

ance with expectations for a nearly linear model.²⁹ The Raman activity of the antisymmetric stretch apparently results from the nonlinearity of the Cl-Hg-Hg-Hg-Cl chain.

In summary, we assign the bands of the Raman spectrum to vibrations of the AlCl_4^- group and to the sym-

(29) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, p 83.

metric and antisymmetric Hg-Cl and Hg-Hg stretching vibrations of the slightly bent Cl-Hg-Hg-Hg-Cl entity.

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Acidity Measurements at Elevated Temperatures.

V. Aluminum Ion Hydrolysis¹

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The hydrolysis of aluminum ion, which is kinetically slow at ordinary temperatures, was studied between 62.5 and 149.8° in 1 *m* KCl to establish better the hydrolysis reactions which occur and their temperature coefficients. Potentiometric measurements were made with hydrogen electrodes in a concentration cell previously described which permits precise acidity measurements at elevated temperatures. The results at low \bar{n} (ligand number) in acidic media and with varying aluminum concentration have led to the choice of two schemes of initial hydrolysis products each containing pairs of species: $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$; $\text{Al}_2(\text{OH})_3^{3+}$, $\text{Al}_3(\text{OH})_5^{4+}$. The authors prefer the first choice because of the apparent absence of 2,3 species in other known hydrolysis schemes. The species AlOH^{2+} , detected by other workers at relatively low aluminum concentration, was not present in detectable amounts under the conditions of these measurements. The identification of the major additional species formed at high \bar{n} values has been narrowed to a polymer with 14 ± 1 Al atoms by least-squares analysis of a large array of alternative species with 11–15 aluminum atoms. The following values of $-\log Q_{x,y}$ have been determined for the most probable scheme (where $Q_{x,y} = [\text{Al}_x(\text{OH})_y]^{(3x-y)+} [\text{H}^+]^y / [\text{Al}^{3+}]^x$ and the numbers in parentheses denote x and y): 25°: (2,2) 7.45, (3,4) 13.36, (14,34) 110.45 (literature data); 62.5°: (2,2) 5.90, (3,4) 10.74; 99.6°: (2,2) 4.81, (3,4) 8.20, (14,34) 67.89; 124.8°: (2,2) 3.95, (3,4) 7.01, (14,34) 55.68. The stabilities of $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, and $\text{Al}_4(\text{OH})_6^{4+}$ as a function of temperature have been used to estimate their thermodynamic parameters at 25°. Results in basic media at 149.8° indicate the presence of one species with a hydroxide-to-aluminum ratio of 4.0. This result combined with literature data indicates this species to be $\text{Al}(\text{OH})_4^-$ or AlO_2^- .

Introduction

The hydrolysis of aluminum ion, the most abundant of the metal ions in the earth's crust, has been studied extensively;² however, the important hydrolysis products produced in aqueous solution have not been well established. It is likely that the principal reasons for this are the slow rate of hydrolysis, first investigated in some detail by Brosset,³ and the severe demands placed on the accuracy of the data by the occurrence of at least one relatively large polymeric ion.

Those species which appear to be the best supported by previous studies are listed in Table I along with selected values for their formation quotients

$$Q_{x,y} = [\text{Al}_x(\text{OH})_y]^{(3x-y)+} [\text{H}^+]^y / [\text{Al}^{3+}]^x \quad (1)$$

Of these, AlOH^{2+} has been reported by numerous investigators, many of whom^{4–9} have found reasonably

(1) Research sponsored by the U. S. Atomic Energy Commission under contract with the Union Carbide Corp.

(2) L. G. Sillén and A. E. Martell, "Stability Constants of Metal-Ion Complexes," The Chemical Society, London, 1964.

(3) C. Brosset, *Acta Chem. Scand.*, **6**, 910 (1952).

(4) (a) J. N. Bronsted and K. Volgvartz, *Z. Phys. Chem., Stoichiomet. Verwandtschaftslehre*, **134**, 97 (1928); (b) W. H. Hartford, *Ind. Eng. Chem.*, **34**, 920 (1942).

(5) R. K. Schonfield and A. W. Taylor, *J. Chem. Soc.*, 4445 (1954).

(6) H. Kubota, *Diss. Abstr.*, **16**, 864 (1956).

(7) C. R. Frink and M. Peech, *Inorg. Chem.*, **2**, 473 (1963).

(8) E. Grunwald and D. W. Fong, *J. Phys. Chem.*, **73**, 650 (1969).

(9) V. A. Nazarenko and E. M. Nevskaya, *Russ. J. Inorg. Chem.*, **14**, 1696 (1969).

concordant values for the equilibrium quotient $Q_{1,1}$. In most of these studies, however, the extent of hydrolysis was measured in a series of dilutions of stoichiometric aluminum salt solutions. Unfortunately such measurements alone cannot uniquely identify a hydrolysis product since the concentration of aluminum and the extent of hydrolysis vary simultaneously. In particular, when such dilution data yield nearly constant values of $Q_{1,1}$, as in the case of aluminum, the same data can yield reasonably constant formation quotients for any species of the general formula $\text{M}_x(\text{OH})_{2x-1}$.¹⁰

The results of Kubota⁶ are therefore noteworthy since, in addition to dilution measurements, a set of

(10) If only one such hydrolysis product is formed in a stoichiometric salt solution, its concentration is given by (charges on complexes omitted)

$$[\text{M}_x(\text{OH})_{2x-1}] = \frac{1}{2x-1} [\text{H}^+]$$

and its formation quotient by

$$Q_{x,2x-1} = \frac{[\text{M}_x(\text{OH})_{2x-1}] [\text{H}^+]^{2x-1}}{[\text{M}]^x} = \left(\frac{1}{2x-1} \right) \left(\frac{[\text{H}^+]^{2x}}{m_{\text{M}} - \frac{x}{2x-1} [\text{H}^+]} \right)^x$$

For small degrees of hydrolysis we therefore obtain the approximation

$$Q_{x,2x-1} = \left(\frac{1}{2x-1} \right) \left(\frac{[\text{H}^+]^{2x}}{m_{\text{M}}} \right)^x$$

Hence, data for slightly hydrolyzed stoichiometric solutions which yield a constant value for $Q_{1,1}$ (*i.e.*, a constant quotient $[\text{H}^+]^2/m_{\text{M}}$) will yield approximately constant values for other quotients, $Q_{x,2x-1}$, as well, and hence be consistent with values of x greater than unity.

