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GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1827-A

U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

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By J. D. HEM *and* C. E. ROBERSON

CHEMISTRY OF ALUMINUM IN NATURAL WATER

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Determination of the effect of pH on aluminum solubility and the determination of the composition of complexes most likely to occur in natural water

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ABSTRACT

Laboratory studies of solutions 4.53×10^{-4} to 4.5×10^{-5} molal (12.2–1.2 ppm) in aluminum, in 0.01 molal sodium perchlorate, were conducted to obtain information as to the probable behavior of aluminum in natural water. When the solutions were brought to pH 7.5–9.5 and allowed to stand for 24 hours, a precipitate was obtained which was virtually amorphous as shown by X-rays, and which had a solubility equivalent to that of boehmite. This precipitate had a hydrolysis constant ($^*K_{S4}$) of 1.93×10^{-13}. When solutions were allowed to stand at this pH range for 10 days, their precipitates gave the X-ray pattern of bayerite ($^*K_{S4}=1.11\times 10^{-14}$). These hydrolysis constants were obtained at 25°C. and corrected to zero ionic strength and are in close agreement with other published values. The predominant dissolved form in this pH range is $Al(OH)_4^-$.

Below neutral pH (7.0) the dissolved aluminum species consist of octahedral units in which each aluminum ion is surrounded by six water molecules or hydroxide ions. Single units such as $Al(OH_2)_6^{+3}$ and $AlOH(OH_2)_5^{+2}$ are most abundant below pH 5.0, and where the molar ratio (r) of combined hydroxide to total dissolved aluminum is low. When r is greater than 1.0, polymerization of the octahedral units occurs. When r is between 2.0 and 3.0, solutions aged for 10 days or more contained colloidal particles between 0.10 and 0.45 μ in diameter. Particles whose diameters were greater than 0.10 μ were identified by X-ray diffraction as gibbsite. Particles smaller than 0.10 μ were also present and were shown by means of the electron microscope to have a hexagonal crystal pattern. Structured material consisting of sheets of coalesced six-membered rings of aluminum ions held together by double OH bridges has a distinctive kinetic behavior. This property was used to determine amounts of polymerized material in solutions having r between 1.0 and 3.0 after aging times ranging from a few hours to more than 4 months. Aging increased the size and orderliness of the polymeric aggregates and was accompanied by a decrease in the pH of the solution.

The kinetic experiments and stoichiometric data for solutions aged for long periods provided a means of determining activities of unpolymerized aluminum. From these values the solubility product for microcrystalline gibbsite was determined to be 2.24×10^{-33}, and its free energy of formation, -272.3 ± 0.4 kcal per mole.

Where polymerization was observed, the process did not stop with small polynuclear complexes containing a few aluminum ions, but proceeded with aging until macromolecules or colloidal-sized particles were formed.

PURPOSE AND SCOPE

Aluminum is an abundant constituent of rock minerals; in fact, only oxygen and silicon exceed aluminum in abundance among the elements present in the outer part of the earth's crust. Aluminum is, however, a very minor dissolved constituent in natural water. In routine water analyses the element is seldom determined, but the available information shows that, except for waters having a pH below 4.0, concentrations rarely exceed a few tenths of a part per million. The chemistry of aluminum in rock-weathering processes seems to favor retention of the element in solids with low solubilities, especially in clay minerals.

Aluminum has a particularly strong tendency to hydrolize in solution, and at any pH above 3.5 various combinations of aluminum with hydroxide ions occur.

The purpose of this investigation was to determine the effect of pH on aluminum solubility and to determine the composition of aluminum hydroxide complexes that are most likely to occur in solution or suspension in natural water. The equilibrium stability of these species, their geometric configuration, and the kinetics of reactions in which they are destroyed were also considered.

ACKNOWLEDGMENTS

During this investigation the many discussions held with colleagues in the U.S. Geological Survey and with others having an interest in the chemistry of aluminum aided in forming the conclusions expressed here. Ivan Barnes and Robert Schoen, of the U.S. Geological Survey, and Dr. George A. Parks, of Stanford University, reviewed the manuscript. Robert Heidel, of the U.S. Geological Survey, aided in the electron-microscope studies.

PREVIOUS STUDIES

The solubility of aluminum hydroxide in water and the form and stability of solute species containing aluminum and hydroxide have been the subject of many research studies from early in the 20th century to the present. The stability constants published prior to 1961 are included in the compilation of stability constants by Sillén and Martell (1964). The published work was reviewed carefully, with particular attention to the studies completed in the past 10–15 years, to provide background information and to aid in planning this investigation.

The results of previous investigations suggest that several different forms of dissolved aluminum species might be expected over the pH range most prevalent in natural waters. Stability constants reported for these species cover a rather wide range of values. The published standard free-energy values for the common solid forms of aluminum hydroxide also disagree.

The chemical behavior of aluminum in dilute solutions presents some serious experimental difficulties. Most reactions involving aluminum and hydroxide proceed slowly at 25°C. Metastable solid species occur and equilibrium conditions are difficult to attain even when long periods of time have been allowed for reactions to proceed. In many reported experiments, equilibrium probably was not obtained. Solid aluminum oxides and hydroxides form a number of of crystalline structures that are chemically similar but differ in solubility; not all investigations ascertained the nature of the solids involved. Experimental conditions—temperature, concentration, and even rate of addition of reagents—strongly influence the results. The accuracy of analytical methods for determining low concentrations of aluminum is not particularly good (below 1.0 ppm, or $<4\times10^{-5}$ molar). Furthermore, aluminum hydroxide tends to form colloidal or subcolloidal suspensions that are difficult to describe thermodynamically.

DISSOLVED AND SUSPENDED SPECIES

Published studies are in general agreement that when the pH of a solution containing Al^{+3} ions is raised, dissolved species consisting of associated Al^{+3} and OH^- are formed, and that when the supply of OH^- is sufficient, a precipitate of the composition $Al(OH)_3$ is produced. If the pH is further increased, this precipitate is redissolved as an anion having more than three hydroxide groups per aluminum. The details of the processes have been described in various ways. Although it is generally assumed that Al^{+3} ions are hydrated, the coordinated water molecules are not usually shown in representations of solution complexes.

In early investigations, the association of aluminum and hydroxide was assumed to be a mononuclear process occurring in steps. The first ion to form would be $AlOH^{+2}$. As pH increased, $Al(OH)_2^+$ would become increasingly abundant. A solid $Al(OH)_3$ would separate as pH increased, and then would be partly redissolved as the anion $Al(OH)_4^-$. However, stability constants generally were obtained only for the species $AlOH^{+2}$ and $Al(OH)_4^-$ and for the crystalline solid.

In recent years, polynuclear complexes have frequently been postulated, with more than one metal atom in the simplest possible representation of the formula of the complex. The ratio of hydroxide ions to aluminum ions in the complex species needs not be integral. Most recent work has shown that polymeric aluminum hydroxide species which have OH:Al ratios less than 3.0 exist below pH 7.0. Although polymeric anions with an OH:Al ratio a little below 4 in alkaline solutions have been reported, the univalent anion has been assigned the composition $Al(OH)_4^-$ in most investigations. $Al(OH)_4^-$ is the form that will be used in this discussion. In some studies the notations AlO_2^- or $H_2AlO_3^-$ (Deltombe and Pourbaix, 1956) have been used to represent the removal of two molecules or of one molecule of water, respectively. Because of the strong tendency for hydration of aluminum ions, these forms seem unrealistic and have not been used in this report.

Among the more recent studies in which the monomeric cation $AlOH^{+2}$ was reported are those by Schofield and Taylor (1954), Frink and Peech (1963), and Raupach (1963a, b, c). The concentrations of aluminum studied ranged from 10^{-5} to 10^{-2} molar. Measurements of pH were made by means of a glass electrode in solutions of aluminum chloride or perchlorate at various concentrations. For the equilibrium

$$Al^{+3}+H_2O=AlOH^{+2}+H^+$$

the mass-law equation for the equilibrium constant is

$$*K_1=\frac{[AlOH^{+2}]\,[H^+]}{[Al^{+3}]\,[H_2O]}.$$

Average values for $*K_1$ at 25°C, reported in these investigations, were $10^{-4.98}$, $10^{-5.02}$, and $10^{-5.05}$ to $10^{-4.97}$, respectively. This is excellent agreement and compares favorably with results of several earlier investigations cited in Sillen and Martell (1964). The lowest individual values of $*K_1$ obtained by Frink and Peech and by Raupach were those applicable to the most dilute solutions and were about half as great as the largest individual values.

Dissolved aluminum species in which the OH:Al ratio exceeds 1.0 appear in solution as the pH increases. A second-step monomeric association product, $Al(OH)_2^+$, was reported by Gayer, Thompson, and Zajicek (1958), whose experimental technique involved preparing a solid $Al(OH)_3$ and reacting it in solutions of NaOH and $HClO_4$. The solubility product for this solid $Al(OH)_3$ was 1.10×10^{-33}, and its standard free energy was -272.73 kcal per mole. Gayer, Thompson, and Zajicek did not obtain a constant value for the ionic product for $AlOH^{+2}$. The average apparent equilibrium constant for the reaction

$$Al(OH)_3(c)+H^+=Al(OH)_2^++H_2O$$

was reported as 2.52. Individual experimental values, however, varied considerably from this average.

Other investigators have reported dimeric or polymeric aluminum ions. Faucherre (1954) reported the cation $Al_2(OH)_2^{+4}$ in solutions where aluminum concentrations exceeded 1.1×10^{-2} molar; at concentrations below 5.1×10^{-3}, however, the monomer $AlOH^{+2}$ was predominant.

Prof. L. G. Sillén and his associates studied polynuclear complexes extensively and published many papers on experimental, mathematical, and graphical techniques for determining the form and stability of these complexes (Sillén, 1954a, b; Heitanen and Sillén, 1954). A general discussion of the subject by Sillén (1959) presents results for various metals. Often the hydrolysis of an element can be explained by assigning most or all the complexed form to a single polynuclear species or to a few such species. Some elements, however, seem to form a considerable number of polynuclear species, which consist of a series of complexes containing a fundamental unit (called by Sillén the core) with a varying number of attached units (the links). As such structures increase in size and complexity, a greater and greater degree of analytical accuracy is needed in evaluating them. Polynuclear aluminum hydroxide species evidently are of such size that they become difficult to evaluate with certainty.

Brosset (1952) made one of the most extensive experimental studies of the chemistry of aluminum hydrolysis. To speed the reactions, the work was done at 40°C. The experimental data were interpreted as indicating polynuclear complexes. The original data were later reinterpreted by Brosset, Biedermann, and Sillén (1954) as indicating that either a single complex $Al_6(OH)_{15}^{+3}$ or a series of complexes with the formula $Al[(OH)_5Al_2]_n^{+(3+n)}$ was formed in acid solution. Brosset at first postulated a polymeric anion complex at pH levels above neutrality; but on recalculation from the data, Brosset, Biedermann, and Sillén (1954) concluded that the results could be explained satisfactorily by postulating that only $Al(OH)_3(c)$ and the anion $Al(OH)_4^-$ formed in alkaline solutions.

The concept of the polynuclear type of complex does not impose any limit on the number of metal atoms or hydroxide groups which are bound together into a unit. Structures containing only a few aluminum ions would obviously behave like other solute ions, and can be so treated in calculations of activity and solubility. As the number of aluminum ions included in the complex increases, the structural units become larger and larger until the system becomes colloidal and finally becomes a suspension of crystalline solid particles. The polynuclear structures appear to be transitional between the dissolved state and the solid state, and when such structures become very large they present difficulties in applying theoretical concepts of activity of solutes and in calculating solubility.

As Brosset and other investigators noted, the pH of a dilute solution of aluminum ions may be raised by adding a base to provide an average of 2.75–2.95 OH groups associated with each aluminum, and no solid will appear to be present. The aluminum in the solutions, after a suitable aging period, is in an ordered state of combination with hydroxide which Brosset (1952, p. 934) stated could be "described as a series of macromolecules with varying numbers of aluminum atoms. It cannot possess a well-defined activity in this form, so *the concept of solubility product will not apply in this case.*" The meaning of this statement is somewhat obscure, but apparently the intent was to explain why solid aluminum hydroxide species were not taken into account in interpreting the experimental data. Certainly, however, at some stage as larger and larger polymerized particles are formed, the polymer will begin to act as a solid rather than as a group of charged solute ions. Just where this point is reached is uncertain but highly polymerized aluminum hydroxide species certainly cannot be expected to behave like simple ions.

The aluminum hydroxide gels have been studied by means of light-scattering and viscosity measurements. Ruff and Tyree (1958) calculated an average molecular weight for the aluminum hydroxide polymer ranging from 256 when the OH:Al ratio was 0.5, to 1,430 when the ratio was 2.25. These solutions were aged for 6 months.

Other investigators, using many different methods, have assigned various formulas to the species of hydroxide polymer they believed to be predominant. Matijevic, Mathai, Ottewill, and Kirker (1961) concluded from experiments involving the coagulation of silver halide sols by means of hydrolyzed aluminum solutions, that the formula $Al_8(OH)_{20}^{+4}$ could be used to represent the first hydrolysis product. Hsu and Bates (1964) suggested a fundamental structure of $Al_6(OH)_{12}^{+6}$ representing a six-membered ring of aluminum ions connected by double OH bridges. Johanssen (1963), from studies of hydroxosulfates of aluminum, described a basic unit of 13 aluminum ions bound to hydroxide in a crystalline solid which formed so rapidly from solution that it was postulated to exist as a unit in hydrolyzed aluminum solutions.

From potentiometric titrations and infrared spectra Fripiat, Van Cauwelaert, and Bosmans (1965) proposed a general formula $Al[(OH)_8Al_3]_n^{4+}$ for the polymer.

All workers are in general agreement that the reactions of aluminum and hydroxide in the pH range from 4.0 to 7.0 are slow and that products formed may be influenced by concentration of reagents, kinds of anions present, and the manner in which the solutions are prepared. The disagreement of results is, therefore, understandable.

Some investigators have preferred to consider the aluminum hydroxide polymers metastable forms which in time could be expected to become an $Al(OH)_3(c)$ phase (Frink and Peech, 1963). The polymers, however, are so slow to change at the temperature of most weathering environments that they must be given consideration in any evaluation of the chemical behavior of dilute solutions of aluminum in natural systems.

The literature describing the behavior of aluminum in alkaline solutions is in somewhat better agreement. The anion $Al(OH)_4^-$ is generally specified. For the equilibrium

$$Al(OH)_3(c) + H_2O = Al(OH)_4^- + H^+$$

the equilibrium constant $*K_{S4}$ was reported by Szabó, Csányi, and Kávai (1955) to be $10^{-12.74}$ at 20°C. The crystal structure of the solid present was not reported, but because of the methods used in preparation, the solid must have been a freshly precipitated form of $Al(OH)_3$. Raupach (1963a) reported a value of $10^{-13.84}$ for this constant at 25°C with a solid that had been aged long enough to develop the crystal structure of bayerite, and Gayer, Thompson, and Zajicek (1958) reported a value of $10^{-14.53}$ and X-ray diffraction data for the precipitate. Feitknecht and Schindler (1963) later concluded that the X-ray data showed the solid to have been bayerite.

NATURE OF PRECIPITATED SOLIDS

Despite an extensive literature, many uncertainties exist as to what solids might be formed under specific conditions of precipitation of $Al(OH)_3$, as the structure of the solids depends on pH, temperature, reagent concentration, and other experimental factors involved in the procedure.

Herbillion and Gastuche (1962) obtained a variety of crystalline and amorphous $Al(OH)_3$ species whose form depended on pH, temperature, and time. Electron-microscope and X-ray studies of similar species reported by Papee, Tertian, and Biais (1958) indicated that an amorphous gel was formed by rapid precipitation at the lower pH they used (pH 8.0). This was the least organized arrangement. A pseudo-boehmite gel was obtained at pH 9, and more crystalline products were obtained at increased pH, in the order pseudo-boehmite, bayerite, gibbsite. Other work in this field (see Fricke and Meyering, 1933) is not in complete agreement as to pH and other conditions that might be expected to favor any given crystalline species. However, it seems reasonable to conclude that the slow downward drift in pH observed in dilute solutions of Al^{+3} species near pH 5, as reported by Frink and Peech (1963) and by Brosset (1952), indicates that a form of $Al(OH)_3$ having a rather low degree of organization and stability forms in weakly acid conditions; and that, on aging, this solid is slowly converted to more stable material. The precipitate first obtained in weakly alkaline solutions, on the other hand, is somewhat more crystalline and stable. This is indicated by the more stable pH observed by Brosset for solutions at pH 9.0 or 10.0 (1952, p. 922). Brosset pointed out this tendency, terming the least stable substance an "α-gel," which, on aging in a neutral or basic environment, passes to a "β-gel" (pseudo-boehmite) and thence, on further aging, to boehmite which has the composition AlOOH. Raupach (1963a) reported bayerite and gibbsite to be the most stable substances in alkaline solutions, and amorphous $Al(OH)_3$ and corundum, in acid solutions.

