

This value is comparable to the rate constant for the Cr^{+2} -catalyzed conversion of trans-CrCl_2^+ to CrCl^{+2} which is of the order of $10^{10} 1.7 \times 10^2 \text{ M}^{-1} \text{ sec.}^{-1}$.

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Hydrolysis of the Aluminum Ion in Dilute Aqueous Solutions¹

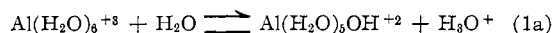
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Reported evidence for the existence of basic polymeric ions in hydrolyzed aluminum salt solutions prompted the present examination of the applicability of the monomeric hydrolysis mechanism, $\text{Al}^{+3} + \text{H}_2\text{O} \rightleftharpoons \text{AlOH}^{+2} + \text{H}^+$, to dilute aluminum salt solutions. Measurements were made of pH and conductance of AlCl_3 and $\text{Al}(\text{ClO}_4)_3$ solutions ranging in concentration from 10^{-5} to 10^{-2} M . The experimental data were found to be most consistent with the assumption that hydrolysis of Al^{+3} proceeds according to the simple monomeric hydrolysis mechanism. The thermodynamic pK value for the first stage hydrolysis was found to be 5.02 at 25°. The equivalent conductance of Al^{+3} at infinite dilution was calculated to be $59.7 \text{ ohm}^{-1} \text{ cm.}^2 \text{ equiv.}^{-1}$ at 25°. Upon dilution, aluminum salt solutions become supersaturated with respect to $\text{Al}(\text{OH})_3$ and remain metastable until the concentration of aluminum salt decreases to about 10^{-6} M , below which the degree of supersaturation reaches a critical level and $\text{Al}(\text{OH})_3$ begins to precipitate.

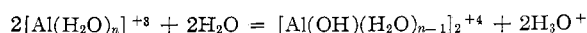
Introduction

Schofield and Taylor³ have determined, from pH measurements, a pK value of 4.98 at 25° for the first stage hydrolysis of the aluminum ion in 0.01 to 0.00001 M solutions of aluminum chloride and potassium aluminum sulfate, assuming the hydrolytic mechanism



They did not, however, attempt to follow changes in pH of the aluminum salt solutions with time. Other reported pK values for the above reaction are: 4.96 by Hartford,⁴ 5.10 by Ito and Yui,⁵ and 5.03 by Kubota.⁶ Notwithstanding these concordant values for the first stage hydrolysis constant, the general applicability of this simple hydrolytic mechanism has been questioned. From measurements of the pH of aluminum perchlorate solutions, Brosset⁷ postulated that the main products of hydrolysis of the aluminum ion were an infinite series of polynuclear complexes with the general formula $\text{Al}[(\text{OH})_6\text{Al}]_n^{+3}$. Subsequent recalculations of the data led Brosset, *et al.*,⁸ to the conclusion that the major product of hydrolysis could be either a single complex such as $\text{Al}_6(\text{OH})_{15}^{+3}$ or an infinite series of complexes with the formula $\text{Al}[(\text{OH})_6\text{Al}_2]_n^{+3+2n}$. Sillén,⁹ in a review of the methods used by Brosset, has suggested still another species, $\text{Al}_{13}(\text{OH})_{32}^{+7}$. Based on similar potentiometric studies, Kubota⁶ found evidence for the existence of dimers of the type $(\text{AlOH})_2^{+4}$, while

Tanabe¹⁰ suggested that the composition of basic AlCl_3 solutions is given by $\text{Al}_{2+n}(\text{OH})_{3n}\text{Cl}_6$. A concentration dependence was reported by Faucherre,¹¹ who found that dimers were formed only in aluminum salt solutions more concentrated than 0.01 M , whereas the monomeric hydrolysis mechanism was applicable to aluminum ion concentrations less than 0.005 M . From a study of the coagulation effect of aluminum salts on aqueous sols of silver halides, Matijević and Tezak¹² concluded that freshly prepared solutions, or those with added acid, contained only trivalent aluminum ions, whereas aging or heating the solutions promoted the formation of dimers



More recently, Ruff and Tyree¹³ have applied the light-scattering method to the determination of the weight number average of aluminum atoms per aggregate in basic aluminum salt solutions and found that the average size of the aggregates increased with the increasing basicity of aluminum ions in solution. The method, however, was not sufficiently sensitive to establish whether or not these aggregates were stable upon dilution.

An attempt has been made in the present investigation to examine critically the hydrolysis of the aluminum ion in dilute aqueous solutions, and to determine which of the several proposed hydrolysis mechanisms is most consistent with the experimental data.

Experimental

Preparation and Purification of Aluminum Salts.—Aluminum chloride was purified by double evaporative recrystallization of

(1) Taken from a Ph.D. thesis submitted by C. R. Frink to the Graduate School of Cornell University, September, 1960. This work was carried out in cooperation with the Tennessee Valley Authority, Wilson Dam, Ala.