TABLE I
 SELECTED HYDROLYSIS SPECIES OF Al^{3+} REPORTED AT 25°

Species	$I(NaClO_4)^f$	M_{Al}	$-\log Q_{x,y}$	Ref
$AlOH^{2+}$	(0)	10^{-5} – 10^{-2}	5.02	a
	0.03	0.001	5.27	b
	0.01	$\sim 2 \times 10^{-5}$	4.9	c
	(0)	10^{-5} – 10^{-2}	4.98	d
$Al(OH)_2^+$	0.1	$\sim 2 \times 10^{-5}$	10.3	c
$Al_2(OH)_2^{4+}$	1	0.003–0.1	7.1	e
$Al_{13}(OH)_{32}^{7+}$	1	0.003–0.1	104.5	e

^a C. R. Frink and M. Peech, *Inorg. Chem.*, **2**, 473 (1963).
^b H. Kubota, *Diss. Abstr.*, **16**, 864 (1956). ^c V. A. Nazarenko and E. M. Nevskaya, *Russ. J. Inorg. Chem.*, **14**, 1696 (1969).
^d R. K. Schonfeld and A. W. Taylor, *J. Chem. Soc.*, 4445 (1954).
^e J. Aveston, *ibid.*, 4438 (1965). ^f Ionic strength adjusted with $NaClO_4$.

measurements is included in which the total aluminum concentration as well as the ionic strength was held constant in a pH range where $AlOH^{2+}$ was clearly shown to be the only hydrolysis product formed. Another important confirmation of the $AlOH^{2+}$ species comes from recent results of Nazarenko and Nevskaya,⁹ who studied hydrolysis at very low aluminum concentrations ($\sim 2 \times 10^{-5} m$) using colored organic ligands which compete with the OH^- ligand. They obtained a value of $Q_{1,1}$ which, though higher than expected, is fairly consistent with other measurements. The results of Kubota and of Nazarenko and Nevskaya leave little doubt that $AlOH^{2+}$ is one of the products of Al^{3+} hydrolysis.

The results of Nazarenko and Nevskaya, since they were obtained at such low concentrations of aluminum, provide the most useful estimate of the stability of $Al(OH)_2^+$. The two mononuclear species, $AlOH^{2+}$ and $Al(OH)_2^+$, are significant only in early hydrolysis at relatively low metal concentrations, where they are soon followed by precipitation of the hydroxide. Frink and Peech¹¹ have measured the solubility in acidic solutions of gibbsite, the stable form of aluminum hydroxide at ordinary temperatures. Their results place upper limits on the stability of $AlOH^{2+}$ and $Al(OH)_2^+$ which are consistent with the values of $Q_{1,1}$ and $Q_{1,2}$ in Table I. It is not too surprising, therefore, that several investigators have studied the more extensive hydrolysis of aluminum at higher concentrations and found no evidence of mononuclear species.

The early work of Brosset³ on more extensive hydrolysis of aluminum in 2 M $NaClO_4$ at 40° was later interpreted¹² by graphical methods of analysis in terms of several proposed species, $Al_6(OH)_{15}^{3+}$, $Al_8(OH)_{20}^{4+}$, etc., or an infinite series $Al[(OH)_5Al_2]_n^{(3+n)+}$ in the acidic range and $Al(OH)_4^-$ or a polymeric species in the alkaline range. The precision needed for a more definite analysis was lacking. In 1965 Aveston¹³ interpreted more extensive and more precise potentiometric data at 25° in terms of $Al_2(OH)_2^{4+}$ and $Al_{13}(OH)_{32}^{7+}$ (Table I). This interpretation, which is also consistent with his ultracentrifuge measurements of the degree of polymerization, was admittedly not a unique one but was selected because of the agreement with the reported¹⁴ cationic species present in $Na_2O \cdot 13Al_2O_3 \cdot 8SeO_3 \cdot 74H_2O$.

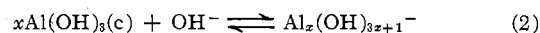
(11) C. R. Frink and M. Peech, *Soil Sci. Soc. Amer., Proc.*, **26**, 346 (1962).

(12) C. Brosset, G. Biedermann, and L. G. Sillén, *Acta Chem. Scand.*, **8**, 1917 (1954).

(13) J. Aveston, *J. Chem. Soc.*, 4438 (1965).

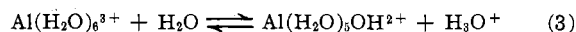
(14) G. Johansson, *Acta Chem. Scand.*, **14**, 771 (1960).

Because of the scatter in the data in the high pH region Brosset, *et al.*,¹² were unable to decide conclusively between an interpretation involving only mononuclear $Al(OH)_4^-$ or one involving anionic polymers with approximately the same aluminum-to-hydroxide ratio. Since that time several investigators^{15–17} have agreed on the charge of the anionic species in equilibrium with the solid phase in dilute basic solutions as -1 . Perhaps the strongest evidence of this is the measurements of Gayer, *et al.*,¹⁵ which show that above pH 9 the solubility of " $Al(OH)_3$ " is proportional to the base concentration, consistent with the general reaction



The recent Raman and infrared spectra of Moolenaar, *et al.*,¹⁸ of sodium aluminate dissolved in H_2O and D_2O are consistent with a tetrahedral structure for the predominant species below about 1.5 m . At higher concentrations their observations are interpreted in terms of a condensation of $Al(OH)_4^-$ to form a dimer of the form $Al_2O(OH)_6^{2-}$.

The generally consistent data obtained by several investigators at low \bar{n} values (< 0.1) suggest that the formation of the initial hydrolysis products of aluminum involve relatively rapid reaction rates. Indeed Holmes, *et al.*,¹⁹ have recently interpreted dissociation field effect relaxation times at 25° in terms of the formation of the $AlOH^{2+}$ species by the equilibrium



They obtained a rate constant of $4.4 \times 10^9 M^{-1} sec^{-1}$ for the reverse reaction at $I \approx 10^{-3} M$ and, from the results of Frink and Peech,⁷ $4.2 \times 10^4 sec^{-1}$ for the forward reaction. That hydrolysis reactions involving such monomeric species are typically rapid is also shown by data²⁰ on the Cr^{3+} ion where the rate constant for the reverse reaction is only one-sixth as large as that for the Al^{3+} ion. The magnitude of these rate constants indicates that these hydrolysis reactions do not involve the exchange of hydration waters—a relatively slow process for Al^{3+} and Cr^{3+} —in the rate-determining step, but simply the removal of a proton from a hydrate water. Some of the subsequent hydrolysis reactions of Al^{3+} and Cr^{3+} , wherein $M^{3+}-OH_2$ bonds presumably are being broken as polymeric species are formed by O^{2-} or OH^- bridging, occur at much lower rates.