Solubility measurements are generally made at an assumed equilibrium condition, in a heterogenous system. True solubility data require equilibrium and exact knowledge of the thermodynamic characteristics of the phases. For aluminum this kind of knowledge is lacking, and for some conditions, nearly impossible to attain.

Table 1 contains selected free-energy values and stability constants which have been obtained from published work, and values obtained in this investigation.

STRUCTURES OF AQUEOUS ALUMINUM SPECIES

The aluminum ion is small and has a high charge, and therefore when dissolved in water it can be expected to be surrounded by a tightly bound shell of oriented water molecules. The sizes of the aluminum ion and the water molecules are such that the aluminum will lie at the center of an octahedron, at each vertex of which is a water molecule. In other words, the coordination number is six, at least for solutions whose pH is near or below neutrality. There may be some tendency toward a four-coordinated arrangement at higher pH; although this is not documented in the literature, the species $Al(OH)_5^{-2}$ and $Al(OH)_6^{-3}$ have not been reported.

The innermost layer of water molecules will be arranged with their negative charge centers directed toward the aluminum ion and their positively charged sides, on which the two protons are located, facing outward. The strong charge on the aluminum ion tends to weaken the forces holding the protons to the oxygen, and thus the protons are relatively easy to dislodge. The typical behavior of aluminum demonstrates this fact, in that a low pH is required to prevent hydrolysis from taking place with the loss of one or more protons from the six adjacent water molecules.

TABLE 1.—*Free energies and stability constants*

Species	*Standard free energy of formation* (ΔG°*kcal*)	*Source of data, and remarks*
Al^{+3}	-115.0	Latimer (1952).
$AlOH^{+2}$	-164.9	Raupach (1963a).
$Al(OH)_2^+$	-215.1	Do.
$Al(OH)_3$(c) amorphous	-271.9	Latimer (1952).
$Al(OH)_3$(c) microcrystalline gibbsite.	-272.3	This report.
AlOOH(c) boehmite	[a] -217.5	Latimer (1952).
$Al(OH)_3$(c) bayerite	-276.2	Deltombe and Pourbaix (1956).
	-274.0	This report.
$Al(OH)_3$(c) gibbsite	-273.9	Latimer (1952).
	-273.5	Barany and Kelley (1961); Frink and Peech (1962).
	-277.1	Raupach (1963a).
	-277.3	Deltombe and Pourbaix (1956).
$Al(OH)_4^-$	-313.9	Raupach (1963a).
	-311.7	This report.

Equilibria	*Log of equilibrium constant*	
$Al^{+3}+H_2O=AlOH^{+2}+H^+$	-5.02	Frink and Peech (1963).
	-4.98	Schofield and Taylor (1954).
	-5.05	Raupach (1963b).
$2Al^{+3}+2H_2O=Al_2(OH)_2^{+4}+2H^+$.	-7.55	Kentamaa (1955).
	$-7.07\pm.06$	Aveston (1965); determined in 1 *M* $NaClO_4$ solution.
$Al^{+3}+2H_2O=Al(OH)^+_2+2H^+$	-8.56	Gayer, Thompson, and Zajicek (1958).
$7Al^{+3}+17H_2O=Al_7(OH)_{17}^{+4}+17H^+$.	-48.8	Sillén and Martell (1964); determined in 3*M* $NaClO_4$ solution.
$13Al^{+3}+34H_2O=Al_{13}(OH)_{34}^{+5}+34H^+$.	-97.6	Sillén and Martell (1964); determined in 3*M* $NaClO_4$ solution.
$Al(OH)_3(c)+H_2O=Al(OH)_4^-+H^+$	[b] -12.74	Szábo, Csányi, and Kávai (1955) at 20°C.
	[b] -12.71	This report.
	[c] -13.84	Raupach (1963a).
	[c] -13.95	This report.

[a] Equivalent to —274.2 when calculated as $Al(OH)_3$.
[b] Fresh precipitate.
[c] Form of solid specified as bayerite.

Figure 1 is a schematic representation of an aluminum-water octahedron. This unit structure upon undergoing the first step in hydrolysis by loss of a proton would become $AlOH(OH_2)_5^{+2}$ and would change slightly in shape to allow the OH^- group to come somewhat closer to the central aluminum ion than a water molecule could. Two monomeric ions may coalesce to form the dimer $Al_2(OH)_2(OH_2)_8^{+4}$ by sharing the two OH^- ions and eliminating two water molecules. This arrangement is shown schematically in figure 2. However, the shared edge should be a little shorter than an unshared edge, rather than the same length as shown. The two

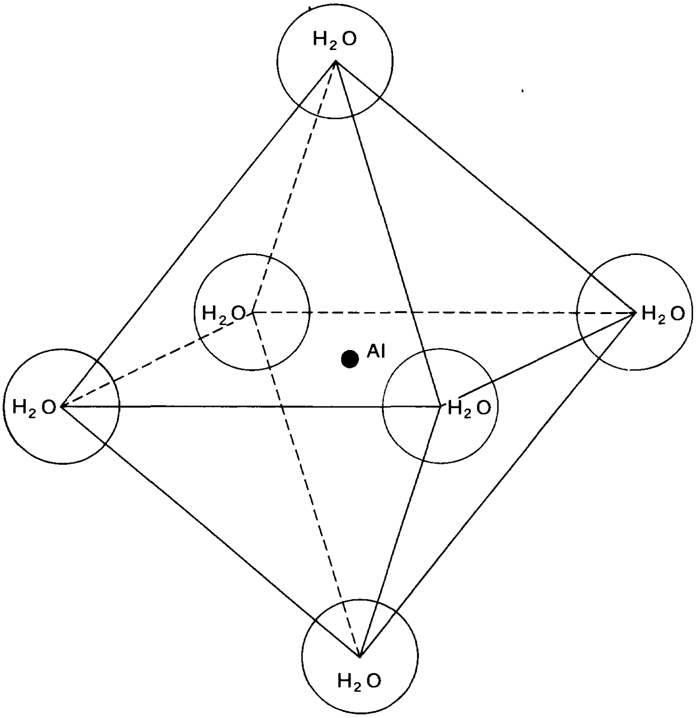

FIGURE 1.—Schematic representation of hydrolyzed aluminum ion $Al(OH_2)_6^{+3}$.

shared hydroxide ions form a double OH bridge connecting the two aluminum ions, an arrangement which is also fundamental in the structure of crystalline aluminum hydroxides. The length of the shared edge in basic aluminum sulfate was reported by Johansson (1963) to be 2.55 A.

Pairs of octahedra in which all six positions are occupied by OH^- make up the structure of the crystalline aluminum hydroxides. In the transition of aqueous forms of aluminum to the crystalline state it is to be expected that polymeric structures having patterns related to those of the solids will occur.

The fundamental principles involved in forming these structures are:

1. Aluminum ions are always surrounded by OH^- or by water molecules.
2. Changes in OH:Al ratio occur by transfer of protons, not by movement of OH^-.

The stereochemical representation of aluminum hydroxide species in solution seems amply justified from theoretical considerations which need not be described in detail here. The reasons for the strong tendency toward polymerization of the individual aluminum octahedra and

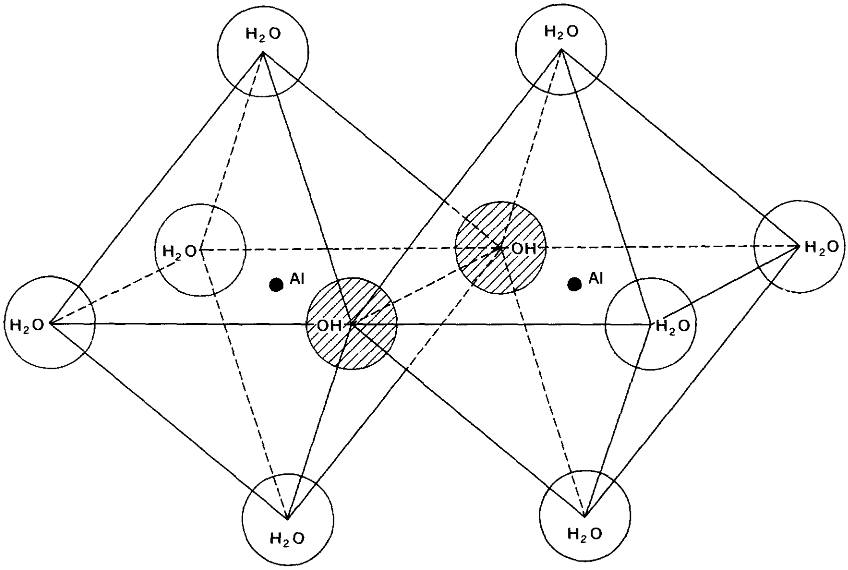

FIGURE 2.—Schematic representation of dimeric cation $Al_2(OH)_2(OH_2)_8^{+4}$.

the preference of the polymers thus formed for a planar or sheet structure rather than a three-dimensional network lie in the preferential directions in which Al–OH bonds are formed and in the nature of the bonding forces. Mattock (1954), for example, pointed out that the tendency for metal ions to form polymeric hydroxides in solution was most pronounced when the metal-OH bond was partly covalent, but that the tendency disappeared both when the bonding was strongly electrostatic and when it was strongly covalent.

HYDROLYSIS EXPERIMENTS

Published information does not provide adequate information for deciding which aqueous species of aluminum are most likely to occur in natural water, what conditions govern the form of precipitated aluminum hydroxide, or to what extent equilibrium conditions can be expected to occur in dilute solutions of aluminum at various pH's. Laboratory studies were designed and carried out to furnish the necessary basic data.

The concentrations of aluminum in natural water are generally much lower than those in solutions studied in most past investigations. Experimental difficulties, however, occur in work with these very low concentrations of aluminum. The maximum concentration selected for the laboratory experiments described here was 4.53×10^{-4} moles, equivalent to 12.2 ppm (parts per million) Al^{+3}. Experiments also were performed with solutions containing 1.2 ppm Al^{+3}, and at intermediate concentrations. In solutions more dilute than 1.2 ppm the sensitivity and precision of analytical procedures, the contamination due to solution of glass (Sackett and Arrhenius, 1962), and the impurities in reagents tend to become critical. Results obtained in the experiments can be extrapolated to the lower concentration ranges found in natural water.

Contact with glass could not be entirely avoided, but contamination from this source was held to a minimum. Polyethylene bottles were used for solutions likely to attack glass and solutions that were aged for long periods. Contamination from atmospheric carbon dioxide was avoided by storing the bottles of solution in a CO_2-free atmosphere. Control tests showed that glass solubility is not a serious problem at the aluminum concentration levels used in this work. Solutions containing 10 ppm and 1.0 ppm aluminum that were stored for 6 months or more in pyrex bottles at pH ≈ 3.0 showed no change in aluminum content greater than the limits of analytical precision.

The first experimental work was designed to indicate the behavior of aluminum over the whole pH range from 2.5 to 11.0. Later experiments studied the systems in more detail, especially in the pH ranges from 4.5 to 6.5 and from 7.5 to 9.5. The procedures were designed to maintain constant total-aluminum concentrations and nearly constant ionic strength. Besides measurement of pH using glass electrodes, information was obtained on the concentration and form of aluminum in solution or suspension by removing particulate matter and examining it by means of X-ray diffraction methods and the electron microscope, and by observing rates and mechanisms of reaction of aluminum hydroxide complexes which did not exhibit particulate behavior. In the concentration range used, other physical properties of the solutions, such as conductivity, did not provide sensitive enough measurements to reflect accurately the changes taking place.

Reactions between aluminum and hydroxide ions are slow at 25°C. The expedient of heating the solutions, used in some studies of these reactions, was not felt to be appropriate in this investigation of reactions taking place under common natural conditions where temperatures are usually not above 25°C.

To simplify the calculations required to convert concentrations to activities, the experiments were made at constant ionic strength in sodium perchlorate solutions. The quantities of aluminum present, however, were small enough that the condition of constant ionic strength could be satisfactorily approximated by using a 0.01 molar concentration of perchlorate. This is a much lower concentration than is normally used in experiments of this type. Stoichiometric composition of all the solutions was known throughout the experiments.

Stock solutions of sodium perchlorate, aluminum perchlorate, and perchloric acid were prepared using de-ionized CO_2-free distilled water. The aluminum perchlorate was prepared from aluminum nitrate and perchloric acid using a technique described by Frink and Peech (1963). A carbonate-free sodium hydroxide standard solution was also prepared. These stock solutions were diluted and combined as required to obtain five types of standard solutions for each set of experiments. One of these solutions (type 1) contained perchlorate, hydrogen, and sodium ions, and had a selected aluminum concentration ranging from 4.53×10^{-4} to 4.53×10^{-5} molar. The type 2 solution contained sodium and perchlorate ions and a concentration of OH^- that was generally a little greater than the combined concentrations of Al^{+3} and H^+ in the type 1 solution. Type 3 solution contained Al^{+3}, Na^+, and ClO^{4-}; the aluminum concentration was twice that in the type 1 solution. Types 4 and 5 solutions were identical with types 1 and 3 except that in place of Al^{+3} they contained an equivalent amount of sodium.

Blank potentiometric titrations were performed on aliquots of solution type 4 by adding equal volumes of both type 2 and type 5. The titrations were done in a covered beaker in a water bath maintained at 25.0 °C ± 0.1 °C. Carbon dioxide was excluded by bubbling nitrogen through the solution. The pH was determined after each addition of titrants by using glass and saturated calomel electrodes and a highly sensitive null-point pH meter (Radiometer pH M4). The response of the electrodes was checked with buffers ranging in pH from 2.00 to 10.00, and all measurements were accurate within 0.01 pH unit. The results of the blank titrations served as a reference for the behavior of the systems in the absence of aluminum.

The reactions of aluminum with OH^- at 25 °C are too sluggish for the reliable use of conventional titration techniques. A "batch" technique was adopted in which a series of aliquots of solution 1 were placed in polyethylene bottles. To each of these the desired volume of solution 2 and an equal volume of solution 3 were added; then the bottles were allowed to stand in a CO_2-free atmosphere long enough to attain a stable pH. In the first experiments, the standing time was 16–24 hours. Although reproducible results were sometimes obtained after this short period of standing, aging effects could not be neglected. In some experiments, aging times of many days to as much as 6 months were used. The temperature was held at 25 °C ± 2 °C during aging. The base (solution 2) was added slowly with vigorous stirring to avoid localized precipitation effects that might delay establishment of equilibrium.

The aged solutions were placed one by one in a water bath, and their pH was measured at 25.0 °C. They were then filtered through plastic membrane filters (Millipore) having pores 0.10 μ or 0.45 μ in diameter. The aluminum content of the filtrate was determined by using the ferron-orthophenanthroline (Rainwater and Thatcher, 1960) procedure and a Beckman model B spectrophotometer, or by using the pontachrome (Donaldson, 1966) procedure and the Turner 111 fluorometer. The latter method is the more sensitive, but for most of the samples the ferron procedure was satisfactory.

A very important quantity in all these solutions is the bound OH; that is, the amount of the total hydroxide present which is chemically bound in some way to aluminum. This quantity is abbreviated as "OH_b" in some places in this paper.

In each set of experimental runs a sufficient number of aliquots were prepared and treated to give a well-defined plot of pH versus volume of titrants. Two curves were prepared; one, the blank or reference curve for solutions containing no aluminum, and the other representing the solutions containing aluminum. The difference between the blank titration and the aluminum titration for any pH is a measure of the bound OH, which can also be calculated from pH and stoichiometric data for solutions of relatively low ionic strength such as the ones used in this work. The amount of aluminum which has precipitated can be computed from differences between amounts originally present and amounts remaining in solution. X-ray diffraction studies were made of the material caught on the plastic filters. A typical set of titration curves is shown in figure 3. The solutions which contained aluminum were allowed to age for 16 hours before their pH was measured.

The results obtained for the solutions which stood for 16–24 hours (1-day aging) showed a fairly consistant relationship of dissolved aluminum to pH between pH 7.5 and 9.5 (fig. 4). Below this pH range, however, the experimental points tended to be scattered. Some solutions having the same pH (between 5.0 and 6.0) gave apparent dissolved aluminum concentrations differing by a factor of 10 or more. This amount of uncertainty is equivalent to more than a log unit in the equilibrium constant and to considerably more than a kilocalorie per mole in the free energy of the precipitate. This difficulty was later overcome by longer aging and modifications in the methods used for determining dissolved aluminum concentrations. The direct equilibrium approach is only applicable above pH 7.5, where ionic species are simple and reactions are rapid.

