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GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1827-B

U.S. DEPARTMENT OF THE INTERIOR
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By J. D. HEM

CHEMISTRY OF ALUMINUM IN NATURAL WATER

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Mathematical procedures used to prepare graphs by which the series of soluble aluminum complexes with fluoride and sulfate are described

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GRAPHICAL METHODS FOR STUDIES OF AQUEOUS ALUMINUM HYDROXIDE, FLUORIDE, AND SULFATE COMPLEXES

By J. D. Hem

ABSTRACT

Published stability constants show that aluminum forms strong complexes with hydroxide, fluoride, and sulfate ions. Equilibrium calculations show that fluoride complexes probably will be the predominant form of aluminum solute species in natural water below neutral pH, when more than a few tenths of a part per million of fluoride, is present. Sulfate complexes of aluminum can be important below neutral pH if sulfate concentrations exceed 500 parts per million.

By means of graphs, the predominant complex species and proportion of uncomplexed aluminum activity to total aluminum concentration are shown as functions of the analytical concentration of aluminum and fluoride, or sulfate, for ionic strengths ranging from zero to that of sea water. In alkaline solutions the species $Al(OH)_4^-$ tends to predominate. The forms of aluminum complexes which can be expected to predominate, and extent of complexing in solutions containing both fluoride and sulfate, and the effects of pH on the complexing of aluminum by fluoride and sulfate also are shown by means of graphs.

INTRODUCTION

The chemical behavior of aluminum in aqueous systems is strongly influenced by the tendency of aluminum to form soluble complex ionic species with various ligands. Earlier work has shown (Hem and Roberson, 1967) that aluminum ions in solution below neutral pH are six-coordinated with respect to water molecules or hydroxide ions. In alkaline water $Al(OH)_4^-$ predominates. Fluoride ions form a six-coordinated series of solute complexes with aluminum. Sulfate also forms soluble complexes with aluminum. Some of these complexing effects are strong enough to interfere in analyses for aluminum.

Thermodynamic data are available for hydroxide, fluoride, and sulfate solution complexes of aluminum. The compilation of stability constants by Sillén and Martell (1964) contains references to some complexes of aluminum with orthophosphate and with organic ligands.

These complexes may be of importance in some natural waters but too little is known of the occurrence of the organic ligands for the complexes to be considered in this paper. The Sillén and Martell compilation also cites studies which found no anionic chloride complexes of aluminum in strong solutions of hydrochloric acid. Whether cationic complexes with chloride or bicarbonate would form is not known, but the absence of data may suggest that such complexes are relatively weak.

Mathematical treatment, assuming chemical equilibrium, can be used to find the predominant dissolved species in systems where any or all of the principal complexing ligands occur; it can also be used to give the proportion of complexed aluminum in solution. In this paper both kinds of calculations have been made for systems containing hydroxide, fluoride, and sulfate. The results of the calculations are presented in the form of graphs which can be used to evaluate directly the degree of complexing and the nature of the species present when total analytical concentrations of aluminum and ligand are known.

SOLUBILITY CALCULATIONS

The calculations and graphs presented in this report are not directly indicative of aluminum solubility. They are intended principally as guides to the type of aluminum solute species and the extent of aluminum complexing if the ionic concentrations that are assumed actually occur.

In the experiments and calculations relating to proportions of the various solute species, no postulations are made as to solid species that might precipitate. Because the graphs given in this paper show some rather high concentrations, it seems likely that solids would form and that they would prevent conditions shown in some parts of the diagrams from being actually attained. The identification of solid species and determination of aluminum solubility in a considerable range of conditions is the subject of continuing research, to be described in separate papers.

One of the purposes of the calculations and the graphs presented here is to ascertain the equilibrium activity of uncomplexed aluminum for a wide span of solution conditions. This value is useful in complicated solubility calculations.

ALUMINUM HYDROXIDE COMPLEXES

Studies described in an earlier report (Hem and Roberson, 1967) indicate that aluminum forms the simple monomeric complex $AlOH^{+2}$ and that it also may form polymeric hydroxide complexes which can grow to colloidal size. An illustration in that report indicated the equilibrium activity of free Al^{+3} and $Al(OH)_4^-$ from pH 4.0 to 9.0 in the presence of three different solid forms of $Al(OH)_3$.

This kind of illustration is a type of solubility diagram and requires knowledge of the specific form of solid which is present. The hydroxide solute species $AlOH^{+2}$ and $Al(OH)_4^-$ can be significant factors in the composition of dissolved forms of aluminum in some ranges of pH as will be shown. A complete treatment of these species is best made in connection with solubility diagrams and will be deferred to a later paper.

Polymeric $Al(OH)_3$ which forms at certain pH ranges is perhaps best thought of as a metastable structural intermediate. This species can evolve into a crystalline form of aluminum hydroxide, or if other solutes of the right kind are present, it may form a part of more complicated aluminum-bearing mineral species.

ALUMINUM FLUORIDE COMPLEXES

Aluminum forms a series of particularly stable complexes with fluoride. Although fluoride is a minor constituent of most natural waters, the complexing action is strong enough to have a considerable influence on the form of dissolved aluminum even when very little fluoride is present.

Brosset and Orring (1943) determined the stepwise constants for the series of complexes from AlF^{+2} to AlF_6^{-3}, at 25°C in solutions of 0.5 ionic strength. For the equilibrium

$$AlF_{n-1}{}^{4-n}+F^-=AlF_n{}^{3-n}$$

for which the concentration equilibrium constant is K_n'', for values of n ranging from 1 to 6, the reported constants are shown below. Also shown are values for the accumulative constants β_n'' where β_n'' represents constants for the reactions:

$$Al^{+3}+nF^-=AlF_n{}^{3-n}.$$

$$K_1''=10^{6.13} \qquad \beta_1''=10^{6.13}$$
$$K_2''=10^{5.02} \qquad \beta_2''=10^{11.15}$$
$$K_3''=10^{3.85} \qquad \beta_3''=10^{15.00}$$
$$K_4''=10^{2.74} \qquad \beta_4''=10^{17.74}$$
$$K_5''=10^{1.63} \qquad \beta_5''=10^{19.37}$$
$$K_6''=10^{0.47} \qquad \beta_6''=10^{19.84}$$

Because these constants include the activity coefficients for the various species at 0.5 ionic strength, they are concentration constants rather than activity equilibrium constants shown in this report as K_n or β_n.

Throughout this paper analytical concentrations are represented by ionic species enclosed in parentheses and activities by species enclosed in square brackets.

SPECIES DISTRIBUTION DIAGRAMS

There are various ways in which the distribution of the dissolved complex species formed in a system containing fluoride and aluminum can be represented graphically. One rather commonly used representation is the species distribution diagram in which the activity or concentration of free F^- is plotted on the x-axis and the percentage distributions of the species are plotted on the y-axis. This gives rise to a series of curves bounding the domains of the species considered. A vertical line drawn on the graph at any desired value of (F^-) will be divided by the curves into segments proportional to the abundance of the species indicated. Figure 1 is a diagram of this type showing the concentration of aluminum fluoride complexes at a fixed ionic strength. The diagram is prepared by a calculation technique similar to one described by Butler (1964) and outlined as follows:

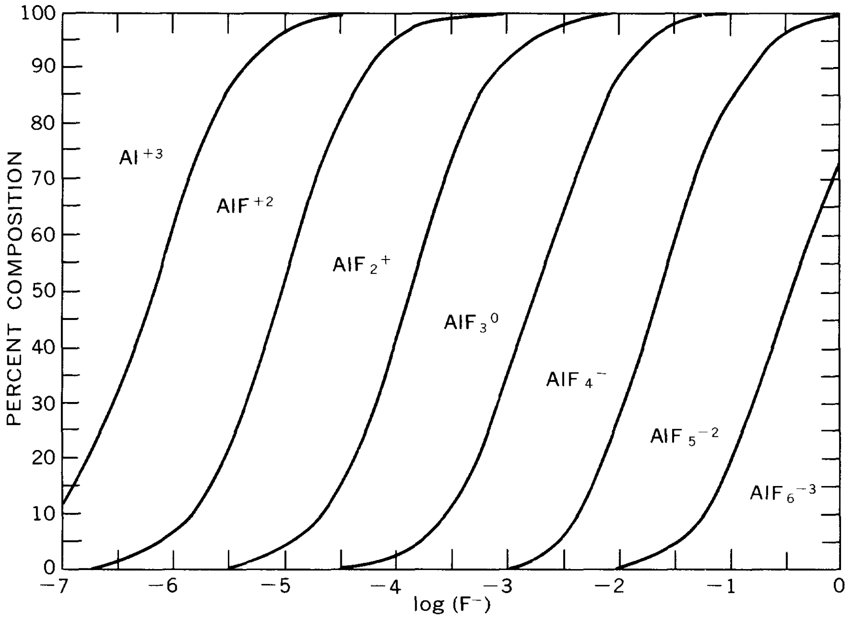

FIGURE 1.—Distribution of dissolved aluminum species as a function of free fluoride concentration (F^-). (Ionic strength 0.5.)