(2) Shell Development Co. Fellow, 1959–1960.

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

(4) W. H. Hartford, *Ind. Eng. Chem.*, **34**, 920 (1942).

(5) T. Ito and N. Yui, *Chem. Abstr.*, **48**, 5613c (1954).

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

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

(8) C. Brosset, G. Biedermann, and L. G. Sillén, *ibid.*, **8**, 1917 (1954).

(9) L. G. Sillén, *Quart. Rev. (London)*, **13**, 146 (1959).

(10) H. Tanabe, *Chem. Abstr.*, **49**, 11482e (1955).

(11) J. Faucherre, *Bull. soc. chim. France*, **21**, 253 (1954).

(12) E. Matijević and B. Tezak, *J. Phys. Chem.*, **57**, 951 (1953).

(13) J. K. Ruff and S. Y. Tyree, *J. Am. Chem. Soc.*, **80**, 1523 (1958).

$\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ in 0.1 *N* HCl solution. After preparing a 0.1 *M* stock solution, the concentration of Al was determined by precipitation with 8-hydroxyquinoline, and the concentration of Cl^- was determined by precipitation as AgCl .¹⁴

Aluminum perchlorate was prepared by prolonged heating of $\text{Al}(\text{NO}_3)_3$ in the presence of an excess of HClO_4 and purified by recrystallization first from the reaction mixture and then again from 0.1 *N* HClO_4 . An approximately 0.1 *M* stock solution was prepared and the concentration of aluminum was determined by precipitation with 8-hydroxyquinoline. The perchlorate concentration was determined¹⁵ by reduction of perchlorate to chloride; the absence of chlorate and chloride was verified by modifications of the same method. The absence of nitrate was confirmed by the brucine method.¹⁶

The free acid content¹⁷ of both stock solutions was determined by a potentiometric method described by Brosset.⁷ This method was found to be more satisfactory than the titration methods which have been proposed.¹⁸ All other chemicals used were of reagent grade, and all solutions were prepared using water redistilled in Pyrex.

Measurement of pH.—The pH was measured independently with two different glass electrodes using a Leeds and Northrup thermionic amplifier and a potentiometer which was accurate to ± 0.01 pH unit. The sample container was mounted in a water bath which was maintained at $25 \pm 0.1^\circ$. The reference electrode, which consisted of a saturated calomel electrode, was provided with a small vessel having a side arm which permitted the test solution to be drawn into the vessel and around the ground glass joint at the base of the electrode. This arrangement prevented contamination of the test solution with KCl in forming the liquid junction. Silver-silver chloride electrodes were prepared as described by Brown.¹⁹ Potassium acid phthalate (pH 4.01) was used as a primary buffer standard, with 0.1 *N* HCl (pH 1.10) and a phosphate buffer (pH 6.86) as secondary standards.²⁰

Measurement of Conductance.—A conductivity apparatus similar to that described by Jones, *et al.*,²¹ which utilizes a cathode-ray oscillograph as a detector, was used. The conductance measurements were made using a fill-type conductivity cell which was mounted in the water bath. The cell constant was determined with standard KCl solutions and was not found to be dependent on the resistance of the solution or the frequency of the oscillator. The Pyrex redistilled water, used in preparation of the aluminum salt solutions, had a specific conductance of approximately 1×10^{-6} ohm⁻¹ cm.⁻¹, which was ignored in calculations of the conductance of the acid aluminum salt solutions.

Calculation of Ion Activities.—While some investigators^{7,11} have chosen to ignore activity corrections in solutions of constant ionic strength, the data obtained in the present study²² indicate that calculation of the ionic activities in solutions of varying ionic strength leads to more concordant values for the hydrolysis constant. Ionic activity coefficients were calculated using the extended Debye-Hückel equation, with values for the parameter a_i , "the distance of closest approach," taken from Kielland.²³

Procedure.—Stock solutions of purified aluminum chloride and aluminum perchlorate were diluted to give aluminum concentra-

tions ranging from 0.00001 to 0.01 *M*. After measuring the initial pH and conductance, the solutions were stored in Pyrex glass stoppered bottles at 25° for varying periods of time after which the conductance and the pH values of the solutions again were measured. Preliminary experiments were conducted to determine the rate at which equilibrium was established and to evaluate the magnitude of the liquid junction potential in pH measurements.