In the following sections, the experimental results for the 7.5–9.5 pH range are discussed first, because the relationships in this range are relatively simple. The experimental results obtained at lower

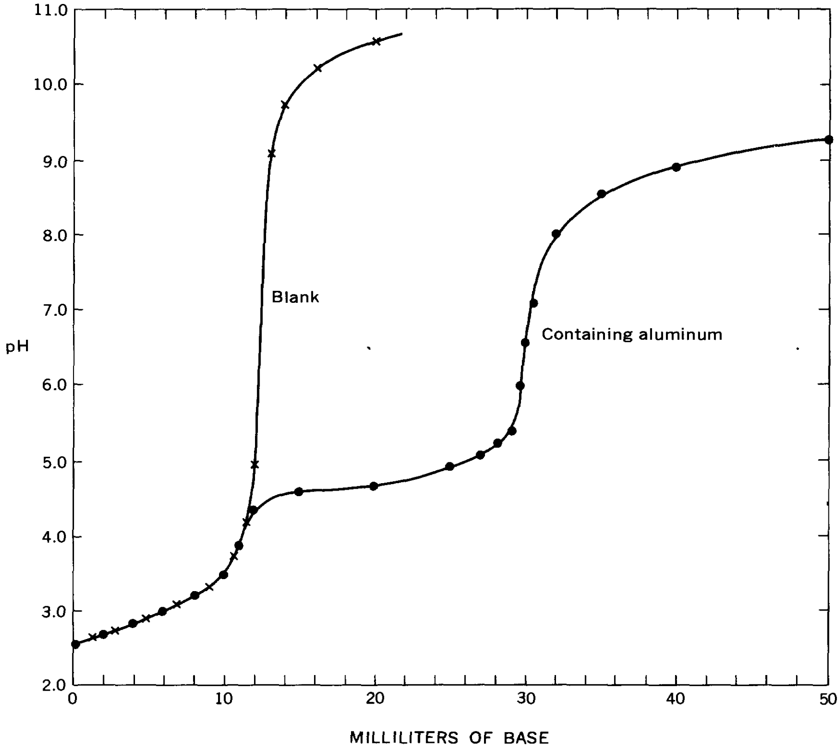

FIGURE 3.—Typical titration curves for solution 4 titrated with solutions 2 and 5 (x's), and for solution 1 titrated with solutions 2 and 3 (dots).

pH are then described and explained in terms of appropriate stereochemical concepts.

BEHAVIOR OF ANIONIC ALUMINUM SPECIES

Solutions to which more than enough OH^- was added to combine with all the aluminum, as $Al(OH)_3$, attained a fairly stable pH after 16–24 hours. The rate of drift in these solutions was generally less than 0.01 pH unit per hour. A fine-grained precipitate was present at that time, and X-ray diffraction patterns were obtained for this material. The plastic filter pads, on which the precipitate had been collected, were placed in the diffractometer and scanned before they had a chance to dry so that the material that had been in contact with the solutions could be identified. The solid obtained after 16–24 hours of aging had a low degree of crystallinity and probably represented what was called pseudo-boehmite in other investigations (Brosset, 1952). The observations of aluminum activity were plotted against pH in figure 4 and gave the line labeled "1-day aging."

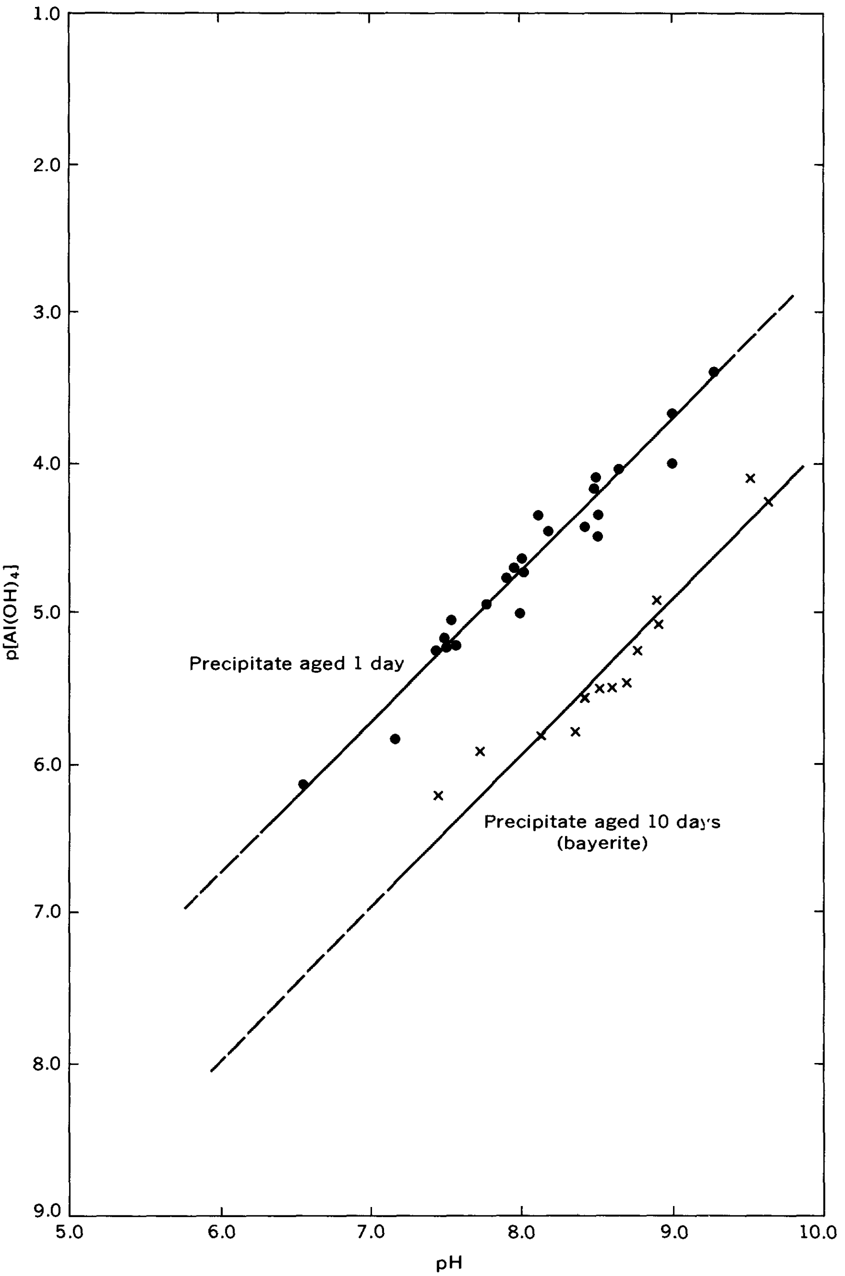

FIGURE 4.—Solubility of aluminum anionic species as affected by aging. Dots represent solutions aged for 16–24 hours (1-day aging); x's represent solutions aged for 10 days.

Solutions that stood for 10 days contained smaller amounts of dissolved aluminum and had a higher pH than the samples aged 1 day, and they gave a second set of points that are plotted as the second regression line in figure 4. Aging periods longer than 10 days produced no further change.

The equilibrium

$$Al(OH)_3(c)+H_2O=Al(OH)_4^-+H^+$$

was assumed to apply to the observations between pH 7.5 and 9.5, where some solid aluminum hydroxide was known to be present. The hydrolysis constant $^*K_{S4}$ for the equilibrium is computed from

$$^*K_{S4}=[Al(OH)_4^-][H^+].$$

Concentration values from the experimental data for dissolved aluminum were converted to activities by using the extended form of the Debye-Hückel equation (Butler, 1964, p. 433), and for the ionic strength of the solutions an activity coefficient of 0.888 was obtained. The measured pH values were considered to represent thermodynamic hydrogen ion activities.

Value for $^*K_{S4}$ were calculated for 22 different samples in which simultaneous observation of total dissolved aluminum and pH were made after 16–24 hours of aging. The pH values ranged from 7.50 to 9.26; and the calculated values for $^*K_{S4}$ ranged from 0.99×10^{-13} to 2.8×10^{-13}, the mean being 1.93×10^{-13}. About one-fourth of the spread of these values could be attributed to analytical errors. The scatter of points, although fairly large, seems to be random among the various observations. Accordingly, a value for $^*K_{S4}$ of $2.0\pm1.0\times10^{-13}$ is indicated by these results for a freshly precipitated form of $Al(OH)_3$. As pointed out earlier in this discussion, several other investigations have produced values very near this for what was probably a similar solid. Values used for the calculation are given in table 2.

Material (identified as bayerite) which had been aged for 10 days had a substantially lower solubility. Data for 12 aged solutions, substituted in the same equations as were used before, gave an average value of 1.11×10^{-14} for $^*K_{S4}$. The maximum value of $^*K_{S4}$ obtained from these data was slightly over 2×10^{-14}, and the minimum, about 0.7×10^{-14}. The observed activities and calculated values for $^*K_{S4}$ for solutions aged 10 days are given in table 3.

TABLE 2.—*Determination of stability constant for freshly precipitated aluminum hydroxide*

[pH 7.50–9.26; aging time 16–24 hours]

Solution No.	pH	C_{Al} (moles per liter)	$[Al(OH)_4^-]$ (moles per liter)	$[H^+]$ (moles per liter)	$^*K_{S4}$
1	7.50	0.063×10^{-4}	0.056×10^{-4}	3.16×10^{-8}	1.77×10^{-13}
2	8.00	$.208\times10^{-4}$	$.185\times10^{-4}$	1.00×10^{-8}	1.85×10^{-13}
3	8.50	$.722\times10^{-4}$	$.641\times10^{-4}$	3.16×10^{-9}	2.03×10^{-13}
4	9.00	2.30×10^{-4}	2.04×10^{-4}	1.00×10^{-9}	2.04×10^{-13}
5	9.26	4.45×10^{-4}	3.95×10^{-4}	5.50×10^{-10}	2.17×10^{-13}
6	7.50	$.067\times10^{-4}$	$.059\times10^{-4}$	3.16×10^{-8}	1.86×10^{-13}
7	8.00	$.240\times10^{-4}$	$.213\times10^{-4}$	1.00×10^{-8}	2.13×10^{-13}
8	8.50	$.440\times10^{-4}$	$.391\times10^{-4}$	3.16×10^{-9}	1.24×10^{-13}
9	7.50	$.067\times10^{-4}$	$.059\times10^{-4}$	3.16×10^{-8}	1.86×10^{-13}
10	8.00	$.240\times10^{-4}$	$.213\times10^{-4}$	1.00×10^{-8}	2.13×10^{-13}
11	8.50	$.480\times10^{-4}$	$.426\times10^{-4}$	3.16×10^{-9}	1.35×10^{-13}
12	9.00	1.11×10^{-4}	$.986\times10^{-4}$	1.00×10^{-9}	$.99\times10^{-13}$
13	8.48	$.963\times10^{-4}$	$.855\times10^{-4}$	3.31×10^{-9}	2.83×10^{-13}
14	8.19	$.407\times10^{-4}$	$.361\times10^{-4}$	6.45×10^{-9}	2.33×10^{-13}
15	7.95	$.111\times10^{-4}$	$.099\times10^{-4}$	1.12×10^{-8}	1.11×10^{-13}
16	7.58	$.111\times10^{-4}$	$.099\times10^{-4}$	2.63×10^{-8}	2.60×10^{-13}
17	7.74	$.119\times10^{-4}$	$.106\times10^{-4}$	1.82×10^{-8}	1.93×10^{-13}
18	8.62	1.07×10^{-4}	$.095\times10^{-4}$	2.40×10^{-9}	2.28×10^{-13}
19	8.11	$.389\times10^{-4}$	$.345\times10^{-4}$	7.76×10^{-9}	2.68×10^{-13}
20	7.55	$.078\times10^{-4}$	$.069\times10^{-4}$	2.82×10^{-8}	1.95×10^{-13}
21	8.45	$.367\times10^{-4}$	$.326\times10^{-4}$	3.55×10^{-9}	1.16×10^{-13}
22	7.94	$.218\times10^{-4}$	$.194\times10^{-4}$	1.15×10^{-8}	2.23×10^{-13}
Mean $^*K_{S4}$					1.93×10^{-13}

TABLE 3.—*Determination of stability constant for aged aluminum hydroxide (bayerite)*

[pH 8.16–9.64; aging time about 10 days]

Solution No.	$[Al(OH)_4]$ (moles per liter)	$[H^+]$ (moles per liter)	$^*K_{S4}$
1	1.32×10^{-5}	1.12×10^{-9}	1.48×10^{-14}
2	8.22×10^{-5}	2.88×10^{-10}	2.37×10^{-14}
3	3.00×10^{-6}	3.31×10^{-9}	9.93×10^{-15}
4	5.90×10^{-5}	2.29×10^{-10}	1.35×10^{-14}
5	1.71×10^{-6}	4.68×10^{-9}	8.00×10^{-15}
6	1.97×10^{-6}	6.92×10^{-9}	1.36×10^{-14}
7	3.00×10^{-6}	2.96×10^{-9}	8.88×10^{-15}
8	3.29×10^{-6}	2.00×10^{-9}	6.58×10^{-15}
9	3.00×10^{-6}	2.50×10^{-9}	7.50×10^{-15}
10	3.29×10^{-6}	2.35×10^{-9}	7.73×10^{-15}
11	8.22×10^{-6}	1.15×10^{-9}	9.45×10^{-15}
12	6.25×10^{-6}	1.58×10^{-9}	9.88×10^{-15}
Mean $^*K_{S4}$			1.11×10^{-14}

Some of the published work seems to report inadequately on the nature of solid species which were present in the experimental solutions. The published values for the standard free energy of formation of the various forms of aluminum hydroxide (table 1) have a rather wide range—from −271.9 kcal per mole for amorphous $Al(OH)_3$, given by Latimer (1952), to −277.3 kcal per mole for gibbsite, given by Deltombe and Pourbaix (1956). Even if the bulk nature of the solid is known, there could be some uncertainty about the crystal structure at the solid-liquid interface.

In some studies, the crystalline nature of the solids was not determined. In other work, the solid used was prepared under conditions that differed greatly from those in the solutions in which it was supposedly later equilibrated. A very long time might be necessary to attain equilibrium in such a system and the reaction times allowed in some experimental studies obviously were inadequate. In this investigation, the solid was formed in the reacting solutions and was identified as nearly as possible without altering the conditions of formation.

Raupach (1963a) reported a value (obtained from published literature) of 1.44×10^{-14} for $*K_{S4}$ and stated that this value was applicable to bayerite. This value agrees very closely with the one computed in the present investigation. Raupach also reported a value of 2.7×10^{-15} for this constant for gibbsite. In the present experiments gibbsite was not identified as a stable solid between pH 7.5 and pH 9.5, and such low solubilities were not observed. However, the report by Gayer, Thompson, and Zajicek (1958), in which a value of 2.98×10^{-15} was given for $*K_{S4}$, was later quoted by Feitknecht and Schindler (1963), who assigned this solubility to bayerite. The value of 1.11×10^{-14} determined for $*K_{S4}$ in the present work, though, appears to be a more reliable figure for a system from which bayerite has precipitated, because this was the form of solid precipitated in the pH range 7.5 to 9.5.

The free energy of formation of the solids cannot be calculated directly from the alkaline-solubility data because the free energy of the species $Al(OH)_4^-$ is not known. The value −313.9 kcal per mole given for this species by Raupach (1963a) (table 1) was based on data in the literature but seemed to fit his experimental results. About the same value for the free energy of $Al(OH)_4^-$ is obtained by calculations using Deltombe and Pourbaix's (1956) value for the free energy of bayerite and the value of $*K_{S4}$ determined for bayerite in present the investigation.

The difference in solubility between the material present after 1 day and that present after 10 days of aging is equivalent to the difference between Latimer's free energy value for boehmite and Deltombe and Pourbaix's value for bayerite. This relationship holds because Deltombe and Pourbaix's value for the free energy of bayerite was calculated from Latimer's value for boehmite and the experimental results of Fricke and Meyering (1933), which are very similar to those of the present study.

The results of calculations such as these are subject to limitations because of the assumptions involved. Positive evidence of boehmite was not obtained from X-ray-diffraction studies of the solids produced in the present experiments. Thus, the solid present after 1 day aging probably cannot justifiably be called boehmite, although its chemical behavior seems similar to what has been called boehmite or psuedo-boehmite by other workers.

Because of the uncertainty in published data regarding the free energy of formation of bayerite, values for the free energy of this solid and of the dissolved species $Al(OH)_4^-$ should be obtained without using any of the $\Delta G°$ values for aluminum species from the literature except that for Al^{+3}. The desired $\Delta G°$ values can be calculated only when sufficient data on the behavior of Al^{+3} have been obtained. Most experimental work has been devoted to the study of the cationic aluminum species.

BEHAVIOR OF CATIONIC ALUMINUM SPECIES

Solutions containing amounts of OH^- less than that required to combine completely with the aluminum present to form $Al(OH)_3(c)$ were prepared using the stock solutions described earlier. The total aluminum concentration was held at 4.53×10^{-4} molal for most of these, but some solutions were 4.5×10^{-5} molal. From the blank titrations and from observed pH values in blanks and in solutions containing aluminum, a concentration of bound OH^- was computed for each of the test solutions. Because the preliminary work had shown that changes were still taking place in solutions aged for a few days, provision was made for longer aging. Solutions having various ratios of bound OH^- to total aluminum ranging from 0.5 to 3.0 were prepared in about 1,000 ml volumes and were, allowed to stand in closed polyethylene containers in a CO_2-free atmosphere at 25°C. At intervals during several months, the pH's of the solutions were measured and aliquots were removed for determination of the state of the aluminum.