In the present investigation, we have examined the hydrolysis of aluminum at higher temperatures, where kinetics are more favorable, using the previously described²¹ hydrogen electrode concentration cell for precise acidity measurements. We hoped to make a more certain identification of principal hydrolysis products and to estimate their thermodynamic parameters from the temperature dependence of their formation equilibria.

Experimental Section

Materials.—All aluminum solutions were prepared by dis-

(15) K. H. Gayer, L. C. Thompson, and O. T. Zajicek, *Can. J. Chem.*, **36**, 1268 (1958).

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

(17) W. Feitknecht and P. Schindler, *Pure Appl. Chem.*, **6**, 130 (1963).

(18) R. J. Moolenaar, J. C. Evans, and L. D. McKeever, *J. Phys. Chem.*, **74**, 3629 (1970).

(19) L. P. Holmes, D. L. Cole, and E. M. Eyring, *ibid.*, **72**, 301 (1968).

(20) L. D. Rich, D. L. Cole, and E. M. Eyring, *ibid.*, **73**, 713 (1969).

(21) R. E. Mesmer, C. F. Baes, Jr., and F. H. Sweeton, *ibid.*, **74**, 1937 (1970).

solution of very high purity aluminum (from K and K Laboratories, Inc.) in Baker Analyzed reagent hydrochloric acid. The only known impurity in the stock solution was iron, equivalent to 0.02 mol % as determined spectrophotometrically with *o*-phenanthroline. The free acid in the solutions was determined at 50° by the titration method described previously,²³ from the stoichiometry, and from the cell voltage in solutions where no significant hydrolysis had occurred. The three methods give an uncertainty of free acid equivalent to about 0.25 mol % of the aluminum.

A potassium chloride stock solution containing less than 10⁻⁵ *m* protolytic impurities in 1 *m* KCl was used for solution preparation. A small amount of CO₂ was removed from Fisher reagent KOH before use by precipitation with Ba(OH)₂. The base solutions were stored in paraffin-coated glass vessels under hydrogen.

The HCl solutions were stored under hydrogen in Pyrex vessels and transferred to a Zircaloy-2 titration reservoir where corrosion was negligible. A solution of 0.6 *m* HCl and 0.4 *m* KCl stored in this vessel for 12 days at 25° exhibited a change of acidity of 1.3 parts per thousand and a zirconium pickup of 4 × 10⁻⁴ *m* as determined by spectrographic analysis.

The ultrahigh-purity grade of hydrogen (99.999%) from J. T. Baker Co. was used.

Potentiometric Cell and Apparatus.—The hydrogen electrode assembly and measuring circuit have been described previously.²¹ The cell representation for the solutions used in this study is



where the half-cell on the right provides a constant reference potential during a titration experiment conducted in the half-cell on the left. That such cells are capable of precise measurement of acidities up to 292° was demonstrated in ref 21 where the apparent ion product of water was determined in this same medium. The estimated error of measurements made with the cell up to 150° is 0.1–0.2 mV. The chloride ion was chosen for the counterion in this study because the common choices of non-complexing anions, NO₃⁻ and ClO₄⁻, are not expected to remain stable at high temperatures in a hydrogen atmosphere. Also, it is known that chloride ion is a very poor complexing ion with small rare gas type cations. Cationic aluminum chloride complexes have not been reported and Kraus, *et al.*,²³ were unable to detect any anionic species of aluminum even in 12 *M* HCl.

Procedures.—The electrodes were replatinized just prior to each run. The air in the cell was removed after assembly by successively pressurizing with hydrogen to 500 psi and venting to atmospheric pressure three times. Then the cell was pressurized to about 500 psi and heated to temperature while limiting the temperature difference between the two compartments to 0.5°. The pressure was then adjusted to the desired level (arbitrarily 580 psi) after temperature equilibration. The high pressure of inert gas reduces the rate of distillation of water although this factor is not very significant at the temperatures investigated in this study. The titrant was added by displacement with mercury driven by a calibrated pressure generator. The titrant was transmitted through platinum tubing and a Zircaloy valve. It was preheated before entering the cell. The total pressure was measured with a Heise gauge and kept constant during a titration by venting a small amount of gas after each addition of titrant.

Precipitation Experiments.—In order to determine as a function of temperature the range of solution composition accessible to hydrolysis measurements without precipitation, several solutions of 0.04 *m* Al³⁺ in 1 *m* KCl with increasing amounts of added base were heated in quartz tubes at various temperatures up to 150°. The turbidity which formed with time was observed visually and with a Hack Turbidimeter (Model 2100). At 100° precipitation commenced at $\bar{n} = 2.2$, at 125° at $\bar{n} = 1.8$, and at 150° at $\bar{n} = 0.6$ where the uncertainties in the \bar{n} value are about 0.1. The solid phases produced at 150° gave a diffuse X-ray diffraction pattern similar to that reported by Levy and Breuil²⁴ for Al₁₇O₁₈(OH)₁₆Cl₃. However, the diffraction patterns for pre-

cipitates formed under different conditions at 150° in the Teflon vessel corresponded to that of boehmite, α-AlO(OH).

Because of these observations and similar observations in preliminary experiments in the potentiometric apparatus, the most extensive set of measurements was made at 125°. Additional measurements were made at 62.5, 100, and 150°. At 150° the accessible region in \bar{n} was limited to 1.0, at 100° the data were less precise because of the slow reaction rates, and at 62.5° the measurements were limited by rate effects to \bar{n} less than 0.16.

Results

Acidity Measurements and Data Analysis.—The potentials, Δ*E*, from cell I are given by the expression

$$\Delta E = (RT/F) \ln (h_r/h) - D_H(h_r - h) - \sum D_i(m_{i,r} - m_i) \quad (4)$$

where *h* is the free acidity in the solution being titrated, *h_r* is the reference acidity, and *m_i* and *m_{i,r}* denote the corresponding molal concentrations of all other ions in the two solutions. The liquid junction potential is given by the terms on the right containing *D_H* and *D_i*, derived from the Henderson equation.²¹ Under the present conditions, wherein the differences (*h_r* - *h*) and (*m_{i,r}* - *m_i*) all are maintained small compared to the ionic strength, the liquid junction potential so calculated was generally less than 1 mV. The validity of this method of estimating the liquid junction potentials has been amply demonstrated in previous work.^{21,25–27}

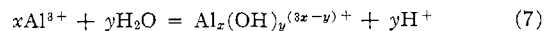
The customary method of analysis of complexing equilibria was employed as described below. The average number of hydroxides bound per aluminum, the hydroxyl number, is given by the measurements as

$$\bar{n} = (h - m_H)/m_{Al} \quad (5)$$

where *m_H* and *m_{Al}* are stoichiometric molal concentrations of acid and aluminum. This observed quantity is compared with values calculated on the basis of various schemes of assumed equilibria. The calculated quantity, \bar{n}_c , is defined by

$$\bar{n}_c = [\sum y Q_{x,y} a^x / h^y] / m_{Al} \quad (6)$$

where *a* is the free aluminum concentration, and *x* and *y* are, respectively, the number of Al³⁺ and OH⁻ ions in each hydrolysis species assumed. The *Q_{x,y}*'s are equilibrium quotients for the reactions



The usual agreement factor, σ(\bar{n}),²⁸ was used as the measure of the goodness of fit of various chosen schemes to the data.