From the cumulative constants β_n, the amount of any of the complex species can be computed as a function of $[Al^{+3}]$ and $[F^-]$. Thus a series of 6 equations results:

$$[AlF^{+2}]=\beta_1[F^-][Al^{+3}]$$

$$[AlF_2{}^+]=\beta_2[F^-]^2[Al^{+3}]$$

$$[AlF_3{}^0]=\beta_3[F]^3[Al^{+3}], \text{ and so forth.}$$

Also, the total of the activity of all dissolved aluminum species in the system is obtained from the summation

$$\Sigma[Al]=[Al^{+3}]+[AlF^{+2}]+[AlF_2{}^+]+[AlF_3{}^0]+[AlF_4{}^-]+[AlF_5{}^{-2}]+[AlF_6{}^{-3}].$$

At zero ionic strength this is equivalent to the total analytical concentration of aluminum. For the purpose of this derivation, zero ionic strength is assumed, but the approach requires only a different set of constants when it is used for other ionic strengths.

There are nine variables in these seven basic equations. The diagram to be constructed assigns a value only to one of the variables. The interrelationships among the other variables then will be expressed in terms of the uncomplexed $[F^-]$.

Substitution of the equations for the activities of the complexes in the summation leads to

$$\Sigma[Al]=[Al^{+3}]+\beta_1[F][Al^{+3}]+\beta_2[F]^2[Al^{+3}]+\beta_3[F]^3[Al^{+3}]$$
$$+\beta_4[F]^4[Al^{+3}]+\beta_5[F]^5[Al^{+3}]+\beta_6[F]^6[Al^{+3}].$$

The fraction of the total aluminum activity present as uncomplexed Al^{+3} is determined by inverting and multiplying all terms by $[Al^{+3}]$,

$$\frac{[Al^{+3}]}{\Sigma[Al]}=\frac{1}{1+\beta_1[F]+\beta_2[F]^2+\beta_3[F]^3+\beta_4[F]^4+\beta_5[F]^5+\beta_6[F]^6}.$$

This fraction is represented as α_0. The fraction α_1, of total aluminum present as AlF^{+2} is

$$\frac{[AlF^{+2}]}{\Sigma[Al]}=\beta_1[F]\alpha_0$$

and

$$\alpha_2=\frac{[AlF_2{}^+]}{\Sigma[Al]}=\beta_2[F]^2\alpha_0, \text{ and so forth.}$$

The sum of the α terms will always be 1.0, or as shown in figure 1, 100 percent.

Thus the fractions, or percentages, of total Al comprised by all seven possible aluminum species are fixed by specifying only the free fluoride activity. The positions of the lines bounding the species are calculated by determining α values for various values of [F]. Normally, not more than three species will be present in significant amounts at one time. The derivation above uses thermodynamic constants and activity values. It is, of course, possible to prepare diagrams for any desired ionic strength using concentrations and appropriate β_n'' values, and this modification in the procedure was used in preparing figure 1.

Figure 1 covers the range of concentration of fluoride from 10^{-7} to 10^0 molal. The stability constants used (Brosset and Orring, 1943) were determined for solutions which were 0.5 molal. Therefore, this diagram applies only for solutions near this ionic strength. The experiments of Brosset and Orring were not carried to high enough fluoride concentrations to determine K_6'', with any degree of certainty, and it is unrealistic to extrapolate data for ionic strength of 0.5 beyond 1 molar concentrations of F^-.

The computations used to prepare the figure assume chemical equilibrium and absence of interfering substances. If the diagram is applied to natural water, high (relative to fluoride) concentrations of ions that compete with the fluoride for complexing of aluminum should not be present. This assumption does not impose a serious limitation at low pH because the fluoride complexes are the most stable of any likely to be present. It does mean, however, that the pH of the system should be below neutrality. The master variable, free fluoride concentration, is mathematically convenient but it cannot generally be directly measured. The only alternative is to assume that the total, or analytical, fluoride concentration is virtually the same as the uncomplexed fluoride. This can be true only if fluoride is present in large excess over the total aluminum. Thus, although the diagram is theoretically correct for systems where most of the fluoride is complexed, it cannot be practically applied to such systems unless free fluoride can be measured.

Even with these limitations, the diagram (fig. 1) suggests some interesting relationships in the chemistry of natural water. In a solution containing around 2 ppm (parts per million) of fluoride (10^{-4} molal) the aluminum would probably be present mostly as AlF_2^+ and AlF_3^0, and nearly all the aluminum would probably be complexed even when only a few tenths ppm of fluoride were present, provided the total Al is always considerably less than the total fluoride. In many natural waters, however, the aluminum content is relatively large compared to the fluoride.

A more useful type of diagram would be one in which the master variables would be readily measurable. Also, one would like to be able to allow for the effects of ionic strengths different from 0.50. Other means of graphic presentation of the behavior of fluoride complexes are therefore desirable. Mathematical and graphical procedures are given here by which one may represent the fields of dominance of the various species in figure 1 on a diagram having analytical concentrations of aluminum and fluoride as abscissa and ordinate. As a first step, some adjustment of stability constants for effects of different ionic strengths is required.

The equilibrium constants reported by Brosset and Orring were used by King and Gallagher (1959) to compute net change in free energy for the stepwise formation of constants up to AlF_5^{-2} in solutions having an ionic strength of 0.07. These authors gave, for the cumulative constants, the following values:

$\beta_1''=10^{6.61}$ $\beta_4''=10^{18.71}$
$\beta_2''=10^{11.97}$ $\beta_5''=10^{20.04}$
$\beta_3''=10^{16.03}$

King and Gallagher did not calculate a free energy for AlF_6^{-3}. An approximate β_6'' value based on the trend of the other figures was estimated as $10^{20.44}$ for this report. In any event, the conditions required for formation of this species in major quantity are unlikely in any natural system.

A further calculation converting the values of King and Gallagher to zero ionic strength was made, using the Debye-Hückel equation to compute the activity coefficients. Values for the parameter *a* (needed for the Debye-Hückel equation) for the various species either were taken from Kielland (1937) or were estimated by analogy with similar forms. The values obtained for the constants for zero ionic strength are

$K_1=10^{7.01}$ $\beta_1=10^{7.01}$
$K_2=10^{5.74}$ $\beta_2=10^{12.75}$
$K_3=10^{4.27}$ $\beta_3=10^{17.02}$
$K_4=10^{2.70}$ $\beta_4=10^{19.72}$
$K_5=10^{1.19}$ $\beta_5=10^{20.91}$
$K_6=10^{-0.05}$ $\beta_6=10^{20.86}$

Table 1 contains standard free energy values for various ionic and other species that enter into calculations in this paper.

TABLE 1.—*Standard free energies*

[Dissolved species indicated by (aq), solid phase by (c), and liquid by (*l*)]

Species	Standard free energy of formation ΔG° (kcal/mole)	Source of data
$Al^{+3}(aq)$	−115. 0	Latimer (1952).
$AlF^{+2}(aq)$	−190. 64	Calculated, from data of King and Gallagher (1959).
$AlF_2^+(aq)$	−264. 55	Do.
$AlF_3^0(aq)$	−336. 46	Do.
$AlF_4^-(aq)$	−406. 22	Do.
$AlF_5^{-2}(aq)$	−473. 92	Do.
$AlF_6^{-3}(aq)$	−539. 93	Do.
$AlSO_4^+(aq)$	−296. 7	Calculated from data of Behr and Wendt (1962).
$Al(SO_4)_2^-(aq)$	−476. 6	Do.
$F^-(aq)$	−66. 08	Latimer (1952).
$AlOH^{+2}(aq)$	−165. 2	Calculated from data of Hem and Roberson (1967).
$AlOH_4^-(aq)$	−311. 7	Hem and Roberson (1967).
$Al(OH)_3(c)$ (microcrystalline gibbsite).	−272. 3	Hem and Roberson (1967).
SO_4^{-2}	−177. 34	Latimer (1952).
OH^-	−37. 595	Do.
$H_2O(l)$	−56. 69	Do.