POTENTIOMETRIC MEASUREMENTS

Techniques used in these experiments are similar in some respects to those which have been summarized by Sillén (1959) who used potentiometric measurements of hydrogen or hydroxide ion activities in describing the polynuclear hydroxide complexes of many metal ions. In applying these techniques, an extensive series of pH measurements is made on solutions having different ratios of

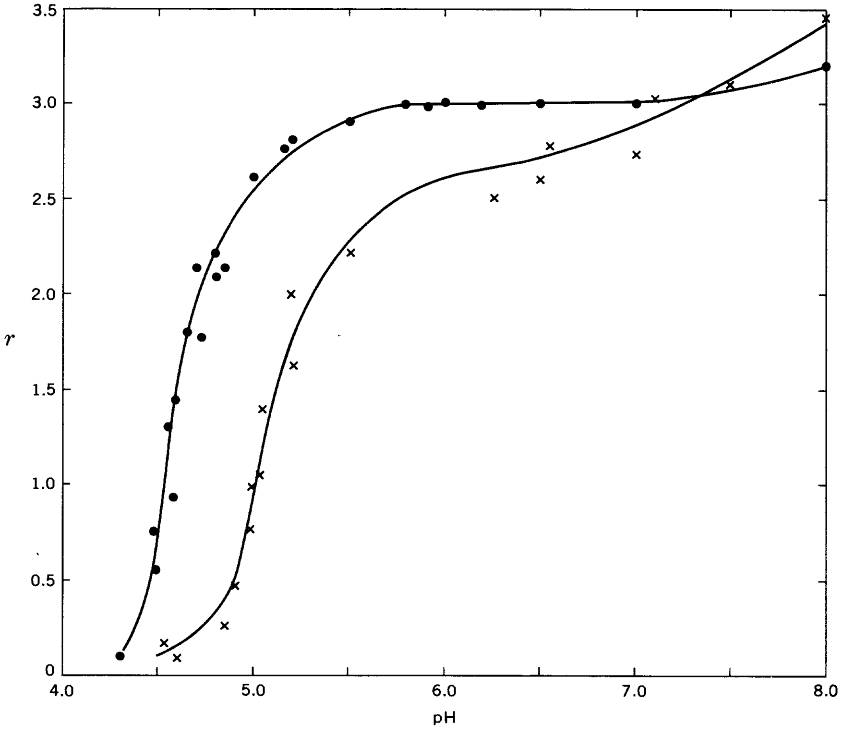

FIGURE 5.—Plot of r (ratio $C_{OH(b)}$: $C_{Al(total)}$) versus pH for solutions 4.53×10^{-4} (dots) and 4.5×10^{-5} (x's) molal in aluminum. All solutions aged 2 days or less.

bound OH to total concentrations of metal ions. When the ratio C_{OH_b}:C_{metal}, r, is plotted against pH, a series of spaced curves results, if polynuclear complexes are formed. The spacing between the curves is a function of the composition or the polynuclear complex species.

Data for two groups of solutions—one 4.53×10^{-4} molal and the other 4.5×10^{-5} molal in aluminum—are plotted in figure 5. The two groups gave rather well-defined curves where only the readings obtained in the first few days were plotted. As aging proceeded, the points for the more concentrated solutions (where r exceeded 1.0) tended to plot to the left of the curve, toward lower pH values. The observed decline in pH indicated that reactions were still taking place and that equilibrium had not been reached.

In interpreting curves such as these, three principal assumptions are required:

1. A reasonable degree of chemical equilibrium is attained.

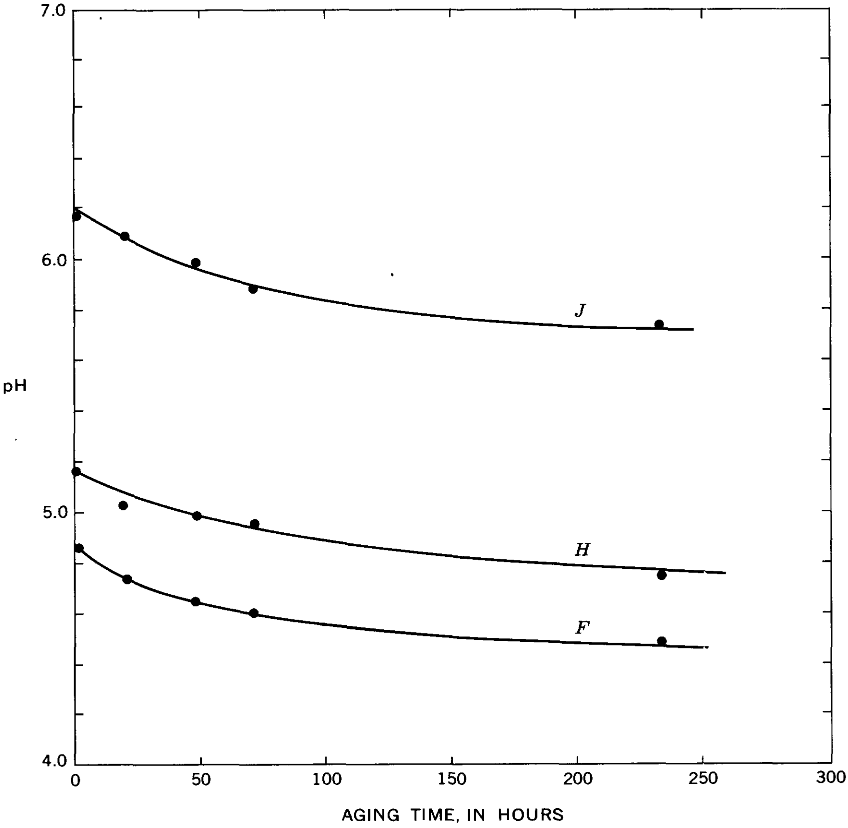

FIGURE 6.—Decline of pH with time for three solutions in which initial value of *r* was 2.99(*J*), 2.74(*H*), and 2.12(*F*).

2. The complex species that are formed are simple enough to be evaluated within the precision of the experimental data.
3. The complex species display ionic properties (as opposed to properties of a colloidal solid) so that they can be treated by thermodynamic calculations.

The assumption of chemical equilibrium is not valid for solutions that have aged only a few days. Characteristically, reactions observed in the laboratory were slow. The pH of weakly acid solutions containing bound OH concentrations equaling or exceeding the total aluminum declined with time. Figure 6 shows the decline of pH over a 10-day period for solutions in which the initial ratio of bound OH to total aluminum was 2.99, 2.74, and 2.12, respectively. Although the rate of decline of pH seemed to be decreasing with time in all three solutions, a decline of a full pH unit was observed in solution J over

25 days; another solution, not shown in figure 6 but equivalent to solution F, showed a slow but continuous decrease in pH for more than 3 months. After several months of aging, some of the solutions in which *r* was more than 2.0 had pH values less than 4.40. The decrease in pH was accompanied by relatively slight changes in total bound OH^-. This suggests that the changing pH must be associated with changes in the way the aluminum and OH^- ions are bound together. It appears erroneous, therefore, to apply methods using pH data and total aluminum and bound OH values alone to characterize the aluminum hydroxide complexes below pH 7.5.

MEASUREMENT AND SIGNIFICANCE OF ALUMINUM CONCENTRATIONS

Aluminum concentrations in solution were determined in the first experiments of the study by means of the ferron-orthophenanthroline procedure (Rainwater and Thatcher, 1960) on aliquots which had been filtered through plastic membranes with a pore diameter of 0.45 mn. This pore diameter had been adequate to remove the precipitated matter observed in solutions aged under alkaline conditions.

First indications were that some aluminum had been filtered out of the solutions except where *r* was less than 1.0 and pH was relatively low, because the aluminum determinations gave lower figures than the total amount known to be present. No solid residue, however, could be observed by examination of the filter pads with a hand lens. On further investigation the aluminum concentrations observed in the filtrate proved erroneous because of the very slow reaction of some of the aluminum species with the ferron organic reagent.

The procedure for the determination of aluminum described by Rainwater and Thatcher (1960) utilizes a complex formed by aluminum and ferron. Interference from iron is avoided by forming a complex of ferrous ions with orthophenanthroline, and the organic reagent used in the determination is therefore a mixed solution of the two chemicals, ferron and orthophenanthroline. The first step in the procedure is the addition of hydroxylamine hydrochloride to the sample aliquot to reduce any ferric iron that might be present. This also brings the pH of the aliquot to about 1.5. Although the samples which were being examined in this study contained no iron, the hydroxylamine is required to attain the proper pH later in the procedure. The prescribed 30 minutes the solutions stand in contact with hydroxylamine at pH 1.5 appeared to insure complete destruction of any aluminum hydroxide complexes and, thus, to prevent any interference with the complexing action of the ferron.

The experimental results, however, show that if aluminum hydroxide species formed in weakly acid solutions are allowed to age, they become highly resistant to attack by acid. A solution containing 12.2 ppm total aluminum and having an *r* value of 2.85 was prepared and allowed to stand in a CO_2-free atmosphere for 4 days. At the end of this aging period the solution had a pH of 6.03. A portion of the solution was then withdrawn into a polyethylene container and brought to pH 1.5 with hydroxylamine hydrochloride. Periodically, portions of this acidified solution were analyzed for aluminum by adding the necessary amounts of the other reagents. Results were as follows:

Time at pH 1.5 (hr)	Al *determined (ppm)*	*Time at pH 1.5 (hr)*	Al *determined (ppm)*
1/6	5.8	24	9.6
1	6.8	48	10.8
3	8.0	96	11.3
9½	8.8	216	11.9

Thus, the aluminum returned very slowly to a determinable state when subjected to moderate acidity. Other similar experiments showed that after about 350 hours the determined aluminum equalled the total known to be present, within the limits of experimental error (±10 percent).

FILTRATION EXPERIMENTS

In further experiments with solutions of aged aluminum hydroxide species, plastic membranes with smaller pores were used for filtration. In solutions which had *r* values below 3.0, practically all the aluminum passed through membranes with a pore diameter of 0.45 μ, although much of this material reacted very slowly with acid. Filtration through membranes with a 0.10 μ pore diameter, however, effectively removed aluminum from solutions in which *r* was near 3.0. Some aluminum was removed by filtration from solutions in which *r* was 2.0, but below this value very little aluminum could be removed by filtration, even by using membranes having pores 0.05 μ or 0.01 μ in diameter. The results of these experiments are given in table 4 and in figure 7.

A plot of percentage of total aluminum passing through the 0.10 μ filter versus *r* indicates that a rather well defined relationship exists for the solutions listed in table 4. Only one point was conspicuously off the curve. This point represented solution 6, which was not aged as long as solution 1 (which had the same *r*). Probably a longer aging time would have decreased the amount of aluminum passing through the filter for solution 6.

TABLE 4.—*Percentage of aluminum hydroxide in filterable state in aged solutions*

[Total concentration of Al=4.53×10^{-4} moles per liter]

Sample	Aging time (days)	pH	r	Percentage passing through given pore diameter	
				0.45 μ	0.10 μ
1	4	4.80	2.47	94	60
1a	11	4.64	2.49	93	57
2	4	4.89	2.65	94	42
3	4	4.99	2.78	99	25
3a	10	4.73	2.80	97	20
4	2	4.68	1.44	100	100
5	2	4.75	1.97	94	93
6	2	4.88	2.47	95	87
7	2	6.54	2.95	80	<1
8	4	6.03	2.88	86	1
9	6	5.58	3.00	----------	2

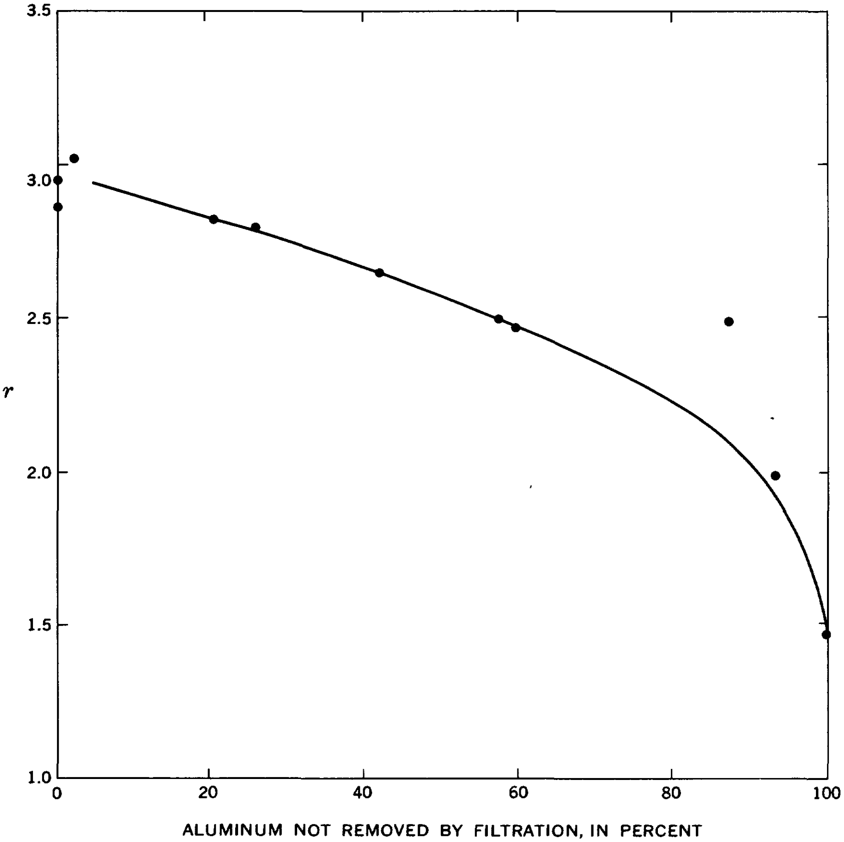

FIGURE 7.—Percentage of aluminum remaining in solutions with various values of r after filtration through membranes with 0.10 μ pore diameter.

CHARACTERISTICS OF FILTERABLE MATERIAL

The material caught on the filters having a 0.10 μ pore diameter was studied by X-ray diffraction. As in the experiments with the precipitates obtained at higher pH, the filters were studied before they had a chance to dry, and the species identified were assumed to have been present in the solutions. The precipitate from the solution having an r value of 2.9 gave a well-defined gibbsite crystal pattern immediately after filtration. Gibbsite peaks appeared a few hours after filtration for systems where r was 2.7 and 2.8. The patterns for material obtained from other solutions, where r was lower, were slower to appear.

The fact that a gibbsite crystal structure can be observed in small particles of hydroxide ($<$0.45 μ in diameter) is very significant. For one thing it implies that the polymeric species of aluminum hydroxide may have a well-defined crystalline structure even when they constitute aggregates too small or too weakly tied together to be isolated by filtration. The gibbsite structure consists of parallel sheets of coalesced six-membered rings, as described by Johansson (1963.) Particles large enough to be held back by the 0.10-μ filter must contain many thousands of these basic ring units, and their behavior must be that of a finely divided solid; certainly, they do not act like solute ions.

Gibbsite particles appear from solutions in which the value of r is 2.0–3.0 only after 2–10 days of aging at 25°C. Processes of polymerization by which these particles are formed may continue for longer periods and may explain some of the pH changes observed during aging

Hsu (1966) reported the synthesis of gibbsite in solutions having r values ranging from 1.8 to 2.7 and aged for 2 years. His solutions were 0.02 molar in aluminum chloride.

STRUCTURE OF ALUMINUM HYDROXIDE POLYMERS

The behavior of aluminum in the pH range below the isoelectric point indicates that relatively large polymeric structures of aluminum and hydroxide ions may occur in solution, and that these structures may enlarge with time. The fundamental structural unit of these polymers is the six-coordinated aluminum ion at the center of an octahedral arrangement of water molecules or OH^- ions, as previously indicated. The rest of this section of the report will be devoted to considering in somewhat greater detail the stereochemical patterns which can be expected from combinations of such octahedral units. In this discussion it is assumed that the bonding between octahedra is through double OH bridges, as in the structure of gibbsite. These structural considerations help explain in detail the chemical behavior of the polymeric species, and provide a model to be tested by the experiments described in this report.

The term "bound OH" where it has been used in this report, has referred in a general way to hydroxide ions bound to aluminum in an unspecified manner. In considering this bound OH in greater detail, it will be helpful to distinguish the nature of bonding more closely. Accordingly, it will be useful to speak of "structural OH," which is the hydroxide present in the double bridges which link the aluminum ions together, and "nonstructural OH," which is the remaining bound OH held in the polymers or complexes by single bonds to aluminum, or otherwise incorporated into the structure where it cannot directly influence the pH of the solution.

The conversion of hydrated aluminum ions to polymerized species can be considered a stepwise process. The first step is hydrolysis, or deprotonation of one of the associated water molecules

$$Al(OH_2)_6^{+3}-H^+=AlOH(OH_2)_5^{+2}.$$

(The proton could also be written with a positive sign on the right side of the equation.) Although this monomeric ion is a little less symmetrical than the Al^{+3} with its octahedral shell of water molecules, there is no apparent reason why such a unit could not have an independent existence, especially in dilute solutions.