Equilibrium Measurements.—Equilibrium was approached slowly under some of the experimental conditions. This is illustrated in Figure 1 which shows potentiometric data as a function of time at 124.8°. The origin on the ordinate represents the equilibrium potential. Equilibration times from several minutes to several hours were observed in the range from 150 to 100°. The region of accessible measurements is further limited by the fact that the maximum attainable value of \bar{n} decreases sharply above 150°. In an experiment at 200° in which the initial composition of the solution was 0.04 *m* Al³⁺ and 0.007 *m* H⁺ in 1 *m* KCl, precipitation occurred immediately. No attempt was

(25) C. F. Baes, Jr., and N. J. Meyer, *Inorg. Chem.*, **1**, 780 (1962).

(26) C. F. Baes, Jr., N. J. Meyer, and C. E. Roberts, *ibid.*, **4**, 518 (1965).

(27) R. E. Mesmer and C. F. Baes, Jr., *ibid.*, **6**, 1951 (1967).

(28) The agreement factor is defined as σ(\bar{n}) = [Σ(W($\bar{n} - \bar{n}_c$)²)/(N_o - N_v)]^{1/2}, where N_o and N_v were the number of observations and variables, respectively. Unit weights *W* were used since this is an adequate representation of the errors in such experiments.

(22) C. F. Baes, Jr., *Inorg. Chem.*, **4**, 588 (1965).

(23) K. A. Kraus, F. Nelson, and G. W. Smith, *J. Phys. Chem.*, **58**, 11 (1954).

(24) L. Levy and H. Breuil, *C. R. Acad. Sci.*, **268**, 262 (1961).

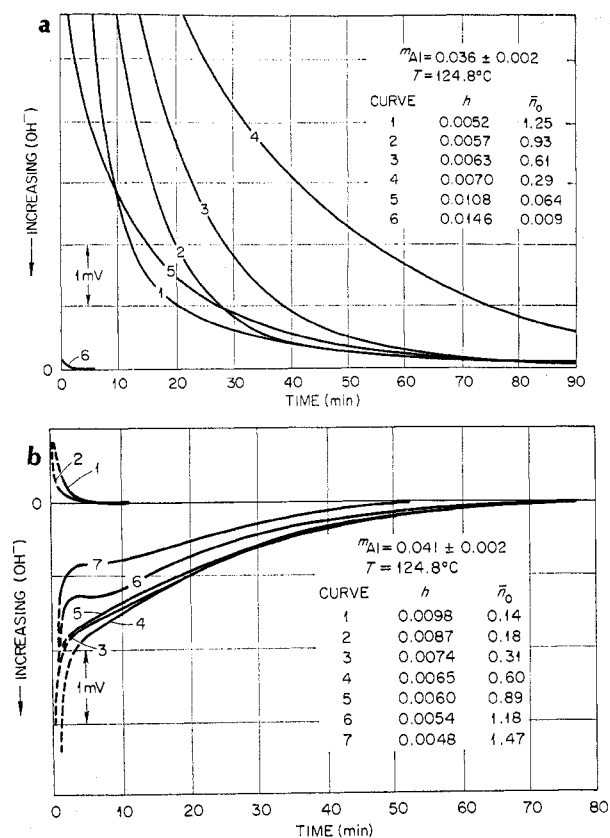


Figure 1.—The kinetics of the approach to the equilibrium potential after additions of acid (a) and base (b) at 124.8°C.

made to find conditions where even a small amount of data could be taken at this temperature.

In the acidic region of pH where cationic complexes are expected to exist, data were taken at low \bar{n} values (<0.2) at 62.5° and over wider ranges of \bar{n} at temperatures from 99.6 to 149.8°. These results are summarized in Table II and Figures 2 and 3. Figure 2

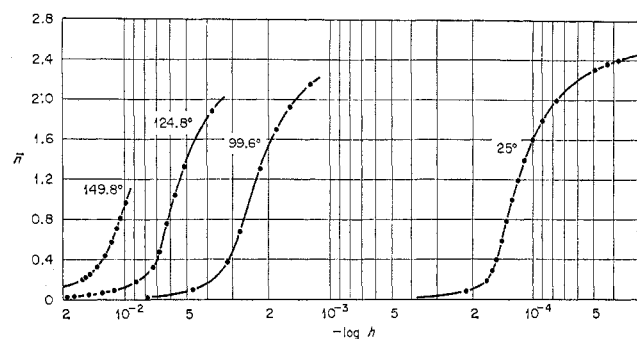


Figure 2.—The shift of hydrolysis of approximately 0.04 m aluminum in 1 m KCl to higher acidities with increasing temperatures.

shows the shift of the pH region of hydrolysis of 0.04 m aluminum solutions with temperature. Figure 3 illustrates the dependence of aluminum hydrolysis behavior on aluminum ion concentration and pH at 124.8°. The open circles on the figure represent data taken in the direction of increasing pH and closed circles represent data taken in the direction of decreasing pH. The small difference between the curves in the two directions results from the decrease of the aluminum ion concentration by dilution during the titrations.