Figure 2 was prepared using the values for β_1 to β_6 for 0.00 ionic strength, the 6 fundamental equilibrium relationships developed earlier for β_1 to β_6 and two summarizations:

$$\Sigma[Al]=[Al^{+3}]+[AlF^{+2}]+[AlF_2^{+}]+[AlF_3^{0}]+[AlF_4^{-}]+[AlF_5^{-2}]+[AlF_6^{-3}]$$

and

$$\Sigma[F]=[F^-]+[AlF^{+2}]+2[AlF_2^{+}]+3[AlF_3^{0}] +4[AlF_4^{-}]+5[AlF_5^{-2}]+6[AlF_6^{-3}].$$

Thus there are 8 equations and 10 unknowns, and if $\Sigma[Al]$ and $\Sigma[F]$ are specified, all other species can then be evaluated.

In any single solution (one total aluminum value corresponding to a certain total fluoride concentration) many of the individual species do not contribute significantly to the total and can be ignored without serious error so that the number of equations needed can be decreased. The lines drawn on figure 2 represent the conditions where the activity of the species above the line is equal to the activity of the species indicated below the line.

In figure 2, for example, the position of the line where $[Al^{+3}]=[AlF^{+2}]$ is calculated from the first two complexing equilibria, and the two summations.

$$[AlF^{+2}]=\beta_1[Al^{+3}][F^-].$$

Since

$$[AlF^{+2}]=[Al^{+3}],$$

$$[F^-]=\frac{1}{\beta_1}=10^{-7.01}.$$

The total complexed will probably also include a significant amount of AlF_2^+. The proportion of this form can be computed from

$$\begin{aligned}[AlF_2^+]&=\beta_2[Al^{+3}][F^-]^2\\&=10^{12.75}[Al^{+3}]\times10^{-14.02}=10^{-1.27}[Al^{+3}].\end{aligned}$$

Higher complex species will be negligible. The summation of Al species will then be

$$\begin{aligned}\Sigma[Al]&=[Al^{+3}]+[AlF^{+2}]+[AlF_2^+]\\&=[Al^{+3}]+[Al^{+3}]+0.0536[Al^{+3}]=2.0536[Al^{+3}].\end{aligned}$$

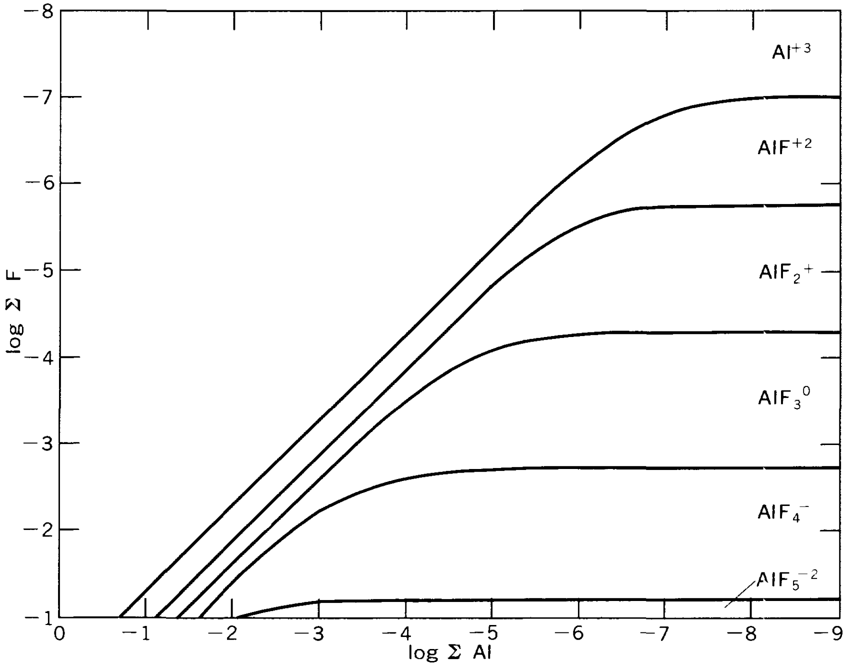

FIGURE 2.—Distribution of dissolved aluminum species as a function of total dissolved fluoride and aluminum. (Zero ionic strength.)

A value for total Al is now arbitrarily selected, and the equation solved for $[Al^{+3}]$. If the value for total Al (ΣAl in fig. 2) chosen is 10^{-5} molal, the value for $[Al^{+3}]$ becomes

$$2.0536[Al^{+3}]=10^{-5}$$

$$[Al^{+3}]=0.487\times10^{-5}.$$

This value which also represents $[AlF^{+2}]$ can now be used to find the total of fluoride species when $\Sigma[Al]=10^{-5}$ from the second summation equation

$$\begin{aligned}\Sigma[F]&=[F^-]+[AlF^{+2}]+2[AlF_2{}^+]\\&=0.978\times10^{-7}+0.487\times10^{-5}+0.522\times10^{-6}\\&=5.49\times10^{-6}=10^{-5.26}\end{aligned}$$

The coordinates of the points for the $Al^{+3}=AlF^{+2}$ line can be determined by repeating this calculation for different values of $\Sigma[Al]$ and solving for the corresponding values of $\Sigma[F]$. Similar calculations using the other equilibria for the higher complexes locate the points for the other lines.

The summation of activities for the various species is, of course, equivalent to the analytically determined concentration of the element here, because the system is at zero ionic strength. Admittedly, zero ionic strength could be approached only in that area on the diagram where dissolved species do not exceed about 10^{-5} molal, but the error introduced by using the diagram for somewhat higher concentrations will be relatively small.

At the right side of the graph where aluminum concentrations are small, the intercepts of the successive lines on the fluoride axis are equivalent to the (F^-) values at points on the lines in figure 1 where activities of the two principal species are equal. As total aluminum concentrations increase, this relationship no longer prevails. The species distribution diagram, figure 1, was specified to be useful only when fluoride was present in excess. These conditions are represented by that part of figure 2 in which the lines on the diagram are parallel to the x-axis. Thus, figure 2 is much more broadly applicable and can be used to indicate the predominant form of complex for any combination of total Al and total F concentrations. This type of diagram, therefore, has advantages over the usual species-distribution diagram for multielectrolyte solutions such as natural water.

As noted previously, figure 2 is in terms of thermodynamic concentrations. Except for very dilute solutions in which the ionic strength is below about 10^{-3} or 10^{-4}, the stoichiometric concentrations will be significantly greater than the thermodynamic concentrations. Where several different forms of aluminum are being considered, having different charges and ion configurations, it is not possible to assign a single activity coefficient which will convert total analytical aluminum concentration to an activity value simply on the basis of ionic strength of the solution. Therefore, the measured total concentration of aluminum cannot be converted accurately to an activity by means of the Debye-Hückel equation.

The simplest method for coping with the more concentrated solutions is to base the calculations on an arbitrarily selected value of ionic strength, and thus to obtain a graph which will apply directly to solutions at or near that ionic strength. This procedure can be extended by drawing several graphs to give as many ranges of ionic strength as desired, subject to the limitations of accuracy imposed by the methods available for calculating individual ion activity coefficients.

The species-distribution diagram based on stoichiometric data is qualitative in that it shows only which form of dissolved species is predominant. To obtain specific indications as to the proportions of complexed to total aluminum, a modified calculation procedure is required, which also obtains results that can be conveniently represented graphically as functions of analytically determined data.

DIAGRAMS SHOWING EXTENT OF COMPLEXING

Figure 3, again having total concentrations of aluminum and fluoride as abscissa and ordinate, shows the ratio of the activity of aluminum in uncomplexed form to the analytical total aluminum for the ionic strength indicated. This ratio provides a simple means of determining the activity of uncomplexed Al^{+3} (denoted by $[Al^{+3}]$), which in turn can be used in considering the various possible equilibria that might control the solubility of aluminum in a system, where the term needing evaluation is $[Al^{+3}]$.

Figure 3 represents a system at zero ionic strength. The effect of different ionic strengths will be shown in other diagrams. The general calculation technique is the same, regardless of ionic strength. Fundamentally, the equations are about the same as the ones used in preparing figure 2. It is necessary to calculate a set of "hybrid" cumulative stability constants which will be applicable at the ionic strengths the diagrams are to represent, and these hybrid constants are represented by the symbol β_n'. These are called hybrid constants because they are used in an equation involving both activity and concentration terms. In this respect these constants are different from those designated by a double prime superscript (for example, β_n''), discussed earlier, which involve only concentrations.