Two deprotonated octahedra can join to form a dimer. This is the smallest structure which contains the characteristic double OH bridge between the aluminum ions, and all the bound OH is structural OH

$$2AlOH(OH_2)_5^{+2}=Al_2(OH)_2(OH_2)_8^{+4}+2H_2O.$$

The dimerization step involves no pH change, but it is not necessarily an end point in the reaction. The configuration of the monomer and dimer were represented in figures 1 and 2. The polymerization process consists fundamentally of deprotonation and dehydration.

Two dimers can join to form a chain structure:

$$2Al_2(OH)_2(OH_2)_8^{+4}-2H^+=Al_4(OH)_6(OH_2)_{12}^{+6}+2H_2O.$$

The shape of this chain structure, however, will depend upon the location of the shared edge, or double OH bridge, which links the dimers. Figure 8 shows that each of the octahedra in the dimers has five edges available for sharing. If no preferential orientation is required because of the nature of the bonding forces, it would be possible for any pair of these edges to be shared—for example, *B–D* and *A′–C′*. One of each five possible combinations would lead to a straight chain structure, equivalent to the joining of two of the dimers in figure 8 along edges *B–C* and B′–C′. The statistical probability of forming long straight chains is therefore low. It also appears that the mutual directional bonding forces between Al^{+3} and OH^- ions which form the double bridges require that no two adjacent bridges

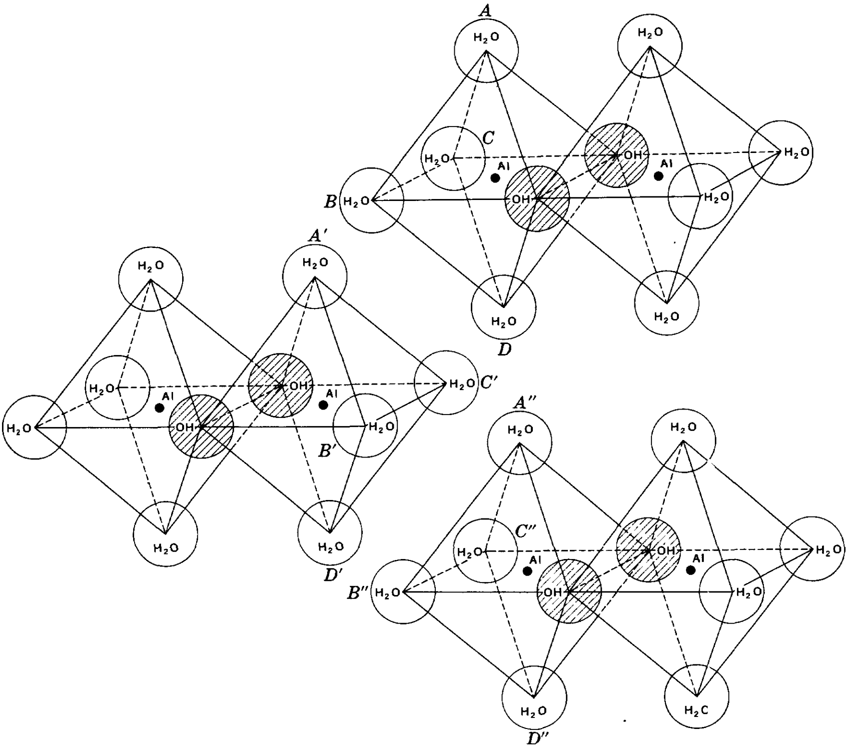

FIGURE 8.—Schematic representation of possible linkages of aluminum hydroxide dimers.

lie in the same plane. The structure of gibbsite follows this rule. Attachment of a third dimer by sharing edges *B′–D′* and A″–C″ would produce a branched chain structure of six aluminum octahedra.

The general formula for a chain structure is

$$Al_m(OH)_{2m-2}(OH_2)_{2m+4}^{+(m+2)},$$

which applies either to straight or to branched chains of finite lengths involving no ring structures. As the chains become longer (as *m* increases) the ratio of structural OH to aluminum approaches 2 as an upper limit. (See fig. 9.) Rapid addition of hydroxide to aluminum solutions probably produces various chain lengths.

The ideal ring structure is composed of six octahedrally coordinated aluminum ions joined together by double OH bridges. This structure, as shown in figure 10, follows naturally from the angles at which the octahedra are joined. A ring containing six octahedra has fewer protons than a six-membered chain, as shown by the equation:

$$Al_6(OH)_{10}(OH_2)_{16}^{+8}-2H^+=Al_6(OH)_{12}(OH_2)_{12}^{+6}+2H_2O.$$

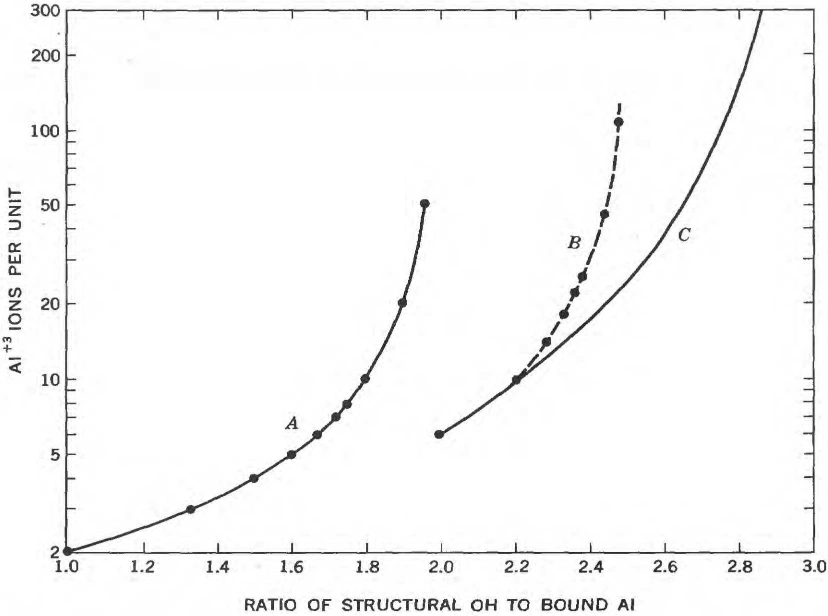

FIGURE 9.—Molar ratio of structural OH to complexed aluminum for different numbers of aluminum ions per unit in chain and ring structures. Curve *A* represents chain structures; *B* and *C* represent different arrangements of ring structures.

The six-membered rings may coalesce in various ways, as a result of further deprotonation and dehydration. As the pH of the solution rises, the structure ultimately forms a planar sheet of aluminum ions octahedrally coordinated with OH^-. The structure may be visualized as coalesced rings, or as joined dimeric units, and has the pattern shown in figure 11. Hsu and Bates (1964) proposed a coalesced-ring structural pattern for the development of aluminum hydroxide polymers.

The enlarging polymeric groups contain an increasing area of neutralized structure involving aluminum ions held together by double OH bridges, and an increasing ratio of structural OH to aluminum, which approaches a limit of 3.0 as the structure increases in size. The increase in the total number of aluminum and structural OH ions is in proportion to the increasing area (radius squared) of the planar unit. At the same time on the perimeter, the aluminum ions, which have potentially unsatisfied positive charges, are increasing in number, but at a slower rate proportional to the increasing perimeter of the aggregate (radius); so the proportion of unsatisfied aluminum ions decreases with increasing grain size. Any nonstructural OH must be held along this perimeter. As the structures become large, the nature of

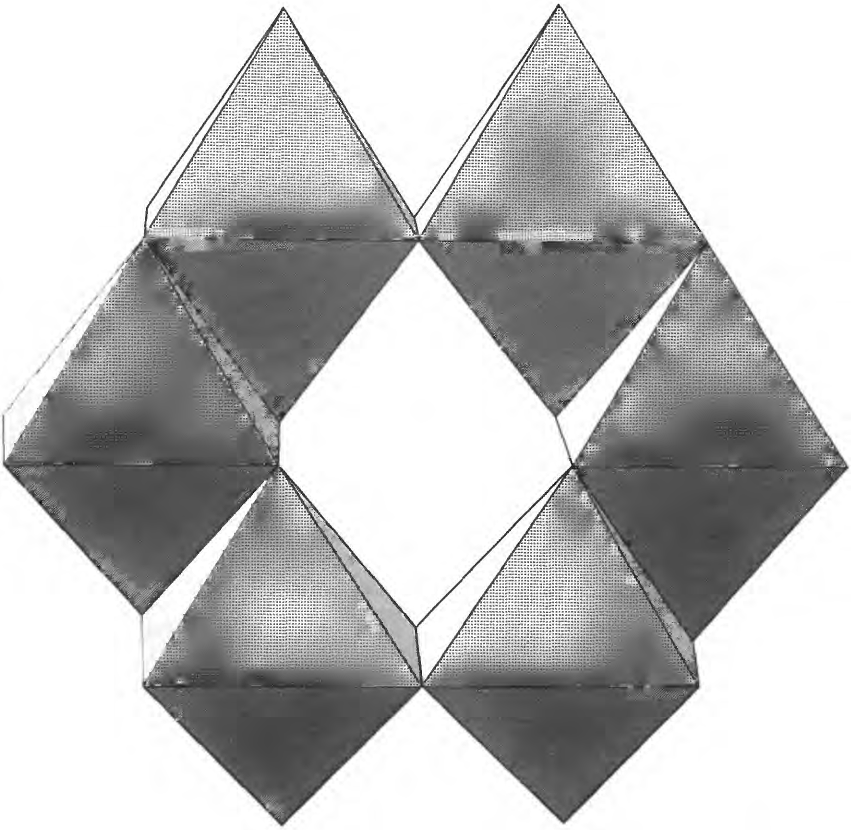

FIGURE 10.—Schematic representation of ring structure formed by six aluminum hydroxide octahedra.

the bonding by which the nonstructrual OH is attached probably evolves into something akin to chemisorption or ion-exchange capacity. The nonstructural OH held by the colloidal particles should be replaceable by other anions of suitable size and charge, or quickly neutralizeo by H^+.

Curve *B* in figure 9 represents the limiting ratio for a straight chain of ring structures arranged side by side. Curve *C* represents a structure built up by adding ring units equally in all directions, in one plane, around a central nucleus. From the trend of the curves it may be deduced that particles containing a thousand aluminum ions probably would have a ratio of structural OH to aluminum about 2.9. To approach a ratio of 3.0, therefore, the aggregates must be large and have a sheetlike rather than a chainlike configuration.

A filter having 0.10 μ pores would catch particles of the order of 1,000 A in diameter. The individual six-membered rings in these

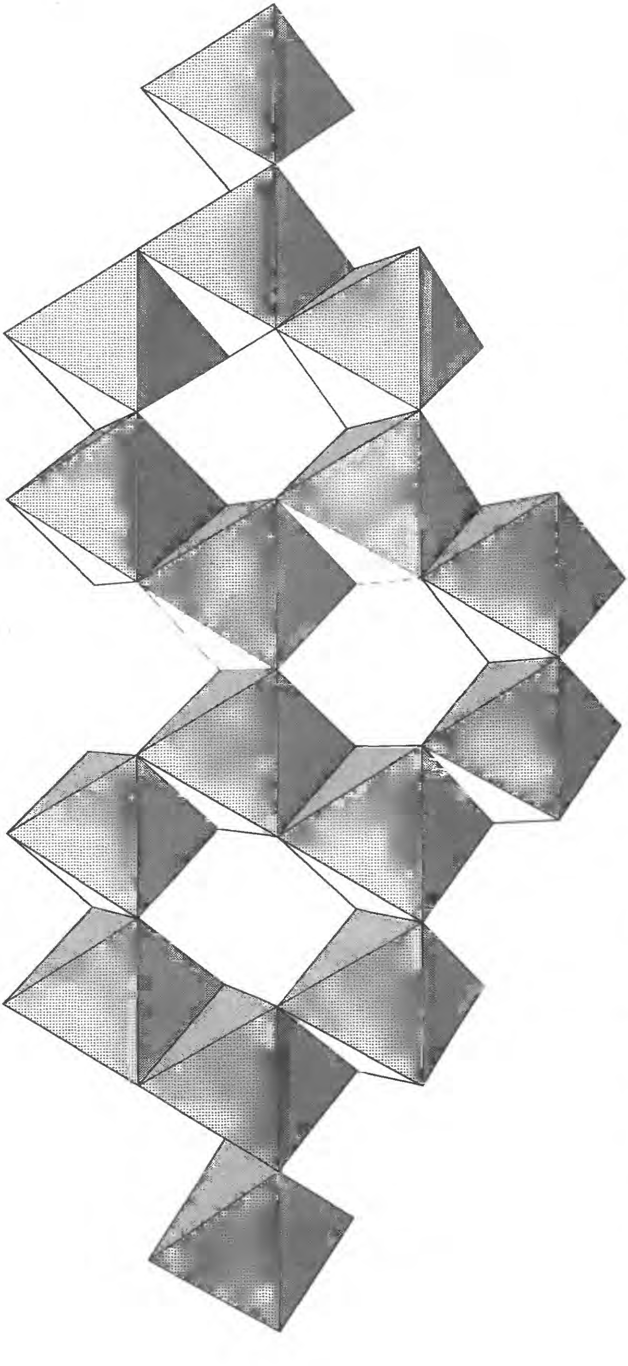

FIGURE 11.—Schematic representation of network of aluminum hydroxide octahedra (gibbsite structural pattern).

structures are about 9 A in maximum width. A particle 0.10 μ in diameter thus would contain many thousands of rings, and nearly all the hydroxide content would be structural.

MECHANISMS OF POLYMERIZATION

Faucherre (1954, p. 262) reported that at concentrations of Al^{+3} over 10^{-2} molar where $r \approx 1.0$, the dimer was predominant, but that the monomer predominated at concentrations below 5×10^{-3} molar. Although the dimer appears to be a symmetrical and perhaps stable configuration, it did not occur and probably should not be expected at the concentrations used in this study. Values of r near 1.0 would tend to favor formation of such units, if aluminum concentrations are high enough.

Polymerization, once begun in solutions of the concentrations here considered, evidently continues until a stable configuration is reached or some other restraint stops the process. Theoretical considerations, however, may be helpful in deciding what would happen. A straight-chain polymer is an unlikely species for reasons which have already been given. No doubt, when OH^- is added to aluminum solutions, rapid hydrolysis and accompanying association of aluminum and hydroxide ions occurs, and the structures are likely to be intricately branched with many rings. In the first-formed structures, water molecules may be in positions where the ideal structure requires OH^-, and OH^- might be where water would normally be expected.

No structural basis exists for supposing that small partly polymerized units such as $Al_4(OH)_8{}^{+4}$, $Al_6(OH)_{15}{}^{+3}$, $Al_6(OH)_{12}{}^{+8}$, and $Al_8(OH)_{20}{}^{+4}$ would be likely to persist over any wide range of pH or r values. Some species proposed in the literature would appear to violate the structural principles which have been outlined here.

The six-member-ring unit is apparently the most stable configuration that can be built up from six AlOH octahedra. However, there seems to be no reason, except perhaps the effects of other ions in the solution, why the polymer should stop growing at that stage. The six-member ring has six octahedral edges on its periphery where additional polymerization could occur. Loss of a proton would result in an OH^- appearing in one of these positions to form a site where an additional octahedron could attach, permitting conjunction of additional rings. The most probable mechanism for ring formation is the rearrangement of the more random structures which form early in the reaction of aluminum with hydroxide, but here again the single ring as a discrete unit would be likely only if some external influence, not considered here, were active in preventing polymeric forms from attaining more than a minimal size for the ratio $r=2.0$.

VERIFICATION OF POLYMERIC STRUCTURE

The assignment of an incipient gibbsite crystal structure to polymerized macromolecules of aluminum hydroxide is based principally on the extrapolation of X-ray diffraction results to aggregates of aluminum and hydroxide which have not reached a sufficient size to be separable from solution by filtration, or which are too small to give a definite diffraction pattern. The electron microscope was also used to study the polymerized material. The kinetic behavior of the bound OH^- in aged solutions provided further evidence of the nature of the structure of both filterable and nonfilterable fractions.

ELECTRON MICROSCOPY

A solution in which the value of r was 2.9 was aged for 48 days. At the end of this time its pH was nearly 4.0, and the solids obtained by filtration of a part of the solution gave the X-ray diffraction pattern of gibbsite. The fine-grained particulate material was also examined by means of the electron microscope. Figure 12 shows several particles of the polymerized hydroxide as viewed through the electron microscope. One of these particles (lower right in fig.12) has a well-defined hexagonal crystal pattern and is about 0.05 μ (500 A) in diameter. The hexagonal pattern is to be expected in a crystal growing at an equal rate in all directions in a single plane.

This photograph is good evidence that the organized crystal structure of gibbsite persists in the very small particles of the polymer. Particles this size cannot be isolated by filtration and are probably too small to give a well-defined X-ray diffraction pattern.