Hydrolysis of Aluminum Chloride Solutions

Attainment of Equilibrium.—The pH of a series of AlCl_3 solutions was measured immediately after preparation and again after ten varying intervals of time during an 8-month period. The first, last, and average values, with their standard deviations, are shown in Table I. The more concentrated solutions reached equilib-

TABLE I
THE pH OF AlCl_3 SOLUTIONS AT 25° MEASURED IMMEDIATELY AND AFTER STORAGE FOR 8 MONTHS

| -log [Al] ^a | pH after indicated time | | | |
|------------------------|-------------------------|-------|------------------|-----------|
| | 0 | 8 mo. | Av. ^b | Std. dev. |
| 2.00 | 3.73 | 3.73 | 3.72 | 0.02 |
| 2.30 | 3.88 | 3.85 | 3.84 | .02 |
| 3.00 | 4.14 | 4.14 | 4.13 | .01 |
| 3.30 | 4.29 | 4.04 | 4.12 | .07 |
| 4.00 | 4.62 | 4.59 | 4.60 | .02 |
| 4.30 | 4.79 | 4.76 | 4.75 | .03 |
| 5.00 | 5.18 | 5.06 | 5.07 | .05 |

^a Brackets indicate total concentration of the aluminum salt.

^b Average pH value of eleven determinations made at different times during the 8-month storage period.

rium immediately as may be seen from the small standard deviation of a pH measurement which was about 0.02 pH unit. Solutions more dilute than 0.0005 *M* tended to become more acid on standing, and the uncertainty of the pH measurement increased correspondingly. The measurements shown for zero time actually were performed 2 to 3 min. after preparation of the solutions, but the changes were gradual so that extrapolation of some of the data to zero time gave virtually identical values. A similar series of solutions was carried through several cycles of heating to 40° and cooling to 25° , with pH measurements made at 25° during each cycle. The data²² indicated that heating the solutions to 40° slightly accelerated the decrease in pH of the dilute solutions but had no effect on those more concentrated than 0.0005 *M*. Several AlCl_3 solutions also were prepared using CO_2 -free water redistilled in Pyrex, but the pH values were identical with those obtained for solutions prepared with water fresh from the still.

Potentiometric Measurements without Liquid Junction.—The pH of separate portions of a series of AlCl_3 solutions was measured with the glass electrode using both the calomel electrode and the silver-silver chloride electrode as a reference. The e.m.f. values observed with the silver-silver chloride reference electrode were

(23) J. Kielland, *J. Am. Chem. Soc.*, **59**, 1675 (1937). The actual values for parameter a used were: H^+ , 9; Al^{3+} , 9; AlOH^{2+} , 9; Cl^- , 3; Ag^+ , 2.5. The Debye-Hückel limiting law was used in estimating the activity coefficients for the polymeric ions for which no published values of parameter a are available.

(14) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," 3rd Ed., The Macmillan Co., New York, N. Y., 1952, pp. 307, 320. The molar Cl to Al ratio found was 3.002.

(15) G. P. Haight, Jr., *Anal. Chem.*, **25**, 642 (1953). The molar ClO_4 to Al ratio found was 2.987.

(16) M. Peech and L. English, *Soil Sci.*, **57**, 167 (1944).

(17) The concentration of free acid in the stock 0.1037 *M* $\text{Al}(\text{ClO}_4)_3$ solution was found to be 4.76×10^{-3} *M*; the AlCl_3 solution was free of either acid or base.

(18) For the use of oxalate as a complexing agent in the titration, see W. J. Blaedel and J. J. Panos, *Anal. Chem.*, **22**, 910 (1950). The use of fluoride is described by R. P. Graham, *Ind. Eng. Chem., Anal. Ed.*, **18**, 472 (1946).

(19) A. S. Brown, *J. Am. Chem. Soc.*, **56**, 646 (1934).

(20) R. G. Bates, "Electrometric pH Determinations," John Wiley, Inc., New York, N. Y., 1954, p. 118.

(21) G. Jones, K. J. Mysels, and W. Juda, *J. Am. Chem. Soc.*, **62**, 2919 (1940).

(22) C. R. Frink, Ph.D. Thesis, "Reactions of the Aluminum Ion in Aqueous Solutions and Clay Suspensions," Cornell University, 1960.

converted to pH values by first obtaining the standard potential of the glass electrode in a potassium acid phthalate buffer, 0.001 *N* in KCl.²⁴ The e.m.f. values observed in the AlCl₃ solutions then were corrected for the potential of the silver-silver chloride electrode calculated from the chloride ion activity using the activity coefficients obtained by the extended Debye-Hückel equation. Appropriate corrections were applied for the solubility of AgCl in solutions containing less than 0.0001 *M* Cl⁻. The close agreement shown in Table II between the pH measurements using cells with and without transference would support the conclusion that the liquid junction potential may be safely ignored and that no aluminum-chloride complexes were present in these solutions, as it would be highly fortuitous if the error due to the liquid junction potential were to compensate exactly for the altered chloride ion activity as a result of complex formation.