TABLE II
ALUMINUM HYDROLYSIS RESULTS IN 1 m KCl

$m_{Al} \times 10^3$	$-\log h$	$\bar{n} \times 10$	$m_{Al} \times 10^3$	$-\log h$	$\bar{n} \times 10$	$m_{Al} \times 10^3$	$-\log h$	$\bar{n} \times 10$
62.5°								
43.00	2.284	0.013	10.67	2.691	2.331	19.40	2.469	16.25
42.53	2.422	0.054	10.36	2.746	4.752	19.19	2.411	13.14
42.14	2.557	0.132	10.12	2.776	6.774	18.98	2.364	9.99
41.69	2.708	0.323	9.81	2.818	9.599	18.78	2.323	6.85
41.16	2.827	0.634	9.51	2.866	12.41	18.58	2.283	3.73
40.94	2.868	0.786	9.22	2.923	15.32			
40.72	2.905	0.954	8.95	2.994	18.19	21.87	2.164	1.508
40.50	2.934	1.124	8.69	3.103	20.98	21.75	2.230	2.565
40.27	2.963	1.301				21.51	2.280	5.306
39.85	3.008	1.647	43.61	2.107	0.161	21.29	2.317	8.076
			43.13	2.328	0.991	21.06	2.356	10.89
43.31	2.254	0.006	42.19	2.510	3.690	20.83	2.403	13.77
42.88	2.321	0.012	41.30	2.559	6.660	20.62	2.457	16.56
42.64	2.389	0.038	40.38	2.604	9.866			
42.16	2.548	0.131	39.51	2.655	13.05	21.43	1.804	0.191
41.71	2.696	0.309	38.50	2.734	16.91	21.31	1.896	0.339
41.26	2.807	0.573	37.92	2.801	19.23	21.18	2.013	0.683
41.04	2.851	0.721	37.35	2.801	19.23	21.07	2.126	1.184
40.82	2.890	0.878		2.900	21.51	20.52	2.320	7.470
40.39	2.949	1.208	43.61	2.109	0.155	20.31	2.359	10.28
39.97	2.997	1.549	43.12	2.333	1.000	20.11	2.402	13.08
			42.18	2.511	3.702			
19.76	2.492	0.000	41.28	2.562	6.714	10.93	2.349	2.469
19.69	2.556	0.055	40.36	2.608	9.959	10.82	2.326	1.793
19.60	2.641	0.128	39.48	2.658	13.18	10.65	2.262	1.080
19.54	2.709	0.191	38.51	2.733	16.87	10.46	2.177	0.564
19.48	2.781	0.250	37.93	2.797	19.17			
19.42	2.847	0.342	37.38	2.897	21.40	9.35	2.616	17.07
19.37	2.910	0.455	37.02	3.008	22.86	9.14	2.565	15.00
19.26	3.010	0.749				8.94	2.528	12.87
19.15	3.085	1.091				8.74	2.498	10.72
19.04	3.143	1.460				8.52	2.465	8.03
						8.30	2.434	5.35
10.93	2.749	0.000	43.61	1.944	0.982			
10.85	2.824	0.064	43.19	2.057	1.735	10.93	2.348	2.479
10.79	2.886	0.134	42.64	2.136	3.191	10.79	2.373	4.009
10.71	2.972	0.248	42.15	2.165	4.717	10.56	2.412	6.566
10.63	3.055	0.404	41.28	2.206	7.553	10.34	2.448	9.159
10.56	3.124	0.586	40.45	2.247	10.40	10.13	2.490	11.73
10.58	3.194	0.832	39.65	2.291	13.34	9.93	2.537	14.27
10.40	3.252	1.108	38.89	2.344	16.06			
10.31	3.311	1.467	38.15	2.421	18.85			
						149.8°		
			43.61	1.942	0.992	43.61	1.795	2.050
			43.37	2.008	1.391	43.12	1.810	2.201
5.577	2.722	0.335	43.19	2.059	1.754	42.38	1.832	2.460
5.534	2.788	1.176	42.66	2.134	3.121	40.73	1.867	3.201
5.476	2.826	2.717	41.75	2.184	5.994	38.59	1.901	4.381
5.352	2.880	6.336	40.88	2.224	8.917	36.47	1.930	5.736
5.242	2.927	9.768	40.05	2.268	11.83	34.58	1.957	7.085
5.134	2.982	13.23	39.24	2.318	14.74	33.24	1.981	8.108
5.025	3.058	16.85	38.99	2.345	15.66	31.40	2.006	9.733
4.923	3.172	20.29	38.14	2.288	12.47	43.61	1.795	2.046
						41.74	1.848	2.713
5.577	2.722	0.335	37.33	2.245	9.250	40.72	1.868	3.199
5.533	2.792	1.154	36.55	2.204	6.050	40.72	1.868	3.199
5.475	2.826	2.730	35.81	2.158	2.896	38.58	1.901	4.388
5.357	2.878	6.198	43.61	1.943	0.987	36.46	1.930	5.741
5.240	2.928	9.809	42.64	1.903	0.776	34.57	1.957	7.090
5.132	2.984	13.28	41.72	1.863	0.605	33.24	1.984	8.093
5.023	3.060	16.91	40.83	1.824	0.471	3.663	2.365	10.91
4.921	3.174	20.34	39.98	1.785	0.382	5.391	2.371	15.05
10.93	2.557	0.909	39.17	1.749	0.301	6.958	2.369	17.13
10.82	2.627	1.384	38.39	1.717	0.229	8.383	2.364	18.38

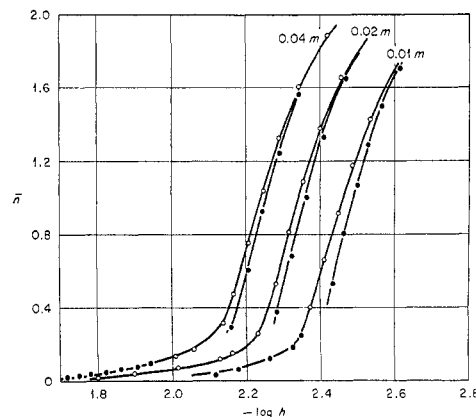


Figure 3.—Hydrolysis data for Al^{3+} in 1 m KCl at 124.8° at the indicated concentrations of aluminum. Open circles represent data taken in the direction of increasing pH or \bar{n} and closed circles represent data taken in the reverse direction. The lines were calculated on the basis of scheme II of Table IV. The spread of the curves in the two directions results from the decrease of the aluminum ion concentration during the experiment.

In the basic region of pH an experiment was conducted at 149.8° in which a solution containing unhydrolyzed aluminum ions was added incrementally to a solution containing 0.03 m KOH in 1 m KCl. The equilibrium was reached rapidly under these conditions.

TABLE III
 HYDROXYL NUMBER OF BASIC ALUMINUM SPECIES AT 149.8°

m_{Al}	(OH ⁻), m	\bar{n}	m_{Al}	(OH ⁻), m	\bar{n}
0.00324	0.01499	4.04 ± 0.06	0.00583	0.002362	4.02 ± 0.02
0.00413	0.01063	4.04 ± 0.04	0.00604	0.001392	4.01 ± 0.02
0.00499	0.006413	4.03 ± 0.03			

The data are summarized in Table III. After the last addition the pH drifted very slowly in the direction expected for the precipitation of α -AlO(OH), boehmite, which was identified by X-ray diffraction after cooling the solution.