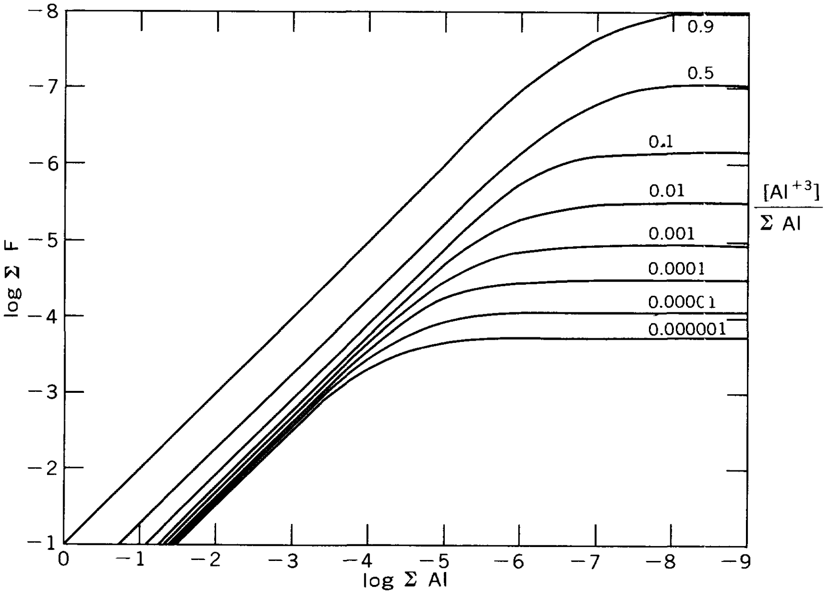

FIGURE 3.—Ratio of free aluminum activity $[Al^{+3}]$ to total dissolved aluminum as a function of total dissolved fluoride and aluminum. (Zero ionic strength.)

The derivation of such a constant (β'_n) is as follows: (Where brackets and parentheses denote activities and concentrations, respectively.)

$$\beta_1 = \frac{[AlF^{+2}]}{[Al^{+3}][F^-]} = 10^{7.01}$$

$$\beta'_1 = \frac{(AlF^{+2})}{[Al^{+3}](F^-)}$$

$$(AlF^{+2}) = \frac{[AlF^{+2}]}{\gamma_{AlF^{+2}}}$$

$$(F^-) = \frac{[F^-]}{\gamma_{F^-}}$$

$$\beta'_1 = \frac{[AlF^{+2}]}{\gamma_{AlF^{+2}}} \times \frac{\gamma_{F^-}}{[Al^{+3}][F^-]}$$

$$\beta'_1 = \beta_1 \frac{\gamma_{F^-}}{\gamma_{AlF^{+2}}}.$$

The activity coefficients can be computed from the ionic strength using the Debye-Hückel equation. The activity rather than the concentration of the uncomplexed form is used because this is the species required in the final answer. The summation equations also are modified by dividing each activity by the appropriate activity coefficient.

In summary, the equations required are

$$(AlF^{+2}) = \beta_1' \, [Al^{+3}](F^-)$$
$$(AlF_2^{+}) = \beta_2' \, [Al^{+3}](F^-)^2$$
$$(AlF_3^{0}) = \beta_3' \, [Al^{+3}](F^-)^3$$
$$(AlF_4^{-}) = \beta_4' \, [Al^{+3}](F^-)^4$$
$$(AlF_5^{-2}) = \beta_5' \, [Al^{+3}](F^-)^5$$
$$(AlF_6^{-3}) = \beta_6' \, [Al^{+3}](F^-)^6$$

$$\Sigma Al = \frac{[Al^{+3}]}{\gamma_{Al^{+3}}} + (AlF^{+2}) + (AlF_2^{+}) + (AlF_3^{0}) + (AlF_4^{-}) + (AlF_5^{-2}) + (AlF_6^{-3})$$

$$\Sigma F = (F^-) + (AlF^{+2}) + 2(AlF_2^{+}) + 3(AlF_3^{0}) + 4(AlF_4^{-1}) + 5(AlF_5^{-2}) + 6(AlF_5^{-3})$$

and

$$\alpha_0' = \frac{[Al^{+3}]}{\Sigma Al}.$$

The fraction present as $[Al^{+3}]$ can be reexpressed as

$$\alpha_0' = \frac{[Al^{+3}]}{\frac{[Al^{+3}]}{\gamma_{Al^{+3}}} + \beta_1'[Al^{+3}](F^-) + \beta_2'[Al^{+3}](F^-)^2 + \beta_3'[Al^{+3}](F^-)^3 \text{ and so forth}}$$

or

$$\alpha_0' = \frac{1}{\frac{1}{\gamma_{Al^{+3}}} + \beta_1'(F^-) + \beta_2'(F^-)^2 + \beta_3'(F^-)^3 + \beta_4'(F^-)^4 + \beta_5'(F^-)^5 + \beta_6'(F^-)^6}.$$

The ionic strength for the diagram can then be assigned and values for the stability constants and $\gamma_{Al^{+3}}$ calculated.

The actual plotting on the diagram of lines representing successively decreasing values of α_0' is done one point at a time. A value of α_0' is chosen and a convenient value for total concentration for aluminum is selected. The ΣF coordinate fixing the point is calculated from the set of equations derived above. Additional points for the same value of α_0' are computed for as many ΣAl values as necessary to define the location of the line. The whole series of calculations is then repeated for additional lines representing other values of α_0'. The procedure will be illustrated by reviewing the computations required for the point representing $10^{-2.00}$ molal total Al concentration on the line $\alpha_0'=0.001$.

Figure 3 represents a solution of zero ionic strength and therefore all activity coefficients have a value of 1.00. For any set of circumstances chosen there will generally not be more than three terms in the denominator which will require consideration. For example, when the value of $\alpha_0'=0.001$,

$$0.001=\frac{1}{1+10^{7.01}(\mathrm{F}^-)+10^{12.75}(\mathrm{F}^-)^2+10^{17.02}(\mathrm{F}^-)^3+10^{19.72}(\mathrm{F}^-)^4}.$$

A trial value of (F^-) of $10^{-5.00}$ gives the fraction a value of 1/770 and the last term in the denominator is very small relative to the others. A somewhat larger value for (F^-) is needed. When $(\mathrm{F}^-)=10^{-4.95}$ the fraction becomes 1/973 and when $(\mathrm{F}^-)=10^{-4.94}$, 1/1021. The last value is the nearest two-place exponent, and better accuracy cannot be shown on the diagram, although greater refinement is obviously possible if needed.

Using $10^{-4.94}$, the value of (F^-) which fits the prescribed conditions, it is now possible to calculate the concentration of the aluminum fluoride complexes from the formula

$$(\mathrm{AlF}_n)=\beta_n'\times(\mathrm{F}^-)^n\times[\mathrm{Al}^{+3}],$$

where the value for $[\mathrm{Al}^{+3}]$ is equal to $\Sigma\mathrm{Al}\times\alpha_0'$, or $10^{-5.00}$.

$$(\mathrm{AlF}^{+2})=10^{7.01}\times10^{-5.00}\times10^{-4.94}=10^{-2.93}$$

$$(\mathrm{AlF}_2^{+})=10^{12.75}\times10^{-5.00}\times10^{-9.88}=10^{-2.13}$$

$$(\mathrm{AlF}_3^{0})=10^{17.02}\times10^{-5.00}\times10^{-14.82}=10^{-2.80}$$

$$(\mathrm{AlF}_4^{-})=10^{19.72}\times10^{-5.00}\times10^{-19.76}=10^{-5.04}$$

The necessary multiples of these species are added together to obtain the total F, fixing a point on the line representing $\alpha_0'=0.001$. Similar computations are required for the other points.

Computations of this type are laborious, especially if diagrams have to be prepared for several different ionic strengths. The data for the series of diagrams in this paper, however, were readily obtained by programming the equations for solution by an electronic computer.

Figure 3 shows the high degree of complexing which can be attained when fluoride is present in sufficient amounts. When used together with figure 2, an indication of proportion of free to complexed aluminum as well as the predominant form of complex present is obtained. Although still subject to some limitations, these diagrams provide a considerably greater amount of useful information than the simpler species-distribution diagram (fig. 1). The effect of increasing ionic strength is to increase the percent of complexing where fluoride is present in excess. Where fluoride is not in excess, the effect of ionic strength is much less important. The closer spacing of the lines as complexing approaches 100 percent is interesting.