TABLE II
THE pH OF AlCl₃ SOLUTIONS AS MEASURED USING CELLS WITH AND WITHOUT TRANSFERENCE

| -log [Al] | e.m.f., ^a v. | pH ^a | pH ^b |
|-----------|-------------------------|-----------------|-----------------|
| 2.00 | 0.162 | 3.72 | 3.75 |
| 2.30 | .138 | 3.85 | 3.81 |
| 2.60 | .114 | 3.97 | 3.96 |
| 3.00 | .082 | 4.15 | 4.16 |
| 3.30 | .058 | 4.27 | 4.26 |
| 4.00 | .000 | 4.57 | 4.61 |
| 4.30 | -.026 | 4.71 | 4.76 |
| 5.00 | -.081 | 5.03 | 5.06 |

^a For the cell: glass|solution x, AgCl|Ag. ^b For the cell: glass|solution x||KCl, sat., Hg₂Cl₂|Hg.

Comparison of Mechanisms of Hydrolysis.—The criterion used in the evaluation of three hydrolysis mechanisms that have been proposed^{3,8,11} was the constancy of the thermodynamic hydrolysis constant obtained under conditions of varying aluminum concentration and ionic strength. In calculating the thermodynamic hydrolysis constant, K_m , for the monomeric hydrolysis mechanism³ given by eq. 1a, the pH was first converted to the H⁺ ion concentration by dividing the H⁺ ion activity by the appropriate activity coefficient. The concentration of AlOH⁺² and Al⁺³ was assumed to be given by

$$[\text{AlOH}^{+2}] = [\text{H}^+]$$

$$[\text{Al}^{+3}] = [\text{Al}^{+3}]_{\text{total}} - [\text{AlOH}^{+2}]$$

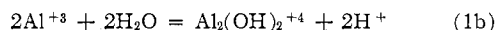
where brackets denote concentrations in moles/l. The activities of Al⁺³ and AlOH⁺² then were calculated by multiplying the concentrations of these ions by their respective activity coefficients.²⁵ The negative logarithm of the thermodynamic hydrolysis constant, pK_m , then was expressed in terms of the negative logarithms of the individual ionic activities as

$$pK_m = \text{pH} + \text{pAlOH} - \text{pAl}$$

The negative logarithm of the concentration hydrolysis constant, pK_m' , also was calculated in order to show the effect of neglecting the ionic activity coefficients on the hydrolysis constant.

The thermodynamic hydrolysis constants K_d and K_p , corresponding to the dimeric¹¹ and polymeric⁸ hydrolysis mechanism, respectively, also were calculated from the data in a similar manner.

For the dimeric mechanism



$$pK_d = 2\text{pH} + \text{pAl}_2(\text{OH})_2 - 2\text{pAl}$$

and for the polymeric mechanism



$$pK_p = 15\text{pH} + \text{pAl}_6(\text{OH})_{15} - 6\text{pAl}$$

Measurements of pH were made on four replications of a series of freshly prepared AlCl₃ solutions. The calculated hydrolysis constants, corresponding to the three proposed mechanisms, are shown in Table III. The data shown in the last two columns of Table III will be

TABLE III
COMPARISON OF THERMODYNAMIC EQUILIBRIUM CONSTANTS CALCULATED FOR THE THREE PROPOSED HYDROLYSIS MECHANISMS

| -log [Al] | pH | $pK_m'^a$ | pK_m^b | pK_d^c | pK_p^d | pK_{ip}^e obsd. | pK_{ip}^f calcd. |
|--------------------|------|-----------|----------|----------|----------|-------------------|--------------------|
| 2.00 | 3.70 | 5.25 | 4.96 | 7.16 | 45.29 | 33.57 | 33.48 |
| 2.30 | 3.84 | 5.24 | 5.01 | 7.02 | 46.25 | 33.33 | 33.30 |
| 2.60 | 3.95 | 5.20 | 5.02 | 6.78 | 46.77 | 33.18 | 33.16 |
| 3.00 | 4.13 | 5.16 | 5.03 | 6.52 | 47.76 | 32.94 | 32.93 |
| 3.30 | 4.29 | 5.19 | 5.09 | 6.40 | 48.79 | 32.70 | 32.79 |
| 4.00 | 4.61 | 5.07 | 5.02 | 5.84 | 50.14 | 32.40 | 32.40 |
| 4.30 | 4.76 | 5.01 | 4.98 | 5.60 | 50.88 | 32.28 | 32.22 |
| 5.00 | 5.13 | 4.67 | 4.65 | 4.50 | 52.21 | 32.22 | 31.77 |
| Mean | | | 5.02 | 6.23 | 48.51 | ... | ... |
| Standard deviation | | | 0.04 | 0.88 | 2.42 | ... | ... |

