]} = k'_2$$

$k_1$  and  $k_2$  are, as suggested by Granér and Sillén<sup>6</sup>, assumed to hold good for all reasonable values of  $n > 2$ .

4. The above assumptions led to the following expression:

$$0 < \bar{n} < 3$$

$$[\text{Al}^{3+}] = \frac{2\bar{n} - 3}{\bar{n} \cdot \frac{k_1}{[\text{H}^+]^3} - \frac{3}{[\text{Al}_t]}}$$

$$\frac{[\text{H}^+]^3}{[\text{Al}_t]} = A_1 + B_1 + \frac{1.5 - \bar{n}}{|1.5 - \bar{n}|} \sqrt{B_1(2A_1 - B_1)}$$

where

$$A_1 = \frac{k_1}{3} (3 - \bar{n}) \text{ and } B_1 = \frac{k'_1}{6} (2\bar{n} - 3)^2$$

$$3 < \bar{n} < 4$$

$$[\text{Al}(\text{OH})_4^-] = \frac{2\bar{n} - 7}{\frac{[\text{H}^+]}{k_2} (\bar{n} - 4) + \frac{1}{[\text{Al}_t]}}$$

$$[\text{H}^+] \cdot [\text{Al}_t] = A_2 \left\{ \frac{1}{A_2} + B_2 + \frac{3.5 - \bar{n}}{|3.5 - \bar{n}|} \sqrt{B_2 \left( \frac{2}{A_2} + B_2 \right)} \right\}$$

where

$$A_2 = \frac{k_2}{3 - \bar{n}} \text{ and } B_2 = \frac{2(\bar{n} - 3.5)^2}{k'_2 (4 - \bar{n})}$$

In the above expression  $[\text{Al}_t]$  denotes the total concentration of aluminium and  $\bar{n}$  the average number of bound hydroxyl groups per aluminium atom.

5. At 40° C and in the presence of  $\text{NaClO}_4$ , 2 *C* as ionic medium, has acceptable agreement between theory and experiment been obtained with the following values for the equilibrium constants:

$$\begin{aligned}
 k_1' &= 5 \cdot 10^{-11} & C^2 \\
 k_1 &= 6 \cdot 10^{-10} & C^2 \\
 k_2' &= 2 \cdot 10^{-11} & C^2 \\
 k_2 &= 2.3 \cdot 10^{-13} & C^2
 \end{aligned}$$

The deviations, which are greatest in the range, where  $2 < \bar{n} < 3$ , are discussed. In this connection it has been pointed out that  $\text{ClO}_4^-$  may possibly enter into the equilibrium.

6. It has been pointed out that *the concept of a solubility product cannot be applied* in the case of  $\alpha$ -gel if, as is assumed, it consists of macromolecules of varying sizes.

I wish to offer my deepest thanks to Professor Arne Ölander for all the interest he has shown in my work and for the continual encouragement I received during this lengthy investigation. Likewise I want to thank Miss Åsa Bränd-Persson for valuable experimental help in the preliminary series of experiments at 25° C. Finally I wish to thank Mrs Stina Nord for her valuable assistance in the experiments.

The investigation was carried out with the financial support of *Statens Tekniska Forskningsråd*.

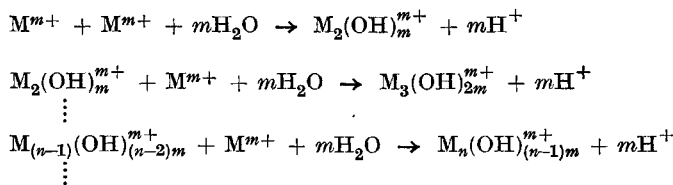
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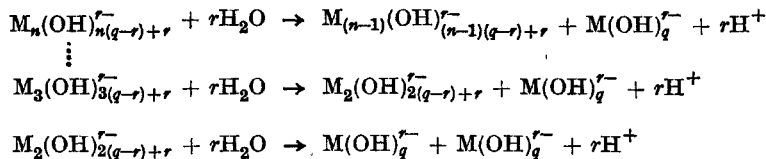
## APPENDIX

In connection with the above calculations of the equilibrium conditions in a system where a hydroxide gel with amphoteric properties is formed, it may be of interest to derive corresponding expressions for the general case.

Assuming that the total concentration of the group  $\text{M}^{m+}$  in a water solution is  $\text{M}_t$ , the group will react with water in the following way:



(The iso-electric point)



where  $m$ ,  $q$ , and  $r$  are positive whole numbers connected by  $m = q - r$ . Let us assume that the equilibrium in the system is determined by the following expressions:

$$\begin{aligned}
 \frac{[M_2(\text{OH})_m^{m+}] \cdot [\text{H}^+]^m}{[M^{m+}]^2} &= k_{1,1} \\
 \frac{[M_3(\text{OH})_{2m}^{m+}] \cdot [\text{H}^+]^m}{[M_2(\text{OH})_m^{m+}] \cdot [M^{m+}]} &= k_{1,2} \\
 \vdots & \\
 \frac{[M_n(\text{OH})_{(n-1)m}^{m+}] \cdot [\text{H}^+]^m}{[M_{(n-1)}(\text{OH})_{(n-2)m}^{m+}] \cdot [M^{m+}]} &= k_{1, (n-1)} \\
 \frac{[M_{(n-1)}(\text{OH})_{(n-1)(q-r)+r}^{r-}] \cdot [M(\text{OH})_q^{r-}] \cdot [\text{H}^+]^r}{[M_n(\text{OH})_{n(q-r)+r}^{r-}]} &= k_{2, (n-1)} \\
 \vdots & \\
 \frac{[M_2(\text{OH})_{2(q-r)+r}^{r-}] \cdot [M(\text{OH})_q^{r-}] \cdot [\text{H}^+]^r}{[M_3(\text{OH})_{3(q-r)+r}^{r-}]} &= k_{2,2} \\
 \cdot \frac{[M(\text{OH})_q^{r-}]^2 [\text{H}^+]^r}{[M_2(\text{OH})_{2(q-r)+r}^{r-}]} &= k_{2,1}
 \end{aligned}$$