Discussion

Kinetic Behavior.—The kinetics exhibited by aluminum hydrolysis during the titrations is illustrated in Figure 1. The curves represent the approach to equilibrium at various points in titrations of solutions containing ~ 0.04 m aluminum conducted at 124.8° (a) by adding acid to initially prehydrolyzed solutions and (b) by adding base to initially unhydrolyzed solutions. In the latter case, at \bar{n} values < 0.2 (curves 1 and 2), equilibrium was approached in a few minutes with the liberation of base. As \bar{n} was further increased, there was a sharp change in behavior; base was consumed during the approach to equilibrium and the rate was much slower. The rate passed through a minimum in the range $\bar{n} = 0.3$ –0.6. Similarly, when acid was added (a) at the higher \bar{n} values, it was consumed at a slow rate and with a minimum in rate in the range $\bar{n} = 0.3$ –0.6. At the lowest value of \bar{n} (curve 6), the rate again was rapid but, interestingly, with the equilibrium being approached from the same direction as when base was added at low \bar{n} values, *i.e.*, with the liberation of base.

We have not attempted a detailed analysis of these rate data because they involve simultaneous changes in the concentrations of several species, some of which very probably are unstable intermediates. The observed rate behavior is consistent, however, with the rapid formation of the initial, small hydrolysis products at low \bar{n} and the much slower formation of large polymers which predominate at the high \bar{n} values. The composition of these species will be discussed in the following sections.

Species in Acidic Media.—From previous work, notably that of Kubota,⁶ it seems clear that AlOH²⁺ is the initial hydrolysis product found at low aluminum concentrations (*e.g.*, 0.001 m). Aveston,¹³ however, found no evidence for this species at the aluminum concentrations (> 0.003 m) which he employed. Rather, he found it necessary to assume only one small polymer and one large polymer—Al₂(OH)₂⁴⁺ and Al₁₃(OH)₃₂⁷⁺ were his choices—to account for all his data.

In order to study more fully the region of existence of the smaller species we made measurements at 62.5° and low \bar{n} values. These data (Table II) were compared by least squares with various schemes of species Al _{x} (OH) _{y} ^{(3 x - y)+} to find the scheme or schemes which best fit these data. Our objective was to find the scheme with the minimum number of species which fits the data within experimental error. There is little justification for the introduction of additional species beyond this point. The agreement factors are given in Table IV for the following species, taken one at a time or two at a time: monomers with y values from 1 to 3, dimers with y values from 1 to 3, trimers with y values from 2 to 5, and tetramers with y values from 3 to 6.

 TABLE IV
 STANDARD DEVIATION OF CALCULATED FROM OBSERVED \bar{n} VALUES FOR TWO SPECIES^d

Species II (x, y) ^c	Species I (x, y) ^c															
	1,1	1,2	1,3	2,1	2,2	2,3	3,2	3,3	3,4	3,5	4,3	4,4	4,5	4,6	4,6	
1,1	35	35	35	29	<i>a</i>	24	20	9.0	10	25	18	12	8.9	16		
1,2		43	<i>a</i>	24	12	<i>a</i>	14	6.1	13	31	11	8.7	13	23		
1,3				25	11	<i>a</i>	14	7.3	14	<i>a</i>	13	12	16	24		
2,1				32	<i>a</i>	16	27	13	7.0	16	28	20	12	12		
2,2					11	11	11	7.7	5.7	9.7	10.0	8.0	5.1	6.5		
2,3						24	9.1	5.8	13	<i>b</i>	8.3	8.7	13	20		
3,2							27	12	7.9	11	<i>b</i>	23	16	12		
3,3								13	8.4	8.5	<i>b</i>	<i>b</i>	13	11		
3,4										13	10	12	13	<i>b</i>		
3,5											30	14	15	18	24	
4,3														18	16	
4,4													23	19	18	
4,5														19	<i>ab</i>	
4,6															24	

^a Contribution of species II was negligible. ^b Contribution of species I was negligible. ^c x is the number of aluminum ions and y the number of OH⁻ ions in the species. ^d Schemes for data in the region $\bar{n} < 0.16$ at 62.5°. Values listed are $\sigma(\bar{n}) \times 10^3$.

We have estimated the uncertainties of the measurements in this region to be equivalent to about 0.005 \bar{n} unit. In agreement with the conclusion of Aveston, the best fit obtained with a single species (those along the diagonal in Table IV) was for the 2,2 species which gave $\sigma(\bar{n}) = 0.011$. To reduce $\sigma(\bar{n})$ to our estimated error, however, it was obviously necessary to examine two-species schemes. The three pairs giving the best fits are as follows: (A) Al₂(OH)₂⁴⁺, Al₃(OH)₄⁵⁺, $\sigma(\bar{n}) = 0.0057$; (B) Al₂(OH)₂⁴⁺, Al₄(OH)₅⁷⁺, $\sigma(\bar{n}) = 0.0057$; (C) Al₂(OH)₃³⁺, Al₃(OH)₃⁶⁺, $\sigma(\bar{n}) = 0.0058$. The initial slope of plots of $\log \bar{n}$ vs. pH at each aluminum concentration studied was in every case greater than 2. It is not surprising therefore that the best pairs of species involve not less than two OH groups per species. The contribution of the 1,1 species is insufficient for a reliable estimate of its stability from these data.

Because of the slow kinetics observed for formation of the large polymers at considerably higher temperatures, we did not expect interference in these experiments at 62.5° in which equilibration times of 5–10 min were used. In any case, a complete analysis of the data, shown below, indicates that only at the highest \bar{n} value in the 0.01 m aluminum solution would there be a significant amount of the large polymer even if sufficient time were allowed for the formation of the species.

The three pairs of species above were further examined by combining each of them with a highly polymeric third species Al _{x} (OH) _{y} ^{(3 x - y)+} in a least-squares analysis of the data at 124.8° covering the entire \bar{n} range, the values of x and y being varied to obtain the best fits. Figure 4 shows the results obtained for pairs A and C plotted as $\sigma(\bar{n})$ vs. y/x . The scheme B did not give a better fit than could be obtained by omission of the Al₄(OH)₅⁷⁺ species, so that this scheme seems much less likely to be the correct one. In Figure 4 the best fit is obtained for the y/x ratio of 2.43, with the lowest minimum obtained in the agreement factor for the tetradecamer Al₁₄(OH)₃₄⁸⁺ combined either with pair A or C. However, only slightly poorer fits are obtained with the tridecamer Al₁₃(OH)₃₂⁷⁺ and the pentadecamers Al₁₅(OH)₃₆⁹⁺ or Al₁₅(OH)₃₇⁸⁺. The distinction among these four polymeric species places a severe strain on the data since the y/x ratio—an important factor in the slope, the spacing, and the limiting value of curves of the type shown in Figure 2—is nearly the same (2.43 ± 0.03) for each species.