^a The negative logarithm of the concentration hydrolysis constant for the reaction shown in eq. 1a. ^b The negative logarithm of the thermodynamic hydrolysis constant for the reaction shown in eq. 1a. ^c The negative logarithm of the thermodynamic hydrolysis constant for the reaction shown in eq. 1b. ^d The negative logarithm of the thermodynamic hydrolysis constant for the reaction shown in eq. 1c. ^e The negative logarithm of the ion activity product of Al(OH)₃ calculated from the experimental data under the assumption that hydrolysis of Al⁺³ proceeds according to the monomeric mechanism shown in eq. 1a. ^f The negative logarithm of the ion activity product of Al(OH)₃ calculated by eq. 3.

referred to later in the Discussion section. Because the data for the monomeric mechanism indicated little or no influence of ionic strength, the pK_m values were averaged to obtain a mean value of 5.02 with a standard deviation of 0.04. The pK_m value for the 0.00001 *M* solution was omitted in calculating this average inasmuch as the deviations of the observed pH values of this solution were found to lie well outside the range of experimental error. The question of whether or not the variability encountered in the seven remaining pK_m observations (Table III) may be attributed to experimental error can be tested as follows: Because

$$K_m' = \frac{[\text{H}^+]^2}{[\text{Al}]_{\text{total}} - [\text{H}^+]}$$

(24) W. J. Hamer and S. F. Acree, *J. Res. Natl. Bur. Std.*, **32**, 215 (1944).

(25) In most of the calculations presented, the ionic strength was taken as six times the molarity of the aluminum salt plus that due to any added electrolyte. While the actual ionic strength may be computed by successive approximations to include the hydrolysis products, calculations showed this to be an unnecessary refinement.

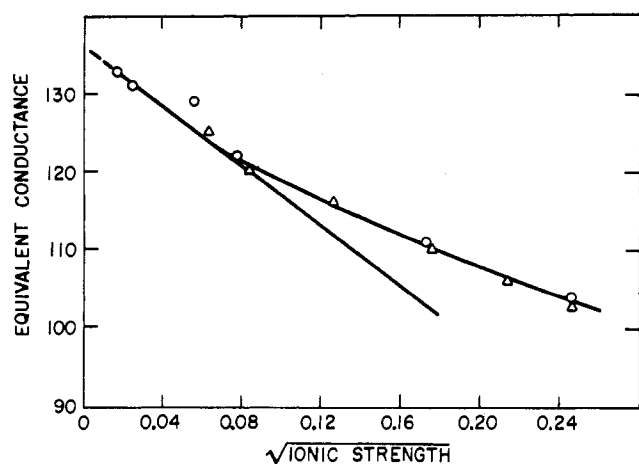
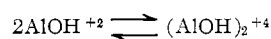


Fig. 1.—The equivalent conductance of AlCl_3 at 25° as a function of concentration: O, in the absence of free acid; Δ , in the presence of 0.001 N HCl . The linear relationship shown in the graph is a plot of eq. 2a.

and $[\text{H}^+]$ is small compared to $[\text{Al}]_{\text{total}}$ over most of the concentration range, the variance of $\text{p}K_m$ should be about two times the variance of pH ; the variance of a pH measurement is $(0.02)^2$, as can be seen in lines 1, 2, and 3 of Table I. Clearly, the variance $(0.04)^2$ of the $\text{p}K_m$ observation is not significantly greater than the variance of $2(0.02)^2$ inherent in its observation. On the other hand, although the error in the pH measurement enters manifold into the estimates of $\text{p}K_p$ and $\text{p}K_a$, the observed variance of these two parameters is many times as great as the error inherent in their observation.

Although the experimental data were found to be most consistent with the monomeric hydrolysis mechanism, the possibility that an appreciable amount of the dimer was formed at the higher concentrations also was tested. When the concentration of the dimer formed according to the reaction



was calculated using values for the dimeric hydrolysis constant reported in the literature (6, 11) it was found that the calculated value for the monomeric hydrolysis constant was no longer constant. This may be construed to indicate that no significant amount of the dimer was present in these dilute solutions.

Conductance Measurements.—Interpretation of the conductance of aluminum salt solutions is difficult, inasmuch as a solution of a metal ion and its hydrolysis products is essentially a mixed electrolyte. Owen and Gurry²⁶ determined the conductance of zinc and copper sulfates by applying corrections for the hydrolysis products, but this presupposes a knowledge of the hydrolysis mechanism. The alternative chosen in the present study was to determine the equivalent conductance of AlCl_3 in solutions containing sufficient added HCl to suppress the hydrolysis of the aluminum ion. These values for the equivalent conductance of AlCl_3 then were compared with those obtained after applying the appropriate corrections to the observed conductance

of hydrolyzed solutions. Measurements were made of the conductance of AlCl_3 solutions ranging in concentration from 0.00001 to 0.01 M and containing 0.001 M of added HCl (an amount adequate to prevent more than 1% hydrolysis in this concentration range). Measurements also were made of the pH and the conductance of a similar series without added HCl .