Figures 4–7 show the values of the ratio of $[Al^{+3}]/\Sigma Al$ for solutions with ionic strengths 10^{-3}, 10^{-2}, 10^{-1}, and 0.71. The first three represent the range that can be covered by the Debye-Hückel equation and amounts to concentrations of up to about 6,000 ppm dissolved solids. The value 0.71 is about the ionic strength of normal ocean water and activity coefficients were taken for this ionic strength partly from Butler's (1964, p. 438) nomograph based on the Davies equation, and partly from Garrels and Christ (1965, p. 103) with some interpolation for a few species. These values are only approximate.

The number of different ionic strengths for which computations are made could be decreased if the contemplated application does not require a high degree of accuracy. The activity coefficients for the ions of interest at various ionic strengths are given in table 2.

Figures 3–7 are directly applicable to solutions where fluoride is the main complexing species. For most natural waters, the other significant ions which need to be considered are hydroxide and sulfate.

TABLE 2.—*Activity coefficients of ion (γ ion) at different ionic strengths*

[All values not footnoted from Butler (1964, p. 435)]

	0.000	0.0001	0.0005	0.001	0.005	0.010	0.025	0.05	0.07	0.10	0.50	0.71	*a* parameter used	Charge
$\gamma_{\mathrm{Al}^{+3}}$	1.000	0.900	0.797	0.738	0.54	0.445	0.325	0.245	0.210	0.18	[1] 0.03	0.03	9	+3
$\gamma_{\mathrm{AlOH}^{+2}}$	1.000	.950	.903	.867	.740	.66	.545	.445	.399	.355	[1] .23	.23	4	+2
$\gamma_{\mathrm{AlSO_4}^{+}}$	1.000	.990	.975	.964	.927	.901	.855	.815	.792	.77	[1] .69	[2] .68	4	+1
$\gamma_{\mathrm{Al(SO_4)_2}^{-}}$	1.000	.990	.975	.964	.927	.901	.855	.815	.792	.77	[1] .69	[2] .68	4	−1
$\gamma_{\mathrm{AlF}^{+2}}$	1.000	.950	.903	.867	.740	.660	.545	.445	.399	.355	[1] .21	[4] .12	4	+2
$\gamma_{\mathrm{AlF_2}^{+}}$	1.000	.990	.975	.964	.927	.901	.855	.815	.792	.77	[1] .69	[2] .68	4	+1
$\gamma_{\mathrm{AlF_3}^{0}}$	1.000	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	[3] 1.11	[2] 1.13	------	0
$\gamma_{\mathrm{AlF_4}^{-}}$	1.000	.990	.975	.964	.927	.901	.855	.815	.792	.77	[1] .69	[2] .68	4	−1
$\gamma_{\mathrm{F}^{-}}$	1.000	.990	.975	.964	.925	.899	.850	.805	.780	.755	[1] .69	[2] .69	3	−1
$\gamma_{\mathrm{SO_4}^{-2}}$	1.000	.950	.903	.867	.740	.660	.545	.445	.399	.355	[1] .24	[2] .12	4	−2
$\gamma_{\mathrm{AlF_5}^{-2}}$	1.000	.950	.903	.867	.740	.660	.545	.445	.399	.355	[1] .24	[4] .12	4	−2
$\gamma_{\mathrm{Al(OH)_4}^{-}}$	1.000	.990	.975	.964	.927	.901	.855	.815	.792	.77	.69	.68	4	−1

[1] Butler (1964, p. 438).
[2] Garrels and Christ (1965, p. 103).
[3] Garrels (1960, p. 35).
[4] Assumed same as SO_4.

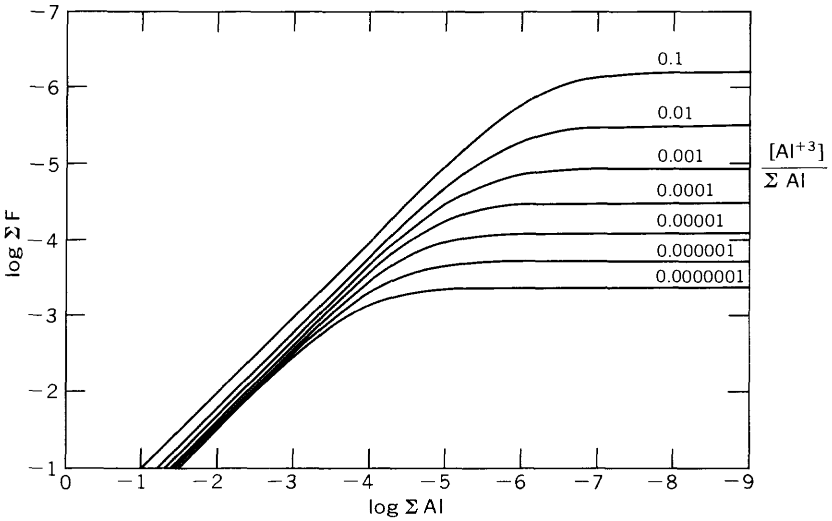

Figure 4.—Ratio of free aluminum activity [Al^{+3}] to total dissolved aluminum as a function of total dissolved fluoride and aluminum. (Ionic strength 0.001.)

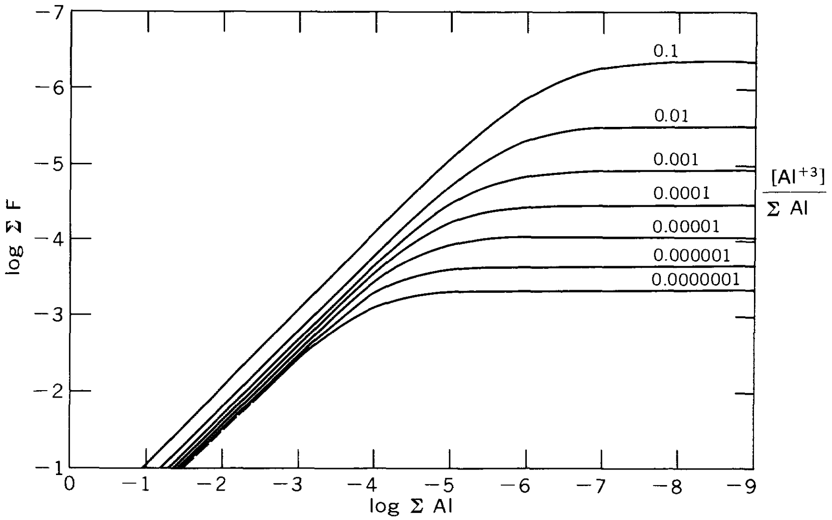

Figure 5.—Ratio of free aluminum activity [Al^{+3}] to total dissolved aluminum as a function of total dissolved fluoride and aluminum. (Ionic strength 0.01.)

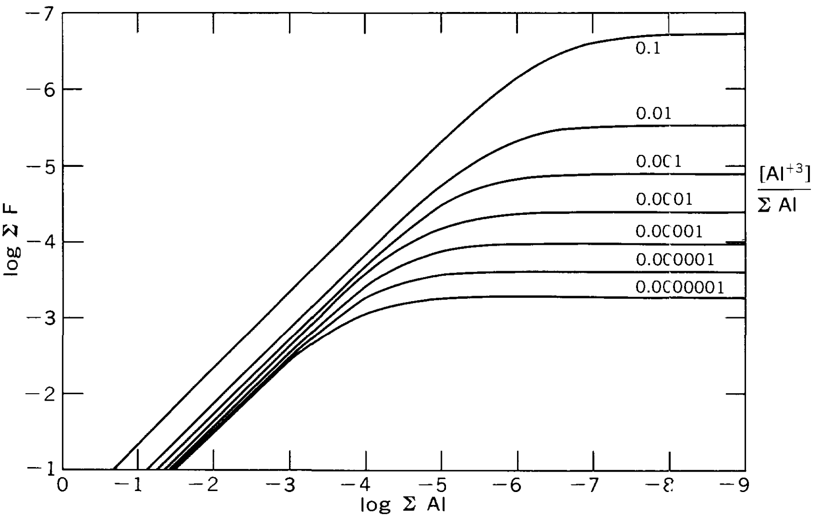

Figure 6.—Ratio of free aluminum activity [Al^{+3}] to total dissolved aluminum as a function of total dissolved fluoride and aluminum. (Ionic strength 0.10.)