TABLE V
 SUMMARY OF LOG Q VALUES FOR ALUMINUM HYDROLYSIS REACTIONS IN ACIDIC MEDIA IN 1 *m* KCl^a

Species	25°	62.5°	99.6°	124.8°	149.8°
Scheme I					
2,3	-11.46 ± 0.16	-9.37 ± 0.04	-7.80 ± 0.10	-6.34 ± 0.03	
3,3	-9.70 ± 0.08	-7.39 ± 0.02	-5.52 ± 0.04	-4.68 ± 0.03	
14,34	-110.55 ± 0.05	...	-67.94 ± 0.03	-55.77 ± 0.02	
$\sigma(\bar{n})^a$	0.044	0.0058	0.022	0.0130	
Scheme II					
2,2	-7.45 ± 0.17	-5.90 ± 0.04	-4.81 ± 0.15	-3.95 ± 0.07	
3,4	-13.36 ± 0.12	-10.74 ± 0.04	-8.20 ± 0.14	-7.01 ± 0.09	
14,34	-110.45 ^b ± 0.06	...	-67.89 ^b ± 0.06	-55.68 ± 0.03	
$\sigma(\bar{n})$	0.037	0.0057	0.028	0.0136	
Scheme III					
2,2	-7.00 ± 0.06	-5.65 ± 0.01	-4.44 ± 0.05	-3.71 ± 0.02	-2.99 ± 0.04
13,34	-110.35 ± 0.06	...	-67.84 ± 0.06	-55.60 ± 0.02	-46.12 ± 0.08
$\sigma(\bar{n})$	0.040	0.0108	0.0310	0.0156	0.032

^a Agreement factors. ^b Value fixed at mean value from schemes I and III.

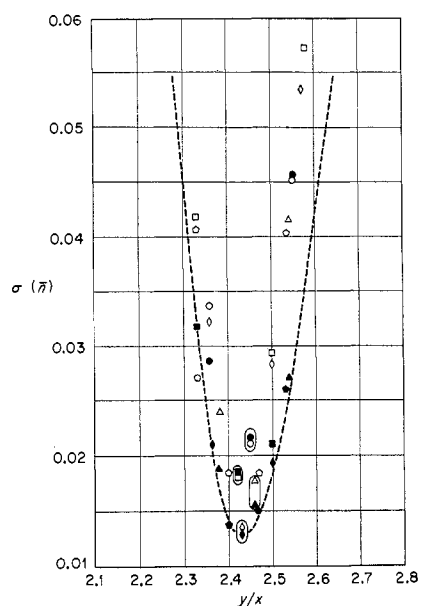


Figure 4.—Agreement factors $\sigma(\bar{n})$ for three-species schemes in the arrays: filled symbols, $\text{Al}_2(\text{OH})_3^{3+}$, $\text{Al}_3(\text{OH})_4^{5+}$, $\text{Al}_2(\text{OH})_y^{(2x-y)+}$; open symbols, $\text{Al}_2(\text{OH})_2^{4+}$, $\text{Al}_3(\text{OH})_4^{5+}$, $\text{Al}_x(\text{OH})_y^{(2x-y)+}$. Symbols: \circ , $x = 11$; \square , $x = 12$; \triangle , $x = 13$; \diamond , $x = 14$; \circ , $x = 15$.

This analysis of the data is in essential agreement with the results obtained by Aveston at 25°; however, our more extensive data in the lower \bar{n} region indicate the need for more than one small species. Of the two schemes A and C, we consider scheme A the more probable because of the absence of 2,3 species and the common occurrence of the 2,2 species among the well-established hydrolysis products of other cations. We cannot make such a judgment among the larger species because of the sparsity of cases where their composition is well established in other systems.

Aveston's ultracentrifuge results indicated that hydrolyzed aluminum solutions of high \bar{n} values ($\bar{n} \approx 2.4$) contained only one polymeric species. The indicated degree of polymerization was in the range 7–17, the exact value depending on the amount of counterion binding assumed. The very rapid rise in the \bar{n} vs. pH curves in the vicinity of $\bar{n} = 0.4$ (Figure 2) clearly means that the principal species being formed contains

a large number of OH^- ions and—since the $\text{OH}^-/\text{Al}^{3+}$ ratio is limited to values ~ 2.5 —a large number of Al^{3+} ions. The absence of one or more intermediate polymers in this range is indicative of the formation of an especially stable high polymer. Finally, the consistency of Aveston's and our \bar{n} vs. pH data above $\bar{n} \approx 0.2$ with a single species containing about 14 Al^{3+} ions adds strongly to the weight of evidence that indeed but one polymeric species is present in significant amounts in this range. Since the stability of a single polymeric species is quite probably conferred by a closed structure, it is tempting to speculate with Aveston and Johansson that this polymeric species is indeed the highly symmetrical ion $\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}^{7+}$ (a 13,32 species) suggested by Johansson to exist in basic aluminum salts precipitated from hydrolyzed solutions. However, if, as suggested above, the small species formed are $\text{Al}_2(\text{OH})_2^{4+}$ and $\text{Al}_3(\text{OH})_4^{5+}$ (scheme A), then quite clearly the polymeric species $\text{Al}_{14}(\text{OH})_{34}^{8+}$ is the most consistent with the present results.

Temperature Dependence of Stabilities.—The formation quotients of the species in the three schemes are given as a function of temperature in Table V. These include the best two-species scheme, III, and the two best three-species schemes, I and II. Because of the extensive hydrolysis at high acidities, the data at 149.8° do not extend to sufficiently low \bar{n} regions to give an estimate of the stabilities of the two small species so that results are given for only the scheme III at this temperature. The expected changes in hydrolysis behavior are observed with increasing temperatures; *i.e.*, the regions of hydrolysis and precipitation both shift to higher acidities.