The equivalent conductance to be assigned to HCl in the presence of AlCl_3 is somewhat uncertain, but it was approximated from the equivalent conductance of HCl in pure solutions²⁷ at the ionic strength of the AlCl_3 - HCl mixture in question. The conductance of the solutions without added HCl was corrected first by subtracting the conductance due to the HCl produced by hydrolysis and then by apportioning the remaining conductance to AlCl_3 and AlOHCl_2 , assuming both species to have the same equivalent conductance.²⁸ The data shown in Fig. 1 were extrapolated to zero ionic strength by means of the Onsager equation, which, upon substitution of the limiting value for the transference number of the chloride ion in solutions of LaCl_3 ²⁹ and the appropriate values for the numerical constants at 25° , has the form

$$\Lambda = \Lambda_0 - (0.751\Lambda_0 + 169.1)\sqrt{C} \quad (2)$$

If the concentration C in equiv./l. is replaced by the ionic strength, μ , in moles/l., and the extrapolated value of 136 for the equivalent conductance of AlCl_3 at infinite dilution, Λ_0 , is substituted in eq. 2, the equation

$$\Lambda = 136 - 191\sqrt{\mu} \quad (2a)$$

is obtained. This limiting equation for the conductance of AlCl_3 , which also has been plotted in Fig. 1, fits the experimental data well up to an ionic strength of about 0.01. Although some question may be raised regarding the application of the Onsager equation to mixed electrolytes and the proper choice of the concentration function, the agreement between the two independent methods for determining the equivalent conductance of AlCl_3 , as shown in Fig. 1, is considered to be supporting evidence for the correctness of the assumed monomeric hydrolytic mechanism. If the limiting equivalent conductance of Cl^- is taken as 76.3, then the limiting equivalent conductance of Al^{+3} is found to be $59.7\text{ ohm}^{-1}\text{ cm}^2\text{ equiv.}^{-1}$ at 25° .

Hydrolysis of Aluminum Perchlorate Solutions

Measurements of pH were made on a series of $\text{Al}(\text{ClO}_4)_3$ solutions, and the monomeric hydrolysis constant was calculated after applying corrections for the free acid present.¹⁷ The pH of another series of $\text{Al}(\text{ClO}_4)_3$ solutions containing sufficient added Na_2CO_3 to exactly neutralize the free acid present also was

(27) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 537.

(28) Obviously these corrections do not require a knowledge of the hydrolysis constant, but only of the mechanism, since the only assumptions necessary are that $[\text{AlOH}^{+2}] = [\text{H}^+]$ and that Al^{+3} and AlOH^{+2} have the same equivalent conductance.

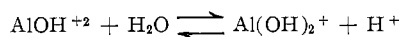
(29) D. A. MacInnes, "The Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, p. 330.

measured. The results were similar to those found with the AlCl_3 solutions. The average thermodynamic pK value found for the solutions containing free acid was 4.97 (standard deviation 0.04), whereas a value of 4.94 (standard deviation 0.05) was found for the solutions in which the free acid was neutralized. Owing to the rather critical dependence of the calculated values on the free acid concentration, the pK value determined in AlCl_3 solutions is considered to be more reliable.

In an attempt to obtain some estimate of the second stage hydrolysis constant, further examination was made of $\text{Al}(\text{ClO}_4)_3$ solutions to which small amounts of Na_2CO_3 had been added. Even at low basicities, corresponding to $[\text{OH}^-]/[\text{Al}^{+3}]$ ratios as low as 0.2, the pH of the solutions continued to decrease slowly with time with concomitant precipitation of aluminum hydroxide, as was verified by analyzing the solutions following high speed centrifugation. Thus it was impossible to extend these studies to include more basic solutions.

Discussion

While the monomeric hydrolysis mechanism appears to be more consistent with the experimental data, it is evident from Table III that there is a tendency for the numerical value of pK_m to decrease on dilution. The calculated pK_m value is quite sensitive to small changes in pH at these low aluminum concentrations, leading to a low value for pK_m if the observed pH is too low. An attempt was made to attribute these low values to second stage hydrolysis



By successive approximations, it was found that a value for pK_2 of 6.0 for the second stage hydrolysis constant would bring the value for pK_m to about 5.0 for the more dilute solutions. This value for pK_2 , however, would appear to be somewhat low in view of the more common ratios of 1:100 that usually are observed between the first and second stage hydrolysis constants.³⁰