Put  $k_{1,1} = k'_1$  and  $k_{2,2} = k'_2$ .

According to Granér and Sillén<sup>6</sup> we can approximately put

$$k_{1,2} = k_{1,3} \dots = k_{1, (n-1)} \dots = k_1 \text{ and } \dots k_{2(n-1)} = \dots k_{2,3} = k_{2,2} = k_2$$

In the same way as before we first calculate  $[M_t]$  and  $\bar{n} \cdot [M_t]$ :

$$\begin{aligned}
 0 < \bar{n} < m: \\
 \left. \begin{aligned}
 [M_t] &= [M^{m+}] + y_1 \frac{2-x_1}{(1-x_1)^2} \\
 \bar{n} \cdot [M_t] &= y_1 \frac{m}{(1-x_1)^2}
 \end{aligned} \right\} \quad (1)
 \end{aligned}$$

where  $x_1 = \frac{k_1 \cdot [M^{m+}]}{[\text{H}^+]^m}$  and  $y_1 = \frac{k'_1 \cdot [M^{m+}]^2}{[\text{H}^+]^m}$

$$m = q - r < \bar{n} < q:$$

$$\left. \begin{aligned} [\text{M}_t] &= [\text{M}(\text{OH})_q^-] + y_2 \frac{2-x_2}{(1-x_2)^2} \\ \bar{n} \cdot [\text{M}_t] &= q \cdot [\text{M}(\text{OH})_q^-] + y_2 \frac{2q-r-qx_2}{(1-x_2)^2} \end{aligned} \right\} \quad (2)$$

where  $x_2 = \frac{[\text{M}(\text{OH})_q^-] \cdot [\text{H}^+]^r}{k_2}$  and  $y_2 = \frac{[\text{M}(\text{OH})_q^-]^2 \cdot [\text{H}^+]^r}{k'_2}$

From the equation systems (1) and (2) we obtain the following relations:

$$0 < \bar{n} < m:$$

$$[\text{M}^{m+}] = \frac{2 \bar{n} - m}{\bar{n} \frac{k_1}{[\text{H}^+]^m} - \frac{m}{[\text{M}_t]}} \quad (3)$$

$$k_1 = \frac{2}{[\text{M}_t]} \left( [\text{H}^+]_{\bar{n} - \frac{m}{2}} \right)^m \quad (4)$$

and

$$\frac{[\text{H}^+]^m}{[\text{M}_t]} = A_1 + B_1 + \frac{\frac{m}{2} - \bar{n}}{\left| \frac{m}{2} - \bar{n} \right|} \sqrt{B_1(2A_1 + B_1)} \quad (5)$$

where  $A_1 = \frac{k_1(m-\bar{n})}{m}$  and  $B_1 = \frac{k'_1(2\bar{n}-m)^2}{2\bar{n} \cdot m}$

$$m = q - r < \bar{n} < q$$

$$[\text{M}(\text{OH})_q^-] = \frac{2 \bar{n} - (2q - r)}{(\bar{n} - q) \frac{[\text{H}^+]^r}{k_2} + \frac{r}{[\text{M}_t]}} \quad (6)$$

$$k_2 = \frac{[\text{M}_t]}{2} \left( [\text{H}^+]_{\bar{n} - q - \frac{r}{2}} \right)^r \quad (7)$$

and  $[\text{H}^+]^r \cdot [\text{M}_t] = A_2^2 \left\{ B_2 + \frac{r}{A_2} + \frac{q - \frac{r}{2} - \bar{n}}{\left| q - \frac{r}{2} - \bar{n} \right|} \sqrt{B_2 \left( \frac{2r}{A_2} + B_2 \right)} \right\} \quad (8)$

where  $A_2 = \frac{k_2}{\bar{n} - q + r}$  and  $B_2 = \frac{r \{ 2\bar{n} - (2q - r) \}^2}{2k'_2(q - \bar{n})}$

The significance of equations (5) and (8) can be expressed in the following manner:

If a substance M occurs with total concentration  $[M_t]$  in a solution and if the ion  $M^{m+}$  reacts with water so as to build up or breakdown a macromolecule (hydroxide) gradually as would be the case with the above assumptions, then the expressions  $\frac{[H^+]^m}{[M_t]}$  and  $[H^+]^r \cdot [M_t]$  for the building-up and breaking-down, respectively, of the macromolecules depend only on the equilibrium constants and on  $\bar{n}$  as the only variable. In these expressions  $m$  and  $r$  are numbers indicating how many hydrogen ions are liberated at each stage of the reaction, and  $\bar{n}$  is the average number of  $OH^-$  groups bound per M atom.

Received August 3, 1951.