REACTION-RATE STUDIES

Differences may be expected between behavior of structural and nonstructural OH^- when aluminum hydroxide species are treated with H^+. For example, the single OH^- of the monomer or the nonstructural OH^- of other species might react quickly when the pH of the system is lowered, because the only process involved would be the transfer of a proton into the OH^- group, making it again a water molecule. Likewise, the aluminum present as Al^{+3} or $AlOH^{+2}$ would be expected to react quickly with the complexing reagents used in the spectrophotometric or fluorometric determination of aluminum. The bridging or structural OH in aluminum hydroxide species, on the other hand, can be expected to react in a more complicated way if H^+ is added. The OH–Al bonds must be broken before protons can combine with the structural OH groups whose charges are satisfied by Al^{+3}. All the aluminum ions are held together by at least one double bridge (shared edge), so there must be a simultaneous break of at least two OH–Al bonds to destroy the structure.

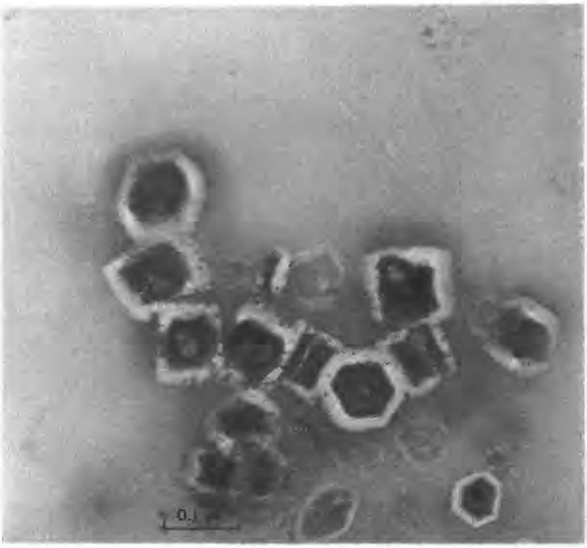

FIGURE 12.—Electron photomicrograph of microcrystalline gibbsite.

Although the details of the reaction mechanism have not been worked out, it seems likely that the structural OH will react more slowly and with a more complex rate law than the nonstructural OH.

A number of different types of experiments were performed to distinguish between and characterize the structural and nonstructural OH, including studies of rate of attack on the bound OH by hydrogen ions, stoichiometric behavior of hydroxide and aluminum, and behavior toward other complexing agents of aluminum held in the polymeric units.

The rate experiments were made with solutions containing 12.2 ppm (4.53×10^{-4} molal) total aluminum and bound OH ranging from $r=0.5$ to $r=3.0$. The solutions were aged in polyethylene bottles in a CO_2-free atmosphere at 25°C. Aliquots of 100 ml were then withdrawn, placed in a closed titration vessel equipped with glass and calomel electrodes, in a temperature-control bath and titrated with 0.101 molal perchloric acid at 25.0°C ±0.1°C in a nitrogen atmosphere. The pH was lowered by rapid addition of the acid to a preselected level, generally between 2.0 and 3.0, and near the pH of the aluminum perchlorate solutions containing no bound OH. This pH was maintained long enough (usually 2–4 hrs) to observe a reasonably steady reaction rate. Some of the titrations were made manually, observing the pH by means of a meter readable to 0.001 pH unit. The pH was held to the nearest 0.01 unit ±0.005 by additions of acid from a microburet. Other titrations were performed using a pH stat which maintained the pH of the test solution at a preselected value, ±0.01 of a pH unit, by automated additions of perchloric acid from a syringe burette. The instrument furnished a chart record of the rate of addition of acid. The pH stat enabled the observation of faster and slower reaction rates than could be followed readily by the manual technique.

In virtually all the rate experiments where the ratio of bound OH to total aluminum exceeded about 1.0, and where enough of the aluminum hydroxide species was present to give an interpretable result, a major part of the hydroxide reacted with the perchloric acid according to a well-defined pattern. The rate was slow, and in these experiments, where only the concentration of the polymer was allowed to vary, a first-order rate law was observed. When log concentration of residual bound OH was plotted against time, a straight line was obtained for solutions where polymerization had proceeded far enough to give a fairly well ordered product. The rate was slower for material aged for longer periods of time, up to about 10 days. Longer aging time had little effect on the rate.

Although the mechanisms which might be involved in setting the observed rate were not studied in detail, a slow rate for the reaction of hydrogen ions with the structural OH of the aluminum hydroxide complexes and polymers is not surprising. Disruption of such structures cannot be accomplished without simultaneous attack on the two OH groups which comprise the double bridges linking the aluminum ions in the structure.

In most of the solutions, a fraction of the bound OH reacted very rapidly with the H^+ added. Probably the fast reaction was caused by the monomeric or nonstructural OH.

Solutions in which r was less than 1.0 contained only fast-reacting hydroxide after about 10 days aging. In some of these solutions, slowly reacting hydroxide was present for a time after the solutions had been prepared, probably as a result of the localized formation of aluminum hydroxide polymers in parts of the solution where a high pH had existed during the addition of the sodium hydroxide reagent. This polymeric material disappeared during aging.

Results of three rate experiments on one of the highly polymeric solutions are given in table 5 and in figures 13 and 14. The solution used in these experiments was made up to have 13.55×10^{-4} moles per liter of bound OH and 4.53 moles per liter of aluminum. After the solution had stood for 2 hours, an aliquot was brought to pH 2.88 with perchloric acid and maintained at this pH by additions of acid for 45 minutes. A moderately rapid reaction took place, and after 45 minutes only about 19 percent of the original bound OH remained. In figure 13, the negative logarithm of the remaining concentration is plotted against elapsed time. The last half of the reaction period shows a straight-line relationship.

During the 2-hour aging period, the aluminum hydroxide polymer in solution J had little time to attain any degree of organization. However, some of the bound OH probably was functioning as bridging hydroxide between aluminum ions. If one extrapolates the approximately straight line attained after about 2000 seconds to its intercept

TABLE 5.—*Reaction rates of aluminum hydroxide polymer at pH 2.88 in relation to aging time*

[Solution J, $\Sigma C_{Al}=4.53\times10^{-4}$ moles per liter]

Age (hrs)	Time (seconds)	Reacted C_{OH_b} (moles per liter)	Residual C_{OH_b} (moles per liter)	$-\log C_{OH_b}$
$\Sigma C_{OH_b}=13.55\times10^{-4}$ moles per liter, pH 6.02				
2	0	0	13.55×10^{-4}	2.87
	60	1.90×10^{-4}	11.65×10^{-4}	2.93
	180	4.57×10^{-4}	8.98×10^{-4}	3.05
	300	6.86×10^{-4}	6.69×10^{-4}	3.17
	540	9.14×10^{-4}	4.41×10^{-4}	3.36
	780	9.79×10^{-4}	3.76×10^{-4}	3.42
	1,020	10.06×10^{-4}	3.49×10^{-4}	3.46
	1,260	10.34×10^{-4}	3.21×10^{-4}	3.49
	1,500	10.46×10^{-4}	3.09×10^{-4}	3.51
	1,740	10.62×10^{-4}	2.93×10^{-4}	3.53
	1,980	10.67×10^{-4}	2.88×10^{-4}	3.54
	2,220	10.78×10^{-4}	2.77×10^{-4}	3.56
	2,700	10.97×10^{-4}	2.58×10^{-4}	3.59
$\Sigma C_{OH_b}=13.56\times10^{-4}$ moles per liter, pH 5.91				
23	0	0	13.56×10^{-4}	2.868
	240	$.56\times10^{-4}$	13.00×10^{-4}	2.886
	480	$.76\times10^{-4}$	12.80×10^{-4}	2.892
	720	$.92\times10^{-4}$	12.64×10^{-4}	2.898
	960	1.02×10^{-4}	12.54×10^{-4}	2.902
	1,200	1.14×10^{-4}	12.42×10^{-4}	2.906
	2,400	1.65×10^{-4}	11.91×10^{-4}	2.924
	3,600	2.03×10^{-4}	11.53×10^{-4}	2.938
	4,800	2.44×10^{-4}	11.12×10^{-4}	2.954
	6,000	2.77×10^{-4}	10.79×10^{-4}	2.967
$\Sigma C_{OH_b}=13.59\times10^{-4}$ moles per liter, pH 5.54				
96	0	0	13.59×10^{-4}	2.867
	240	0	13.59×10^{-4}	2.867
	1,200	$.28\times10^{-4}$	13.31×10^{-4}	2.876
	2,400	$.51\times10^{-4}$	13.08×10^{-4}	2.883
	3,600	$.76\times10^{-4}$	12.83×10^{-4}	2.892
	4,800	1.02×10^{-4}	12.57×10^{-4}	2.901
	6,000	1.24×10^{-4}	12.35×10^{-4}	2.908
	7,200	1.35×10^{-4}	12.24×10^{-4}	2.912
	8,400	1.52×10^{-4}	12.07×10^{-4}	2.918
	9,600	1.73×10^{-4}	11.86×10^{-4}	2.926

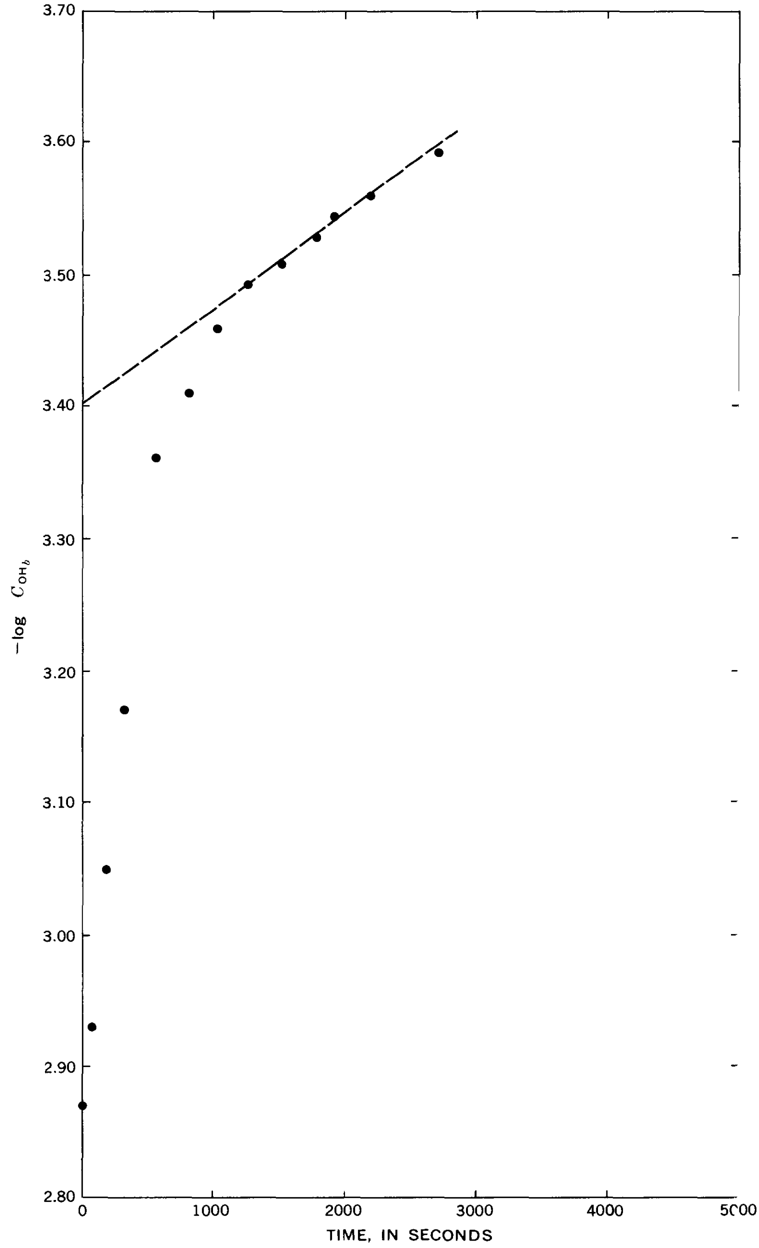

FIGURE 13.—Rate of reaction of freshly formed aluminum hydroxide with acid. Solution J aged 2 hours.

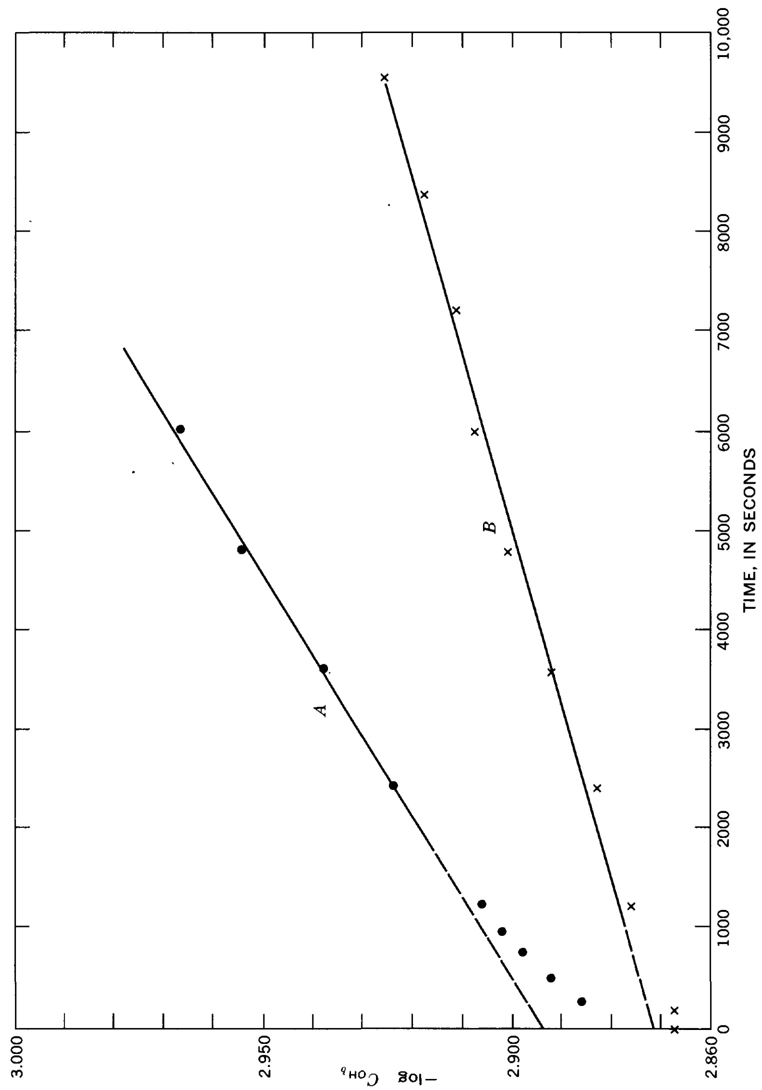

Figure 14.—Rates of reaction of aged aluminum hydroxide with acid. *A*, Solution *J* aged 23 hours. *B*, Solution *J* aged 96 hours.

at zero time (dashed line in fig. 13), the original content of structural OH appears to be about 3.8×10^{-4} moles per liter, or about 28 percent of the total.

Aging of the aluminum hydroxide produces definite changes in its behavior. Shown in table 5 and in figure 14 are the results obtained for aliquots of solution J after 23 hours and 96 hours of aging, respectively. The structural OH constituted about 95 percent of the total bound OH after 23 hours, and about 99 percent after 96 hours. Increasing the aging time also slowed the rate at which the structural OH was attacked at pH 2.88. The apparent rate constant decreased from 2.8×10^{-5} sec^{-1} after 23 hours aging to 1.3×10^{-5} sec^{-1} after 96 hours.

Another aliquot of solution J, aged for 11 days, produced results similar to those for the material aged 96 hours, but gave an apparent rate constant of 0.8×10^{-5} sec^{-1}. This was the lowest rate observed, and it was difficult to measure precisely. In most of the experiments the rate did not decrease much after 10 days of aging.

Results of a number of rate experiments for solutions where *r* values ranged from 0.97 to 3.00 are given in table 6. The dissolution was performed at the same pH (2.88) in most of these experiments, and a few general trends were found. The apparent rate constant decreases with aging of the solutions, and somewhat similar rates are observed for the solutions aged for comparable periods. Experimental error in the measurement of the rate constant becomes greater for solutions having smaller amounts of bound OH, and for some of the solutions there were inconsistencies in behavior. Not all experimental results could be duplicated. These difficulties probably stemmed from failure to attain an equilibrium distribution of species during aging. The small amount of the particulate species being studied may also have influenced the results.

The results of the experiments using different dissolution pH levels show that the aluminum hydroxide species are attacked more rapidly at lower pH. Additional experiments to determine the kinetic behavior of the polymer are needed before final conclusions on this phase of the research can be drawn. However, the differences in reaction rates permit calculation of species concentrations and aid in postulating the structure of the species.