A more plausible explanation of the cause for the decrease in the value of pK_m in the two most dilute solutions was suggested by an observation, which has not been reported previously, that, on dilution, an aluminum salt solution becomes supersaturated with respect to gibbsite, the thermodynamically stable phase of $\text{Al}(\text{OH})_3$. The solubility product of pure, crystalline gibbsite has been determined by Frink and Peech,³¹ who reported a value of 33.5 for pK_{sp} of $\text{Al}(\text{OH})_3$ at zero ionic strength and at 25°. The "observed" values for the negative logarithm of the ion activity product of $\text{Al}(\text{OH})_3$, pK_{ip} , listed in the seventh column of Table III, were calculated from the experimental data under the assumption that hydrolysis of Al^{+3} proceeds according to the monomeric mechanism shown in eq. 1a. It is obvious that the degree of supersaturation of the AlCl_3 solutions with respect to $\text{Al}(\text{OH})_3$ increased markedly with dilution. The very slow decrease of pH with time

would indicate that these solutions were metastable with respect to precipitation of $\text{Al}(\text{OH})_3$.

It is possible to calculate fairly accurately the effect of dilution on the ion product of $\text{Al}(\text{OH})_3$. Neglecting H^+ ions produced by second and third stage hydrolysis as well as those present in the water used in diluting the aluminum salt solution, the concentration of ionic species resulting from the first stage hydrolysis is given by

$$[\text{AlOH}^{+2}] = [\text{H}^+] = x[\text{Al}]_t$$

where x is the degree of hydrolysis and the subscript t denotes the total concentration of aluminum in solution. The thermodynamic hydrolysis constant may be written as

$$\frac{x^2[\text{Al}]_t \gamma_{\text{H}^+} \gamma_{\text{AlOH}^{+2}}}{(1-x)\gamma_{\text{Al}^{+3}}} = K_m$$

If V is the volume of dilution, in l./mole, then $[\text{Al}]_t = 1/V$. The activities of OH^- and Al^{+3} may be expressed as

$$(\text{OH}^-) = \frac{K_w \sqrt{V}}{\sqrt{K_m(1-x)\gamma_{\text{Al}^{+3}}\gamma_{\text{H}^+}}}$$

and

$$(\text{Al}^{+3}) = \frac{(1-x)\gamma_{\text{Al}^{+3}}}{V}$$

Upon substituting the numerical value for the ion product of water and taking $K_m = 9.55 \times 10^{-6}$, the ion activity product of $\text{Al}(\text{OH})_3$ becomes

$$K_{ip} = (\text{Al}^{+3})(\text{OH}^-)^3 = \frac{3.39 \times 10^{-35} \sqrt{V} \gamma_{\text{AlOH}^{+2}}^{3/2}}{\sqrt{(1-x)\gamma_{\text{H}^+}^{3/2} \gamma_{\text{Al}^{+3}}^{3/2}}} \quad (3)$$

Since the degree of hydrolysis, x , increases with dilution, it is obvious from eq. 3 that the ion activity product of $\text{Al}(\text{OH})_3$ should increase with dilution. Upon very high dilution, the ion activity product of $\text{Al}(\text{OH})_3$ should, of course, begin to decrease rather than continue to increase indefinitely, as predicted by eq. 3, owing to neglect of the H^+ from dissociation of water in the derivation of eq. 3. It can be seen from the data given in Table III that the predicted values for pK_{ip} (calculated by eq. 3) are in good agreement with the observed values except for the most dilute solution for which the predicted value is lower than the observed value. The higher observed value for pK_{ip} , as compared with that predicted by eq. 3, for the most dilute solution must be attributed to precipitation of $\text{Al}(\text{OH})_3$. Indeed, it has been shown elsewhere³¹ that while it is necessary to seed such supersaturated solutions with gibbsite in order to hasten the establishment of the solubility product of gibbsite, unseeded dilute solutions will suffer some loss of aluminum after a period of 3 months, presumably due to precipitation of $\text{Al}(\text{OH})_3$. Thus, the slow decrease of pH with time (Table I) and the low value for pK_m (Table III) found for the $10^{-5} M$ AlCl_3 solution may be attributed to precipitation of $\text{Al}(\text{OH})_3$ in this solution in which the degree of supersaturation with respect to $\text{Al}(\text{OH})_3$ had reached a critical level. It is interesting

(30) A. B. Lamb and A. G. Jacques, *J. Am. Chem. Soc.*, **60**, 967, 1215 (1938).

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

to note here that the solubility of this freshly precipitated $\text{Al}(\text{OH})_3$ is much higher than that of gibbsite.