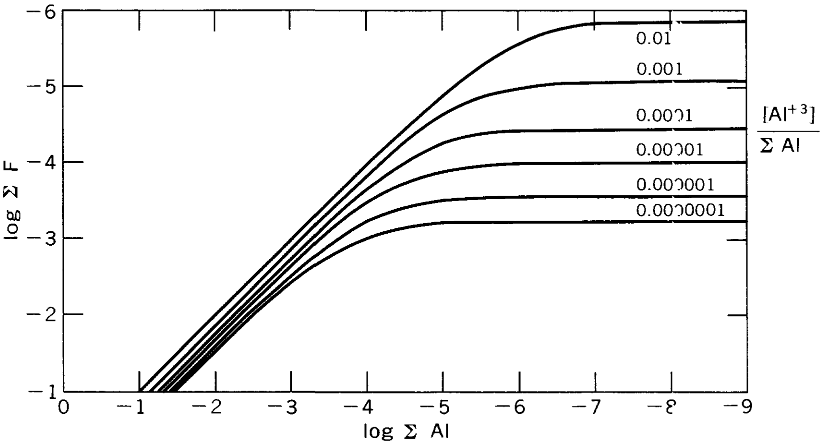

Figure 7.—Ratio of free aluminum activity [Al^{+3}] to total dissolved aluminum as a function of total dissolved fluoride and aluminum. (Ionic strength 0.71.)

EFFECTS OF HYDROXIDE

The principal hydroxide species which would be present in ionic solution below neutral pH would be $AlOH^{+2}$. Aluminum (Al^{+3}) reacts with water to form $AlOH^{+2}$, as follows,

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

The equilibrium constant ($^*K_1$) for this reaction is $10^{-4.75}$ (Hem and Roberson, 1967), hence

$$\frac{[AlOH^{+2}]}{[Al^{+3}]}=\frac{10^{-4.75}}{[H^+]}.$$

From this it is clear that at a pH of 4.75, $[AlOH^{+2}]=[Al^{+3}]$, and at a pH of 3.75, $[AlOH^{+2}]=0.1[Al^{+3}]$. Therefore, from a pH of 3.75 to neutrality, in a system where OH^- is the only complexing ligand, $AlOH^{+2}$ becomes important relative to Al^{+3}. However, they both may be analytically unimportant when other ligands (for example, fluoride) are present in the system, and then it is necessary to consider all reactions at the same time. Figure 8 is based on computations where the species $AlOH^{+2}$, in addition to fluoride, is considered.

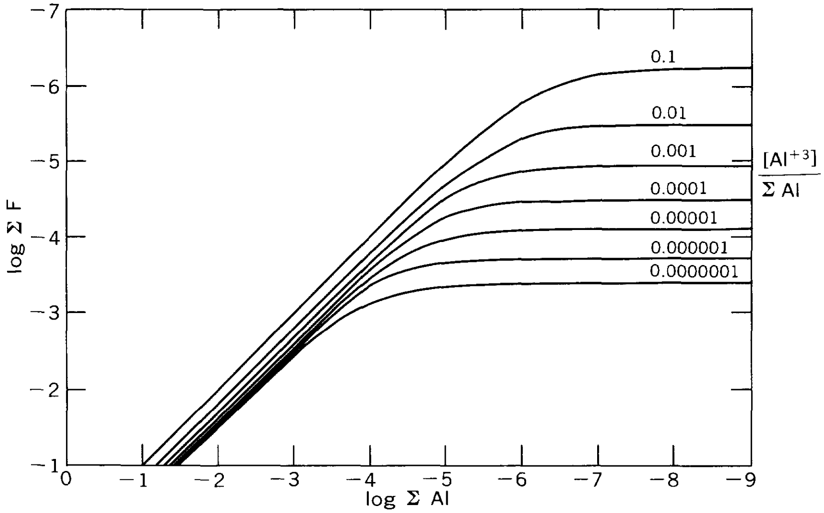

FIGURE 8.—Ratio of free aluminum activity $[Al^{+3}]$ to total dissolved aluminum as a function of total dissolved fluoride and aluminum. This graph differs from figure 3 in that here the aqueous species $AlOH^{+2}$ is considered (pH 5.00).

The basic equation for α_0 at zero ionic strength becomes

$$\alpha_0=\frac{1}{1+\frac{{}^*K_1}{[H^+]}+\beta_1'[F^-]+\beta_2'[F^-]^2+\ \ldots\ \beta_5'[F^-]^5}$$

where ${}^*K_1/[H^+]$ represents the additional term for $AlOH^{+2}$. The stoichiometric summation equation for fluoride remains the same as discussed in the preceding section, and the summation equation for aluminum now contains a term for ($AlOH^{+2}$). Figure 8, based on electronically computed and drawn curves, shows the ratios $[Al^{+3}]/\Sigma Al$ at a pH of 5.0 and zero ionic strength. Similar graphs (not shown) were prepared for pH values 3.0, 4.0, 4.5, 5.0, 5.5, 6.0, and 6.5, for each of the ionic strengths: 0.0000, 0.0005, 0.005, 0.07, and 0.71. Comparison of figure 8 with figures 3–7 shows that in the region where fluoride is in excess of the aluminum (that is, the horizontal portion of the curves) the calculated amount of aluminum complexed is increased when effects of OH^- are considered. For example, for ΣF and ΣAl of 10^{-6} and 10^{-7}, respectively, and at zero ionic strength, the ratio $[Al]/\Sigma Al$ decreases from 0.1 (fig. 3), where OH^- was neglected to about 0.09 (fig. 8) where OH^- at a pH of 5 was considered. At a pH of 6.5 (figure not shown), the ratio decreases to about 0.05 as compared to 0.1 when OH^- is neglected (fig. 3).

In summary, the effect of neglecting the species $AlOH^{+2}$ in preparing the graphs (figs. 3–7) is usually relatively small when fluoride is in excess of aluminum and even less when it is not present in excess. This suggests that in most natural waters below neutral pH the $AlOH^{+2}$ form is an insignificant part of the total content of aqueous aluminum species.

In considering the effect of hydroxide on dissolved species at rather low pH, however, one should not lose sight of the important solubility effects and the formation or dissolution of solid aluminum hydroxide species. This is especially important above neutral pH where the anion $Al(OH)_4^-$ is likely to predominate. Solubility diagrams, in which pH is a master variable, show the influence of hydroxide to better advantage and will be given in another paper.

ALUMINUM SULFATE COMPLEXES

Behr and Wendt (1962) studied the equilibria

$$Al^{+3}+SO_4^{-2}=AlSO_4^+$$

and

$$AlSO_4^++SO_4^{-2}=Al(SO_4)_2^-.$$

They obtained equilibrium constants for the two reactions of $10^{3.2}$ and $10^{1.9}$, respectively.

In the terms used for evaluating the fluoride complexes one may then write

$$\frac{[AlSO_4{}^+]}{[Al^{+3}][SO_4{}^{-2}]}=\beta_1=10^{3.2}$$

$$\frac{[Al(SO_4)_2{}^-]}{[Al^{+3}][SO_4{}^{-2}]^2}=\beta_2=10^{5.1}$$

$$\Sigma[Al]=[Al^{+3}]+[AlSO_4{}^+]+[Al(SO_4)_2{}^-]$$

$$\Sigma[SO_4]=[SO_4{}^{-2}]+[AlSO_4{}^+]+2[Al(SO_4)_2{}^-].$$

If the values for $\Sigma[Al]$ and $\Sigma[SO_4]$ are specified, all the other species can be evaluated. Figure 9 is a species distribution graph which shows areas of dominance for the three aluminum species as functions of total aluminum and sulfate. The diagram represents a solution of zero ionic strength.