The initial concentration of structural OH is obtained by extrapolation of the first-order reaction rate to zero time, and the nonstructural OH represents the difference between this value and the original calculated total concentration of bound OH. The experimental error in the determination of nonstructural OH by this procedure may be considerably more than 10 percent, and some of the

TABLE 6.—*Form of bound hydroxide deduced from rates of dissolution of aluminum hydroxide polymers and related species*

C_{OH_b} (moles per liter)	r	Age	pH		1st-order rate constant, k (sec^{-1})	OH (moles per liter)		Percent structural OH
			Initial	Dissolution		Structural	Nonstructural	
6.52×10^{-4}	1.44	94 hrs	4.59	2.88	3.8×10^{-5}	4.29×10^{-4}	2.23×10^{-4}	66
8.02×10^{-4}	1.77	72 hrs	4.58	2.88	1.4×10^{-5}	7.12×10^{-4}	$.90\times10^{-4}$	89
8.18×10^{-4}	1.80	36 days	4.43	2.88	1.5×10^{-5}	7.64×10^{-4}	$.54\times10^{-4}$	93
8.23×10^{-4}	1.82	49 days	4.38	2.88	1.4×10^{-5}	7.88×10^{-4}	$.35\times10^{-4}$	96
9.69×10^{-4}	2.14	72 hrs	4.62	2.88	2.7×10^{-5}	8.70×10^{-4}	$.99\times10^{-4}$	90
		144 hrs	4.63	2.88	1.7×10^{-5}	9.34×10^{-4}	$.35\times10^{-4}$	97
9.72×10^{-4}	2.15	35 days	4.47	2.88	1.9×10^{-5}	8.80×10^{-4}	$.98\times10^{-4}$	91
9.78×10^{-4}	2.16	49 days	4.42	2.88	1.2×10^{-5}	9.10×10^{-4}	$.68\times10^{-4}$	93
12.44×10^{-4}	2.75	24 hrs	5.22	2.88	2.6×10^{-5}	12.30×10^{-4}	$.14\times10^{-4}$	99
12.65×10^{-4}	2.77	96 hrs	5.10	2.88	2.0×10^{-5}	12.45×10^{-4}	$.20\times10^{-4}$	98
12.50×10^{-4}	2.76	260 hrs	4.78	2.39	4.3×10^{-5}	12.27×10^{-4}	$.23\times10^{-4}$	98
13.55×10^{-4}	2.99	2 hrs	6.02	2.88	17.0×10^{-5}	3.85×10^{-4}	9.70×10^{-4}	28
13.56×10^{-4}	2.99	23 hrs	5.91	2.88	2.8×10^{-5}	12.91×10^{-4}	$.65\times10^{-4}$	95
		25 hrs	5.92	2.50	4.3×10^{-5}	12.58×10^{-4}	$.98\times10^{-4}$	93
13.59×10^{-4}	3.00	96 hrs	5.54	2.88	1.3×10^{-5}	13.51×10^{-4}	$.08\times10^{-4}$	99+
		260 hrs	5.54	2.88	$.8\times10^{-5}$	13.51×10^{-4}	$.08\times10^{-4}$	99+

differences in nonstructural OH observed after different aging times are probably the result of lack of precision in the calculated values. In some of the solutions aged for short periods, equilibrium distributions of aluminum species obviously had not been attained and the results of the kinetic study should, therefore, be interpreted with caution.

INTERPRETATION OF RESULTS OF RATE STUDIES

In several respects, the results of the dissolution rate experiments give significant insights into the nature of the aluminum hydroxide combinations. The three general conclusions which may be drawn are:

1. The slow rate of reaction with respect to hydrogen ion concentration is additional evidence of the existence in the structure of the aluminum hydroxide polymer of double OH bridges already postulated from the crystal structures observed in filtered residues.
2. The rate experiments provide a basis for estimating the proportion of structural to total bound OH, and thus the degree of polymerization which exists. Where considerable polymerization has occurred, it is possible to calculate the concentrations of uncomplexed aluminum in the solutions for use in determining equilibrium solubilities.
3. The calculated apparent rate constants provide information showing the increasing degree of order within the polymerized aggregates and the rate at which equilibrium conditions among the dissolved and particulate species are approached.

It should be emphasized that these rate studies do not constitute a rigorous investigation of the kinetics of the system. In such an investigation, more attention would have to be paid to the actual chemical mechanisms and to the activation energies and other properties of the aluminum hydroxide species. The results used here were obtained only to aid in understanding the general behavior of the aluminum hydroxide species. The more detailed characterization of their kinetics remains to be investigated.

The reaction mechanism whereby aluminum hydroxide species are brought into solution in acid probably involves various intermediate stages in which some form of double OH bridging is attacked by H^+ to yield hydrated Al^{+3}:

$$(H_2O)_4Al(OH)_2Al(H_2O)_4^{+4}+2H^++2H_2O=2Al(OH_2)_6^{+3}.$$

The structural model proposed for the aluminum hydroxide polymer is based on a lattice of aluminum ions bound together by double OH bridging. For the reaction of H^+ to hydrolyze such a structure, the OH linkages would have to be destroyed two at a time. Thus, the fundamental process, probably the one which is rate determining, is bimolecular in nature and can be written

$$\text{bridged } (OH^-)_2 + 2H^+ = 2H_2O.$$

It is logical to expect, and satisfying to note, that the rate data support the postulated structure of the complex polymers. Although the size of the aggregates must be inferred from other considerations, the fundamental nature of the structure seems clearly indicated.

The rate experiments typically showed that a somewhat greater amount of acid had to be added to attain the desired dissolution pH than could be accounted for by the free OH content and by dilution effects. This difference is ascribed to bound OH^-, which, so far as can be determined, reacts rapidly with the added H^+, but not according to well defined rate law. The fraction of the bound OH^- which enters into this initial rapid reaction is largest in the solutions which were relatively fresh, and decreased on aging. The rapidly reacting fraction became very small in the solutions having r values of about 2 or more. In solutions where r was 0.5 or less, the entire amount of bound OH^- generally reacted rapidly, regardless of aging.

Results of rate experiments were used to compute concentrations of $AlOH^{+2}$ and Al^{+3} on the basis of the following assumptions:

1. Slowly reacting bound OH^- is polymerized in a form in which, as a first approximation, the OH:Al ratio is 3.0.
2. Fast reacting bound OH^- is present as the equivalent of $AlOH^{+2}$.

The concentrations of aluminum present as Al^{+3}, $AlOH^{+2}$, and $Al(OH)_3$ polymerized are computed from the known total concentrations of bound OH and aluminum:

$$C_{AlOH} = C_{OH_b\,(\text{fast reacting})}$$

$$C_{Al(OH)_3} = 1/3\, C_{OH_b\,(\text{slowly reacntig})}$$

$$C_{Al^{+3}} = \sum C_{Al} - C_{AlOH} - C_{Al(OH)_3}$$

Neither assumption is correct for all conditions. From figure 9 it is evident that the assumption that the polymerized aluminum hydroxide contains three structural OH ions per Al^{+3} ion is a good approximation only when the polymeric units contain considerably more than 100 Al^{+3} ions.

The assumptions probably tend to assign too much aluminum to the $AlOH^{+2}$ form and not enough to the polymer. They do, however, provide a basis for computing the concentration of uncomplexed Al^{+3} and the monomer $AlOH^{+2}$. Values obtained for 12 aged solutions are given in columns 5 and 6 in table 7.

TABLE 7.—*Rapidly reacting aluminum determined by ferron compared with calculated values for* Al^{+3} *and* $AlOH^{+2}$

Solution	Age (days)	pH	Total $C_{Al\ detn.}$	$C_{Al^{+3}calc.}$	$C_{AlOH^{+2}calc.}$	Total $C_{Al\ calc.}$
C	49	4.49		2.73×10^{-4}	0.56×10^{-4}	3.29×10^{-4}
	136	4.50	3.48×10^{-4}			
D	49	4.34		2.00×10^{-4}	$.56\times10^{-4}$	2.56×10^{-4}
	136	4.24	2.25×10^{-4}			
E	49	4.38		1.41×10^{-4}	$.56\times10^{-4}$	1.97×10^{-4}
	136	4.31	1.89×10^{-4}			
F	48	4.43		$.90\times10^{-4}$	$.41\times10^{-4}$	1.31×10^{-4}
	135	4.38	1.41×10^{-4}			
G	11	4.43		3.42×10^{-4}	$.41\times10^{-4}$	3.82×10^{-4}
	98	4.45	3.86×10^{-4}			
H	11	4.78		$.21\times10^{-4}$	$.23\times10^{-4}$	$.44\times10^{-4}$
	98	4.50	$.44\times10^{-4}$			
J	11	5.25		0.00	$.12\times10^{-4}$	$.12\times10^{-4}$
	98	4.92	$.12\times10^{-4}$			
K	62	4.61				$.44\times10^{-4}$
	69	4.75	$.43\times10^{-4}$			
L	62	4.78		$.26\times10^{-4}$	$.18\times10^{-4}$	$.44\times10^{-4}$
	69	4.96	$.32\times10^{-4}$			
M	62	4.85		$.17\times10^{-4}$	$.15\times10^{-4}$	$.32\times10^{-4}$
	69	5.03	$.27\times10^{-4}$			
N	62	4.84		$.083\times10^{-4}$	$.11\times10^{-4}$	$.19\times10^{-4}$
	69	5.08	$.13\times10^{-4}$			
O	62	5.74		$.11\times10^{-4}$	$.01\times10^{-4}$	$.12\times10^{-4}$
	69	6.05	$.02\times10^{-4}$			

DIRECT DETERMINATION OF UNPOLYMERIZED ALUMINUM

An independent check on the accuracy of the calculated values for aluminum in table 7 was made by determining dissociated aluminum, using a modification of the ferron procedure. The modification was intended to decrease to a negligible level the response of the procedure to polymerized forms of aluminum hydroxide.

Some indication of the behavior of ferron toward Al^{+3} and $AlOH^{+2}$ can be gained from published stability constants. The ferron reagent (8-hydroxy 7-iodoquinoline 5-sulfonic acid) forms a colored complex with aluminum which absorbs visible radiation most effectively at a wavelength of 370 millimicrons. The association constants quoted by Sillén and Martell (1964, p. 614) for ferron indicate that the reagent has two dissociable hydrogens, but that at pH 5.0 only the first dissociation step has taken place. The stability data quoted for the aluminum complex indicate that an uncharged species with three ferron units per Al^{+3} would probably be formed. The stability constants for the stepwise complexing process are:

$$Al^{+3}+HL^{-}=AlHL^{+2},\ K_1=10^{7.6}$$

$$AlHL^{+2}+HL^{-}=Al(HL)_2{}^{+},\ K_2=10^{7.1}$$

$$Al(HL)_2{}^{+}+HL^{-}=Al(HL)_3{}^{0},\ K_3=10^{5.6}$$

where HL^{-} represents the half-dissociated ferron.

In any event, the first step is the critical one. If the equilibrium

$$Al^{+3}+H_2O=AlOH^{+}+H^{+}$$

for which various investigators have reported $^{*}K_1$ to be near 10^{-5} is subtracted from the first step in the ferron complexing process, we obtain

$$AlOH^{+2}+H^{+}+HL^{-}=AlHL^{+2}+H_2O$$

for which $K_{eq}=10^{12.6}$. From the mass law relationship

$$\frac{[AlHL^{+2}]}{[AlOH^{+2}]}=10^{12.6}\ [H][HL].$$

The ratio in the analytical solutions at pH 5.0 in the presence of 10^{-4} moles per liter of ferron, is strongly weighted in favor of the ferron complex, hence it seems safe to assume the AlOH form will be fully determined at equilibrium, and probably the reaction will be rapid. Okura, Goto, and Yotuyanagi (1962) found that a solution of 8-quinolinol did not complex polymeric aluminum hydroxide species. The ferron reagent has the same basic structure as 8-quinolinol but with additional substituted iodide and sulfonic acid groups.

In the standard ferron procedure, the aliquots are treated with hydroxylamine as a first step which lowers the pH to about 1.5. At this pH some polymerized aluminum will be converted to a determinable form, in time, especially if the polymer is freshly formed. The order in which reagents were added in the ferron procedure was altered so that the hydroxylamine was the last reagent added. Under these conditions the polymerized aluminum hydroxide is not exposed to a pH less than about 5. Hopefully, the results should include only Al^{+3} and $AlOH^{+2}$. This hope was not completely realized, as the intensity of the color of the aluminum-ferron complex increased slowly on standing. However, readings of the spectrophotometer taken a few minutes after adding the reagents probably represent Al^{+3} and $AlOH^{+2}$ with relatively insignificant amounts of polymerized forms.

If the aluminum determined includes only Al^{+3} and $AlOH^{+2}$, then the amount of aluminum which is rapidly reacting in these experiments should be comparable to the amount which was calculated from the studies of rate of dissolution by acid. In column 4 of table 7 are shown the concentrations of aluminum determined after 5 minutes of contact with ferron at pH 5 for 12 of the solutions used in the studies of dissolution in acid. For comparison, the last column of the table gives calculated values for the total of the Al^{+3} and $AlOH^{+2}$ fractions calculated from the kinetic experiments. Although the aging times were different for these sets of data, all solutions were aged at least 11 days. Aging longer than 11 days produced only minor changes in the polymerization; therefore, all the results are presumed to be comparable.

The total of the two calculated values agrees fairly well with the determined value given in table 7 for each of solutions C through J. This general agreement of results suggests that the same forms of dissociated aluminum were probably observed in both sets of experiments.

REPLACEMENT OF HYDROXIDE BY FLUORIDE IONS

Kinetic experiments were not made on the more dilute solutions K through O in table 7. To obtain some information on the free-aluminum content of these solutions, a procedure more sensitive than that used in dissolution-rate experiments was developed. In this revised procedure a solution of 0.1 *M* sodium fluoride was added to the aged samples, and the effect on pH determined. The dimensions and charge of F^- ions are similar to those of OH^- ions. The relative stability of the complexes can be evaluated from the equilibrium

$$AlOH^{+2}+F^-=AlF^{+2}+OH^-,$$

for which the equilibrium constant is $10^{-2.02}$ (calculated from free-energy data). At pH 5, the activity of OH^- is 10^{-9}; therefore, at equilibrium the fluoride complex will be strongly predominant, and F^- should quickly replace any OH^- held to aluminum by single bonds. The F^- also would probably tend to replace some of the structural or bridging OH in the complexes and polymers, but at a relatively slow rate.

The predicted behavior was generally observed—a rapid rise in pH occurred following addition of F^- ions. The released OH was calculated from the initial pH, and the observed pH change was assumed to be equivalent to the initial $AlOH^{+2}$ content. The remaining OH bound to aluminum was assumed to be polymeric, as it was in the acid-dissolution experiments, and the aluminum remaining as Al^{+3} could thus be computed for solutions L through O. Solution K contained so little bound OH that the amount of $AlOH^{+2}$ was negligible. The agreement for determined and calculated aluminum species for solutions K through O was not quite as good as for the more concentrated solutions.

The approximate agreement of the results in table 7 indicates that the Al^{+3} and $AlOH^{+2}$ concentration estimates may be used to calculate a solubility product for the colloidal $Al(OH)_3$ polymer, and to compute values for the first hydrolysis constant $*K_1$, from the equilibrium

$$Al^{+3}+H_2O=AlOH^{+2}+H^+.$$

CALCULATION OF ALUMINUM HYDROXIDE SOLUBILITY

Values of $C_{Al^{+3}calc.}$ from table 7 were converted to activities using the activity coefficient 0.427 previously calculated, and the negative logarithms of the activities were plotted against pH in figure 15. Some additional points were obtained from acid-dissolution experiments not included in table 7.

Most of the points in figure 15 are clustered near pH 4.50 and p[Al] 4.20. A line with a slope of −3.0 was drawn through the approximate centroid of these points. Solutions H, L, M, and N gave results that plotted very close to the line. The point for solution O is considerably out of line, and agreement between calculated and determined aluminum values is not good, so this point was not considered significant. The points for these five solutions are represented in figure 15 by the symbol "x".

The value of K_{S0} given by the expression

$$K_{S0}=[Al][OH]^3$$

can be determined from the relationships shown in figure 15 as $10^{-32.65}$. The $\Delta G°$ for the solid microcrystalline gibbsite identified in the experiments in this investigation is −272.3 kcal. This is more than a kilocalorie less negative than the values given by Latimer (1952) and by Barany and Kelley (1961) for gibbsite, but is a little more negative than the value of −271.9 kcal per mole given by Latimer for amorphous $Al(OH)_3$. The scatter of points used in drawing the solubility curve in figure 15 is equivalent to an uncertainty in the K_{S0} value of about ±0.3 log units and ±0.4 kcal in $\Delta G°$ for microcrystalline gibbsite. The activities of dissolved aluminum in equilibrium with 1-day-aged $Al(OH)_3$ and bayerite are indicated by dashed lines in figure 15 which was taken from figure 4.

Figure 15 is a synthesis of all the solubility data obtained during this investigation. It indicates the minimum dissolved activity of aluminum would be reached between pH 5.5 and 6.0.