The thermodynamic parameters in Table VIA were calculated from the $Q_{x,y}$ values for scheme II in Table V. For these calculations the assumption of a constant ΔC_p was found sufficient to describe the variation of each $Q_{x,y}$ with temperature. The data of Aveston,¹³ taken in 1 *M* NaClO_4 rather than 1 *m* KCl, were included; we do not expect any appreciable activity coefficient differences in these two media at 25°. The values of ΔH° and ΔS° for the reactions of Al^{3+} with OH^- ions, Table VIB and C, are derived from the values in Table VIA and from ΔH° and ΔS° for the dissociation of water in 1 *m* KCl (13.67 kcal/mol and -17.18 cal/deg).²¹ These results are expressed in

TABLE VI
 SUMMARY OF THERMODYNAMIC PARAMETERS CALCULATED FOR THE HYDROLYSIS REACTION IN SCHEME II AT 25°^a

Species	ΔH , kcal	ΔS , cal/deg	$\Delta H/\gamma$, kcal	$\Delta S/\gamma$, cal/deg	ΔC_p , cal/deg
A. Reaction: $x\text{Al}^{3+} + \gamma\text{H}_2\text{O} = \text{Al}_x(\text{OH})_\gamma^{(3x-\gamma)+} + \gamma\text{H}^+$					
Standard State: Hypothetical 1 <i>m</i> Solutions in 1 <i>m</i> KCl					
$\text{Al}_2(\text{OH})_2^{4+}$	18.3 ± 2.6	27 ± 8	9.2 ± 1.3	14 ± 4	12 ± 44
$\text{Al}_3(\text{OH})_4^{5+}$	30.9 ± 3.4	42 ± 11	7.7 ± 0.8	11 ± 3	90 ± 62
$\text{Al}_{14}(\text{OH})_{34}^{8+}$	262.8 ± 1.9	377 ± 6	7.73 ± 0.06	11.1 ± 0.2	733 ± 42
B. Reaction: $x\text{Al}^{3+} + \gamma\text{OH}^- = \text{Al}_x(\text{OH})_\gamma^{(3x-\gamma)+}$					
Standard State: Hypothetical 1 <i>m</i> Solutions in 1 <i>m</i> KCl					
$\text{Al}_2(\text{OH})_2^{4+}$	-9.0 ± 2.6	61 ± 8	-4.5 ± 1.3	31 ± 4	
$\text{Al}_3(\text{OH})_4^{5+}$	-23.4 ± 3.4	111 ± 11	-5.8 ± 0.8	28 ± 3	
$\text{Al}_{14}(\text{OH})_{34}^{8+}$	-201.6 ± 2.1	961 ± 7	-5.93 ± 0.06	28.3 ± 0.2	
C. Reaction: $x\text{Al}^{3+} + \gamma\text{OH}^- = \text{Al}_x(\text{OH})_\gamma^{(3x-\gamma)+}$					
Standard State: Hypothetical Mole Fraction Unity in 1 <i>m</i> KCl					
$\text{Al}_2(\text{OH})_2^{4+}$	-9.0 ± 2.6	85 ± 8	-4.5 ± 1.3	43 ± 4	
$\text{Al}_3(\text{OH})_4^{5+}$	-23.4 ± 3.4	159 ± 11	-5.8 ± 0.8	40 ± 3	
$\text{Al}_{14}(\text{OH})_{34}^{8+}$	-201.6 ± 2.1	1339 ± 7	-5.93 ± 0.06	39.4 ± 0.2	

^a Uncertainties include the covariance of ΔH , ΔS , and ΔC_p .

terms of mole fraction standard states as well as the molal standard states. Only in the former case (Table VIC) is the value of ΔS° independent of the change in the number of species in a reaction.

We see from Table V that, within the estimated uncertainties, the values of $\Delta H^\circ/\gamma$ and $\Delta S^\circ/\gamma$ each are constant for the three aluminum hydrolysis species of scheme II. Similar results have been observed previously²⁷ for a number of other sets of hydrolysis species, and this behavior may be generally true in cation hydrolysis. The $\Delta H^\circ/\gamma$ values for $\text{Al}_3(\text{OH})_4^{5+}$ and $\text{Al}_{14}(\text{OH})_{34}^{8+}$ in Table VIC are near the lower limit of the range of corresponding values for the other systems (-6.0 to -9.2). Th^{4+} ion—like Al^{3+} , a rare gas type ion—yields the most nearly similar values (-6.0, -6.2, and -6.0 kcal) for three polynuclear species. The $\Delta S^\circ/\gamma$ values for the aluminum species are near the

value (37 cal deg⁻¹) predicted by the equation $\Delta S^\circ/\gamma = 28 + 1.0Z^2$ proposed previously.²⁷

Species in Basic Solution.—The present results in basic solutions (Table III) are consistent with the observations of Brosset at 40°; *i.e.*, within the small uncertainties of the data they show the hydroxide-to-aluminum ratio to be equal to 4. This result, together with our observation of rapid kinetics and the reported solubility measurements,¹⁵⁻¹⁷ suggests a mononuclear species with -1 charge. The Raman spectra of Moolenaar, *et al.*,¹⁸ indicate that the species of this type formed at low temperatures is tetrahedral $\text{Al}(\text{OH})_4^-$.

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Vibrational Spectra and Solution Studies on Iodyl Compounds

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Infrared and Raman spectra of the iodyl compounds IO_2F , IO_2AsF_6 , and $\text{IO}_2\text{SO}_3\text{F}$ are reported together with vibrational spectra for IOF_3 and KIO_2F_2 . A polymeric structure with a bridging SO_3F group and discrete IO_2 groups are found for $\text{IO}_2\text{SO}_3\text{F}$. Solution studies of this compound in HSO_3F indicate incomplete ionization of the solute.

A number of inorganic compounds containing the IO_2 group have been reported over the years. They include iodyl fluoride,¹⁻⁴ IO_2F , and its interaction products with the Lewis acids AsF_5 and BF_3 ,⁵ commonly regarded as, *e.g.*, $\text{IO}_2\text{AsF}_6^{5,6}$ and not as $\text{AsF}_4^+\text{IO}_2\text{F}_2^{-7}$

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as assumed previously. The other known iodyl compounds can be regarded as salts of strong oxyacids and include the compounds $(\text{IO}_2)_2\text{S}_2\text{O}_7$,^{8,9} $\text{IO}_2\text{SO}_3\text{F}$,¹⁰ $\text{IO}_2\text{-CF}_3\text{CO}_2$,¹¹ $(\text{IO}_2)_2\text{SeO}_4$, and $(\text{IO}_2)_2\text{HSeO}_4$.¹²

All these compounds are white or pale yellow non-volatile compounds, previously thought to contain the

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