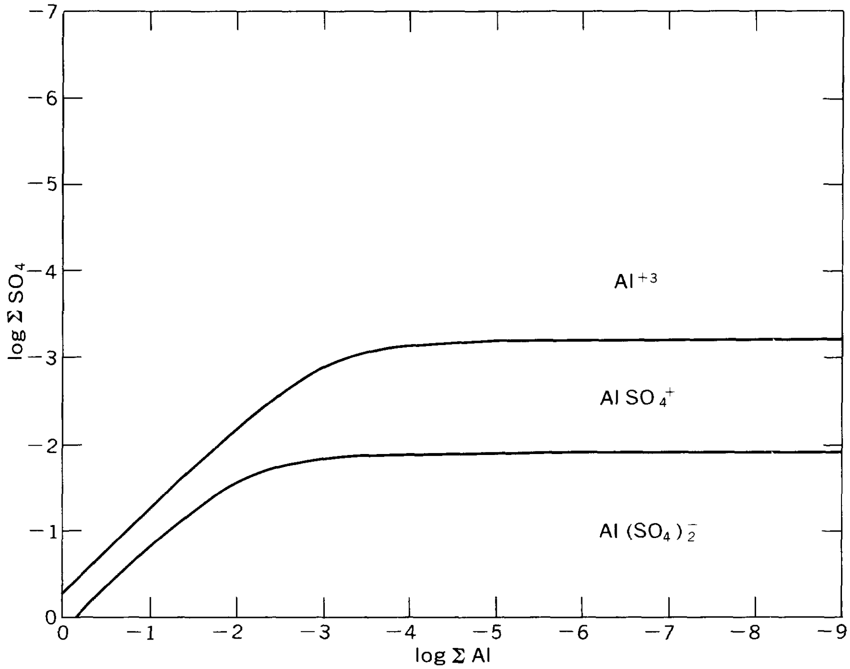

FIGURE 9.—Distribution of dissolved aluminum species as a function of total dissolved sulfate and aluminum. (Zero ionic strength.)

The same set of equations was used, with a specification of the ratio of [Al^{+3}] to stoichiometric total aluminum (ΣAl) to prepare figure 10. This diagram resembles figure 4 in that it represents the effect of complexing without taking into account the effects of ionic strength. A more realistic picture is given by figures 11–14 which represent the same kind of calculation, for solutions of ionic strength 10^{-3}, 10^{-2}, 10^{-1}, and 0.71.

The procedures used in preparing figures 11–14 are directly analogous to those used in preparing the diagrams for the fluoride species, and, therefore, will not be discussed in detail. The activity coefficients used are given in table 1.

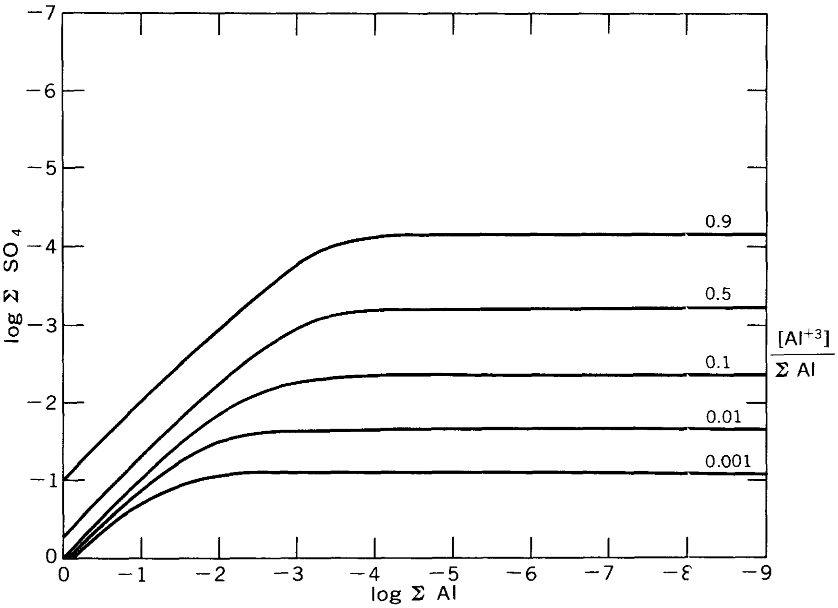

FIGURE 10.—Ratio of free aluminum activity to total dissolved aluminum as a function of total dissolved sulfate and aluminum. (Zero ionic strength.)

It may be of interest to note that the value of the ratio [Al^{+3}]/Σ(Al) cannot be greater than the value of the activity coefficient for Al^{+3}. This sets an upper limit for the ratio on each diagram.

The complexing effect of sulfate is obviously much weaker than that of fluoride, but is still significant. For example, if the total sulfate concentration is 500 ppm in a solution having an ionic strength of 0.10, only a tenth of the total aluminum will be uncomplexed. In systems where sulfate complexing is potentially important, there rarely will be enough dissolved aluminum to use up more than a small fraction of the available sulfate.

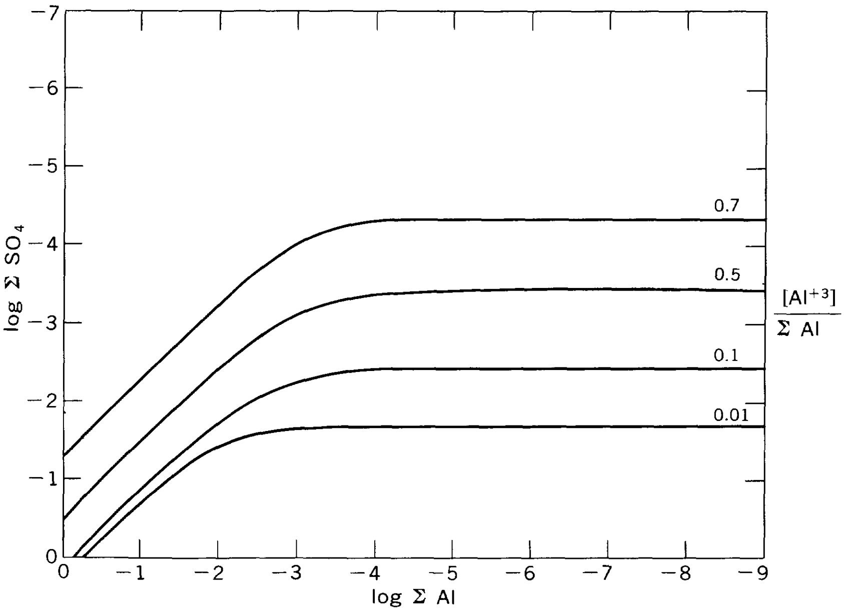

Figure 11.—Ratio of free aluminum activity to total dissolved aluminum as a function of total dissolved sulfate and aluminum. (Ionic strength 0.001.)

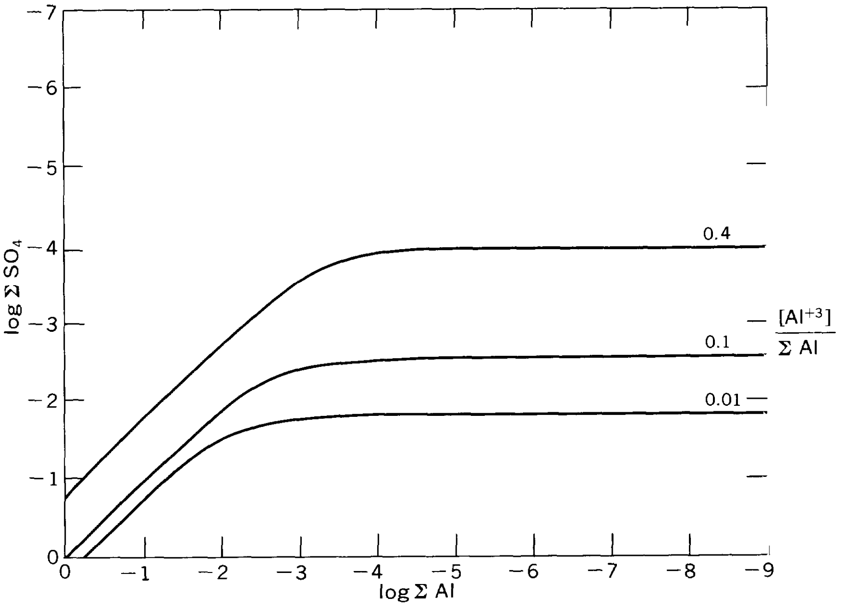

Figure 12.—Ratio of free aluminum activity to total dissolved aluminum as a function of total dissolved sulfate and aluminum. (Ionic strength 0.01.)