Free-energy values for both the solid and the solute species of aluminum present above the isoelectric point could not be calculated

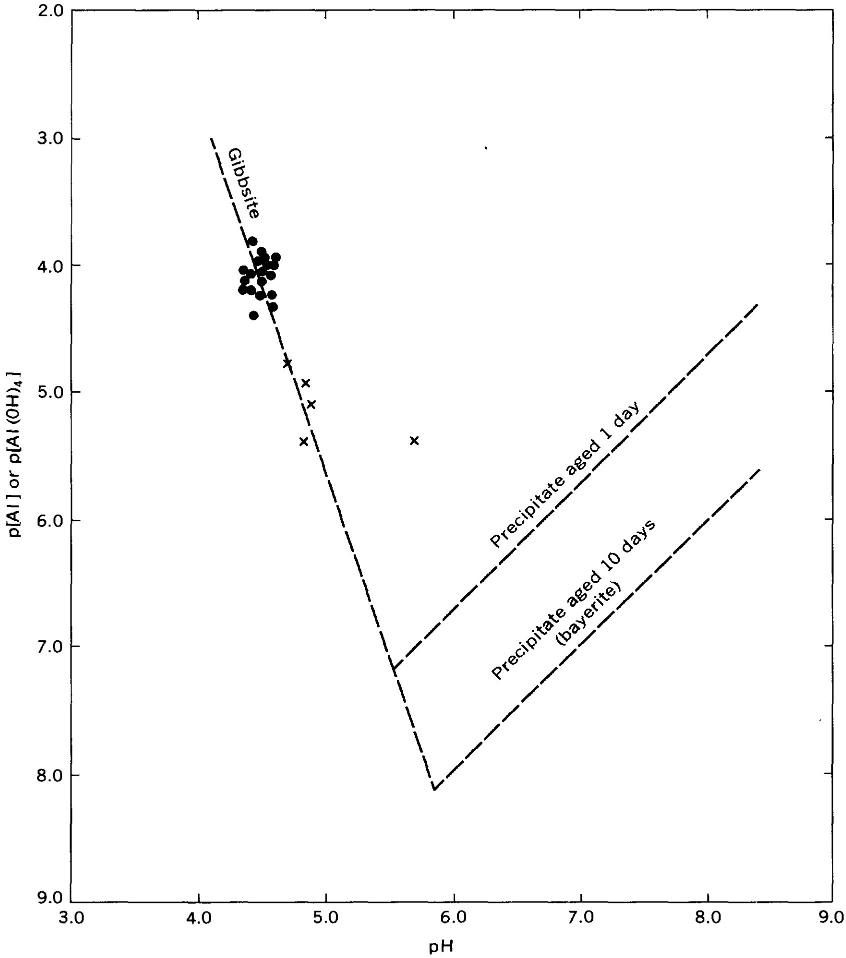

FIGURE 15.—Solubility of microcrystalline gibbsite and other aluminum hydroxide species.

directly from the solubility experiments conducted in alkaline solutions. It is now possible, however, to evaluate both, using the free energy for microcrystalline gibbsite determined in experiments below the isoelectric point as representative of the free energy of formation of the first solid to appear above the isoelectric point. Although this assumption cannot be proved, it seems reasonable, especially because both amorphous aluminum hydroxide and microcrystalline gibbsite were identified by X-ray in solutions whose pH was near 7.0.

If the free energy of formation calculated for microcrystalline gibbsite is used with the solubility values obtained in the experiments above the isoelectric point, a value for free energy of $Al(OH)_4^-$ can be obtained from the relationship

$$\Delta G^\circ_{Al(OH)_4} = \Delta G^\circ_{Al(OH)_{3(c)}} + \Delta G^\circ_{H_2O} - RT \ln {}^*K_{S4}$$
$$= -311.67 \text{ kcal per mole.}$$

This value is in good agreement with values of ΔG° that can be calculated from published results of other investigations (for example, Szábo and others, 1955) in which precipitation from supersaturated solutions was studied. It is less negative than values obtained by calculations based on the published values for well-crystallized solids (Deltombe and Pourbaix, 1956), or based on experiments in which well-crystallized material was exposed to undersaturated solutions (Raupach, 1963a).

It is further possible to calculate the free energy of formation of bayerite and the amorphous material present after 16–24 hours. The value obtained for 1-day aged material is the same as that for microcrystalline gibbsite ($\Delta G^\circ = -272.3$ kcal per mole). The value calculated for bayerite is -274.0 kcal per mole.

Upon very long aging, the microcrystalline gibbsite may be converted to a less soluble form having larger crystal aggregates. Aging periods in the experiments described here (up to 6 months) were not long enough to produce such material.

CALCULATION OF $^*K_1$

The equations required for the computation of $^*K_1$ include

$$\sum C_{Al} = \frac{[Al^{+3}]}{\gamma_{Al^{+3}}} + \frac{[AlOH^{+2}]}{\gamma_{AlOH^{+2}}}$$

$$C_{AlOH^{+2}} = \frac{[AlOH^{+2}]}{\gamma_{AlOH^{+2}}}$$

$$^*K_1 = \frac{[AlOH^{+2}][H^+]}{[Al^{+3}]}.$$

The total concentration of dissolved aluminum, ΣC_{Al}, is the value obtained from the kinetic studies of unpolymerized aluminum, and the concentration of $AlOH^{+2}$ also was obtained from the kinetic studies, as previously described. The activity coefficients were computed from the extended Debye-Hückel equation. The results of the computation of $^*K_1$ are given in table 8. The 19 sets of data give a mean value for the activity product of 1.8×10^{-5}; extreme

TABLE 8.—*Computation of* $^*K_1$

[Concentrations in moles per liter]

C_{OH_b}	Age (hrs)	pH	$C_{AlOH^{+2}}$	$C_{Al^{+3}}$	[AlOH^{+2}]	[Al^{+3}]	[H$^+$]	$^*K_1$
2.40×10^{-4}	430	4.50	0.71×10^{-4}	3.26×10^{-4}	0.48×10^{-4}	1.39×10^{-4}	3.16×10^{-5}	1.1×10^{-5}
2.48×10^{-4}	23	4.48	$.49\times10^{-4}$	3.38×10^{-4}	$.33\times10^{-4}$	1.44×10^{-4}	3.31×10^{-5}	$.76\times10^{-5}$
2.51×10^{-4}	260	4.43	$.41\times10^{-4}$	3.42×10^{-4}	$.28\times10^{-4}$	1.46×10^{-4}	3.72×10^{-5}	$.71\times10^{-5}$
4.20×10^{-4}	90	4.58	1.10×10^{-4}	2.40×10^{-4}	$.75\times10^{-4}$	1.02×10^{-4}	2.63×10^{-5}	1.9×10^{-5}
4.29×10^{-4}	70	4.50	$.79\times10^{-4}$	2.57×10^{-4}	$.54\times10^{-4}$	1.10×10^{-4}	3.16×10^{-5}	1.6×10^{-5}
4.24×10^{-4}	140	4.52	$.84\times10^{-4}$	2.52×10^{-4}	$.57\times10^{-4}$	1.08×10^{-4}	3.02×10^{-5}	1.6×10^{-5}
4.28×10^{-4}	860	4.50	$.84\times10^{-4}$	2.54×10^{-4}	$.57\times10^{-4}$	1.09×10^{-4}	3.16×10^{-5}	1.7×10^{-5}
4.28×10^{-4}	1180	4.49	$.56\times10^{-4}$	2.73×10^{-4}	$.38\times10^{-4}$	1.17×10^{-4}	3.24×10^{-5}	1.1×10^{-5}
6.59×10^{-4}	138	4.50	$.35\times10^{-4}$	2.10×10^{-4}	$.24\times10^{-4}$	$.90\times10^{-4}$	4.50×10^{-5}	1.2×10^{-5}
6.34×10^{-4}	72	4.57	$.86\times10^{-4}$	1.84×10^{-4}	$.58\times10^{-4}$	$.79\times10^{-4}$	2.69×10^{-5}	2.0×10^{-5}
6.32×10^{-4}	142	4.58	$.96\times10^{-4}$	1.79×10^{-4}	$.65\times10^{-4}$	$.76\times10^{-4}$	2.63×10^{-5}	2.2×10^{-5}
6.44×10^{-4}	860	4.38	$.71\times10^{-4}$	1.91×10^{-4}	$.48\times10^{-4}$	$.82\times10^{-4}$	4.17×10^{-5}	2.4×10^{-5}
6.48×10^{-4}	1180	4.34	$.56\times10^{-4}$	2.00×10^{-4}	$.38\times10^{-4}$	$.85\times10^{-4}$	4.56×10^{-5}	2.0×10^{-5}
8.12×10^{-4}	143	4.59	$.74\times10^{-4}$	1.33×10^{-4}	$.50\times10^{-4}$	$.57\times10^{-4}$	2.57×10^{-5}	2.3×10^{-5}
8.18×10^{-4}	860	4.43	$.48\times10^{-4}$	1.51×10^{-4}	$.33\times10^{-4}$	$.64\times10^{-4}$	3.72×10^{-5}	1.9×10^{-5}
8.23×10^{-4}	1180	4.38	$.56\times10^{-4}$	1.41×10^{-4}	$.38\times10^{-4}$	$.60\times10^{-4}$	4.17×10^{-5}	2.6×10^{-5}
$.25\times10^{-4}$	1490	4.78	$.18\times10^{-4}$	$.26\times10^{-4}$	$.12\times10^{-4}$	$.11\times10^{-4}$	1.66×10^{-5}	1.8×10^{-5}
$.55\times10^{-4}$	1490	4.85	$.15\times10^{-4}$	$.17\times10^{-4}$	$.10\times10^{-4}$	$.073\times10^{-4}$	1.41×10^{-5}	1.9×10^{-5}
$.88\times10^{-4}$	1490	4.84	$.11\times10^{-4}$	$.083\times10^{-4}$	$.075\times10^{-4}$	$.035\times10^{-4}$	1.45×10^{-5}	3.1×10^{-5}
Mean $^*K_1$								1.8×10^{-5}

values are 0.71×10^{-5} and 3.1×10^{-5}. It would appear from the results of this computation that a reasonable value would be $(1.8 \pm 1.0) \times 10^{-5}$ for the first hydrolysis constant $*K_1$. In log units the range of the values would be -4.55 to -5.10. As noted previously, the values given for $*K_1$ in recent literature are generally near 10^{-5}.

Solutions in which $AlOH^{+2}$ is likely to constitute a major part of the dissolved aluminum evidently have a narrow range of pH. The value of $*K_1$ is fairly consistent for a considerable range of r and for total aluminum concentrations of 0.45×10^{-4} as well as 4.53×10^{-4}. The spread of the individual values would have been increased by by assuming the presence of $Al(OH)_2^+$, or of polymeric species in which r was less than 3.0.

FACTORS CONTROLLING pH

Owing to the high proportion of structural OH present in polymerized species, no close relationship of pH to degree of polymerization was found. For example, a pH of 4.43 was measured in a solution in which over half the aluminum was slowly reacting or polymerized, and the same pH was measured in a solution in which only 15 percent of the aluminum was polymerized. Also, the same, or nearly the same, pH was observed where the ratio of Al^{+3} to $AlOH^{+2}$ was near 8 as where the ratio was near 4. In general, however, the pH does appear to correlate to a limited extent with the relative and total concentrations of the dissociated species. Correlation with the polymeric forms, especially if they are present as colloidal suspensions, is not really to be expected.

The polymeric aggregates grow during aging, and a general downward drift in pH takes place as protons are transferred from H_2O molecules held in the octahedra and ultimately appear in solution, as all the internal positions on the Al octahedra are occupied by OH^- ions. The ability of bridging OH to enter into equilibria related to the solution pH is limited by the slow rate at which such bridges can be broken once they have become established. Effective buffering can only be exerted by more active and available species such as $AlOH^{+2}$.

As the polymerization nears completion, the amounts of free Al^{+3} and $AlOH^{+2}$ decrease to very low levels. When ions with buffering capacity are scarce, the pH is controlled by sorption-desorption reactions along the edges of polymerized particles where unsatisfied chemical bonds may exist. Effects of polymeric species on solution pH were observed qualitatively in several experiments. Filtration through filters having 0.10 μ pore diameters caused increases of several tenths of a pH unit in solutions where r was very near 3.0. These solutions were very poorly buffered, however.

SUMMARY AND CONCLUSIONS

The results of the experimental studies can be summarized as follows:

1. Aluminum hydroxide precipitates formed in dilute perchlorate solutions from pH 7.5 to pH 9.5 are initially composed of material having the solubility of boehmite, $*K_{S4}=2.0 \pm 1.0 \times 10^{-13}$.
2. Aging in solution for 10 days alters the precipitate formed between pH 7.5 and pH 9.5 to bayerite, $*K_{S4}=1.11 \times 10^{-14}$.
3. The predominant dissolved aluminum species between pH 7.5 and pH 9.5 is the anion, $Al(OH)_4^-$, when competing ligands are absent.
4. Aluminum ions in solution in water below about pH 7.5 are octahedrally coordinated with respect to water molecules or hydroxide ions.
5. When the average number of hydroxide ions bound to each aluminum ion rises above 1.0, polymerization of the octahedra through sharing of edges takes place. This polymerization process ultimately gives rise to planar sheets in which each aluminum ion shares three pairs of hydroxide ions with three other aluminum ions; this is the crystal structure of gibbsite.
6. Any explanation of the behavior of aluminum in solution below pH 7.5 in the presence of hydroxide ions must be compatible with a structural pattern which leads to a gibbsitelike lattice.
7. In solutions 10^{-4} molal in aluminum and having a ratio of bound OH to Al ranging from about 1 to 3, the pH tends to decrease on aging. This decrease in pH, which may continue for many months, is brought about by polymerization of aluminum hydroxide species. In solutions 10^{-5} molal in aluminum, the effects of polymerization on pH during aging are less marked than at higher concentrations.
8. After polymerization, solutions in which the ratio of bound OH to aluminum is 2.0 or more have filterable aluminum hydroxide (gibbsite) particles more than 0.10 μ in diameter.
9. Polymers less than 0.10 μ in diameter cannot be filtered out. The polymers react very slowly both with complexing reagents used in determining dissolved aluminum, and with H^+.
10. The polymers dissolve in acid at a slow rate because H^+ must react with two OH bridges simultaneously to break down the structure.

11. From reaction-rate data, the ion $AlOH^{+2}$ was found to be a significant part of the dissociated aluminum species in most solutions studied. The equilibrium constant for the reaction

$$Al^{+3} + H_2O \rightleftarrows AlOH^{+2} + H^+$$

is $(1.8 \pm 1.0) \times 10^{-5}$.

12. From calculated Al^{+3} activities, polymeric $Al(OH)_3$ has a solubility product of 2.24×10^{-33}. The standard free energy of formation for this microcrystalline gibbsite is −272.3 kcal per mole. The material to which this value applies consists of particles near 0.10 μ in diameter.
13. Although the processes involved in solution or precipitation of aluminum hydroxide are commonly summarized in a simple chemical equilibrium, a relatively complicated reaction scheme would probably be nearer reality. In this reaction scheme there are slow steps and fast steps. For example, the first precipitate to appear may be the product of a fast process, but the aging of this material to a less soluble and more highly crystalline form is a much slower process. A reasonable understanding of the chemistry of such a system requires attention to the various steps and cannot be attained merely by generalized equilibrium treatment.

APPLICATION TO NATURAL CONDITIONS

Geochemical systems often involve complex stepwise reactions, and proper attention to the reaction mechanisms is required in studying them. Also, the conditions under which a reaction is taking place may change greatly with time. In weathering reactions, for example, periodic dehydration and probably drastic pH changes will occur. Thus the simple application of reversible chemical thermodynamics will often fail to give a useful interpretation of geochemical behavior.

The experiments designed for this study utilized solutions which contained more aluminum than is generally found in natural water. Some waters of low pH no doubt do contain as much as, or more than, the 12.2 ppm aluminum which was used for most of the experiments, but concentrations this high are unusual. Most natural waters contain considerably less than 1 ppm in solution. Polymerization of aluminum hydroxide species may take place at concentrations near 1 ppm, and, possibly, routine wet methods for aluminum analysis will give low results.

The behavior of aluminum in natural water is complicated by the fact that most such waters contain solutes such as silica, fluoride, and sulfate which are likely to influence the behavior of aluminum. Precipitates containing aluminum and silica were obtained in dilute solutions by Harder (1965). Siffert (1962) reported a synthesis of kaolinite from a mixture of dilute solutions of silicic acid and an organic complex of aluminum.

Aluminum is known to form complexes with fluoride, and the tendency for aluminum hydroxide polymers to form in solution may be decreased in the presence of fluoride. In the experiments conducted during this investigation, the presence of about 100 ppm F^- had a very decided effect on aluminum behavior. This, however, is a much higher fluoride concentration than is normally to be expected in natural solutions, but the mole ratio of fluoride to aluminum (about 10) is in the range of normal expectancy.

The effects of dissolved fluoride, silica, and sulfate on behavior of aluminum will be described in another report in this series.

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