Assuming the hydrolysis of the Al^{+3} to proceed according to the three-stage hydrolysis mechanism, there must be in solution an extremely low equilibrium concentration of molecular $\text{Al}(\text{OH})_3$ as given by

$$[\text{Al}(\text{OH})_3] = \frac{K_1 K_2 K_3 [\text{Al}]_t}{[\text{H}^+]^3}$$

in which $[\text{Al}]_t$ is the total concentration of AlCl_3 in solution, and K_1 , K_2 , and K_3 are the three-stage hydrolysis constants. It can be shown that, like the ion activity product, $(\text{Al}^{+3})(\text{OH}^-)^3$, the concentration of molecular $\text{Al}(\text{OH})_3$ also should increase with dilution, pass through a maximum value, and then should decrease upon further dilution of the AlCl_3 solution. As the total concentration of AlCl_3 is decreased to about $10^{-5} M$, the degree of supersaturation of the solution with respect to molecular $\text{Al}(\text{OH})_3$ reaches a critical value and $\text{Al}(\text{OH})_3$ begins to precipitate. This precipitation of $\text{Al}(\text{OH})_3$ will cause further hydrolysis of AlCl_3 as the equilibrium concentrations of the hydrolysis products will tend to be restored. Consequently, the observed pH values will be lower than those predicted by the first stage hydrolysis reaction, which, in turn, will lead to a

slightly higher value for the monomeric first stage hydrolysis constant, K_m , calculated with the assumptions that $[\text{H}^+] = [\text{AlOH}^{+2}]$ and that all the aluminum has remained in solution. This increase in the apparent value of K_m , upon dilution or addition of base to an aluminum salt solution, has been interpreted¹¹ as failure of the classical monomeric hydrolysis mechanism to describe the hydrolysis reaction, whereas it actually is due to precipitation of $\text{Al}(\text{OH})_3$ when the degree of supersaturation of the diluted aluminum salt solution has reached a critical level. Thus, the behavior of an aluminum salt solution resembles to some extent that of a ferric chloride solution³⁰ which also becomes supersaturated with respect to $\text{Fe}(\text{OH})_3$ upon dilution but from which $\text{Fe}(\text{OH})_3$ begins to precipitate immediately. On the other hand, an aluminum salt solution tends to remain metastable, upon dilution, over a wide range of supersaturation with respect to $\text{Al}(\text{OH})_3$. Although the presence of a variety of polymeric basic ions in partially neutralized solutions has been postulated, such solutions are obviously not at equilibrium and it seems quite likely that any polymeric complexes that may be present in such solutions represent transient stages in the aggregation of molecular $\text{Al}(\text{OH})_3$ and its ultimate precipitation.

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The Kinetics of Ammonia Exchange between Nickel Ammine Complexes and Ammonia in Aqueous and Anhydrous Ammonia Solutions Measured by Nuclear Magnetic Resonance of N^{14}

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Rate data are reported on the exchange of NH_3 with $\text{Ni}(\text{NH}_3)_6^{++}$ in aqueous and anhydrous ammonia solutions. The aqueous exchange is represented by the rate law, $R = 6k_1[\text{Ni}(\text{NH}_3)_6^{++}]$, where k_1 is $5.6 \pm 0.5 \times 10^4 \text{ sec}^{-1}$ at 25° and the activation parameters are $\Delta H^* = 9.5 \pm 1.1 \text{ kcal./mole}$ and $\Delta S^* = -5 \pm 4 \text{ e.u.}$ Addition of NH_4^+ and some other ions had no effect on the rate. The limited data in anhydrous ammonia can be represented by the same rate law and the rate parameters are essentially the same; k_1 at 25° is $4.7 \pm 0.5 \times 10^4 \text{ sec}^{-1}$, $\Delta H^* = 10 \pm 1 \text{ kcal./mole}$ and $\Delta S^* = -3 \pm 4 \text{ e.u.}$ Possible mechanisms are discussed and comparisons with related reactions are given. No chemical shift in the N^{14} resonance in NH_3 was produced by Ni^{++} .

Introduction

Preliminary results have been reported for NH_3 exchange with nickel ammine complexes employing both tracer³ and n.m.r.⁴ line broadening techniques. This report represents an extension and improvement of the n.m.r. data to yield more detailed results on the kinetics of the fast exchange reactions. Very little work has been done on the kinetics of complex ion reactions in liquid ammonia (especially little at room temperature). Studies of the present sort may serve to aid in obtaining

a start on a more detailed understanding of kinetic behavior in anhydrous ammonia. The exchange results reported here also should be useful in correlating the kinetic behavior of metal complexes with properties of the metal ion and ligands as well as with the nature of the solvent used. In addition, it is of considerable importance to compare results of different methods for studying fast reactions in order to establish their reliability.

Experimental

The n.m.r. spectra were obtained using a spectrometer which employed a standard marginal oscillator and a phase-sensitive detector. The N^{14} resonances in the uncomplexed NH_3 were ob-

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- (3) J. R. Sutter and J. P. Hunt, *J. Am. Chem. Soc.*, **82**, 6420 (1960).
- (4) J. P. Hunt and H. W. Dodgen, *J. Chem. Phys.*, **35**, 2261 (1961).