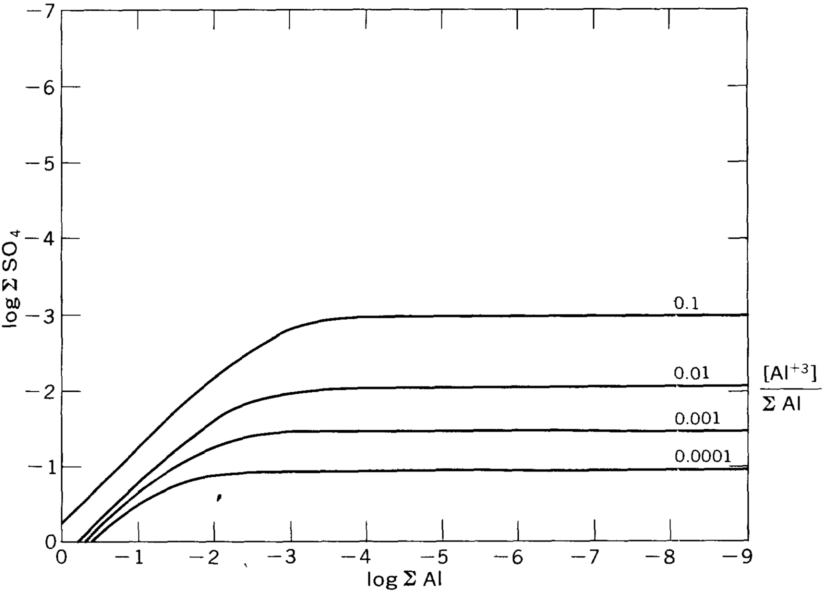

FIGURE 13.—Ratio of free aluminum activity to total dissolved aluminum as a function of total dissolved sulfate and aluminum. (Ionic strength 0.10.)

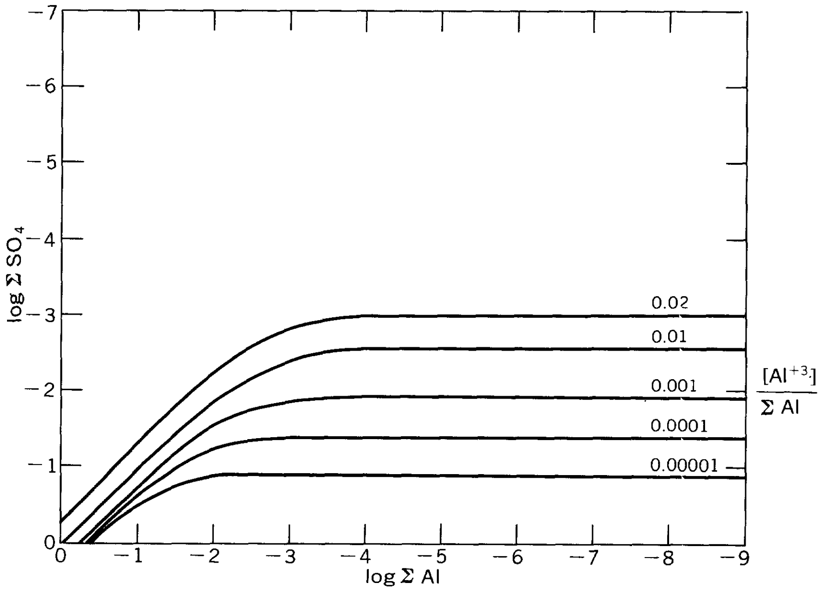

FIGURE 14.—Ratio of free aluminum activity to total dissolved aluminum as a function of total dissolved sulfate and aluminum. (Ionic strength 0.71.)

To apply these calculations to natural systems certain assumptions will be needed. These include:

1. Ligands other than SO_4 are absent or negligible;
2. No other ion which might complex sulfate is present in significant quantity.

The first assumption will not hold for many systems, except perhaps for some acid waters that are low in fluoride. The tendency for sulfate to form ion pairs with the more common cations of natural waters is well known and may need to be considered in relating stoichiometric total sulfate to actual SO_4^{-2} activity.

MIXED SOLUTE SYSTEMS

By extension of the procedures already given, it is possible to evaluate all the possible dissolved species of aluminum up to about pH 7.00 by considering simultaneously the complexing reactions involving F^-, SO_4^{-2}, and OH^-, and to express the results as a diagram like those of figures 3–8 or 10–14, provided that the concentrations of only two components are allowed to vary at once. To cover any significant range of conditions a very large number of diagrams would be required, but by means of a computer program the ones of particular interest could easily be prepared. On a three-dimensional diagram or model, three variables could be handled at once. Three-dimensional plots were not used in this report because, aside from the difficulties in drawing and interpreting a diagram in perspective, the treatment would still be correct for only one ionic strength.

By making the simplifying assumption that complexing ligands are present in considerable excess, the activity of free ligand becomes nearly equal to the total concentration at zero ionic strength. It is now possible to evaluate the relative importance of complexes formed by two competing ligands over a considerable range of ligand concentration. Figure 15 was prepared in part from figures 3 and 10, by extending the segments of the lines representing equal $[Al^{+3}]/\Sigma Al$ ratios which are parallel to the ΣAl axis. For example, the line labeled 0.5 corresponds to $\log \Sigma F = -7.03$ and $\log \Sigma SO_4 = -3.23$. Where these lines would intersect represents a point at which the fluoride complex species and those containing sulfate are present in equivalent amounts. Competition between the complexing ligands causes the lines to meet in a smooth curve.

The location of the curved part of the $[Al^{+3}]/\Sigma Al = 0.5$ line can be determined simply by a procedure described by Hem (1963), if only two complex species need to be considered at a time.

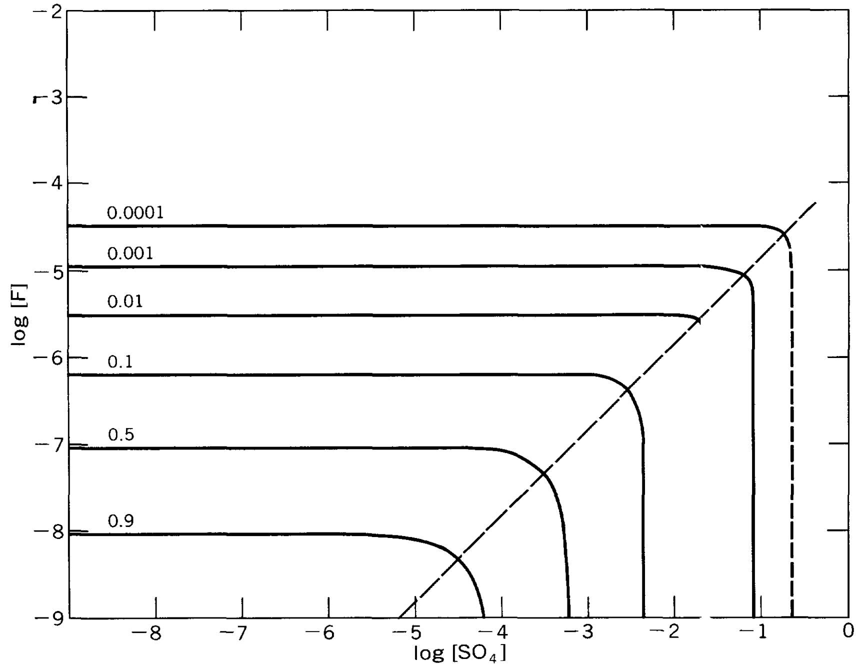

FIGURE 15.—Ratio of free aluminum activity to total dissolved aluminum as a function of the two competing ligands, fluoride and sulfate. (Zero ionic strength.)

From the complexing equilibria previously considered, it can be shown that

$$\frac{[AlSO_4^+][F^-]}{[AlF^{+2}][SO_4^{-2}]}=10^{-3.81}$$

and

$$\frac{[Al(SO_4)_2^-][F^-]^2}{[AlF_2^+][SO_4^{-2}]^2}=10^{-7.65}.$$

For the area of interest in figure 15, these two equations define a nearly continuous straight line for any single ratio of complexed sulfate species to complexed fluoride species. The diagonal line in figure 15 represents a ratio of 1.0. Along this line

$$\Sigma[AlF \text{ species}]=\Sigma[AlSO_4 \text{ species}].$$

Where the only complexed forms of importance are AlF^{+2} and $AlSO_4^+$

$$[AlF^{+2}]=[AlSO_4^+].$$

Where 50 percent of the total activity of aluminum is complexed

$$\frac{[\mathrm{AlF}^{+2}]+[\mathrm{AlSO}_4{}^{+}]}{\Sigma[\mathrm{Al}]}=0.5$$

and

$$[\mathrm{Al}^{+3}]=[\mathrm{AlF}^{+2}]+[\mathrm{AlSO}_4{}^{+}]$$
$$=2[\mathrm{AlF}^{+2}].$$

From the first complexing step for aluminum and fluoride we know that

$$\frac{[\mathrm{AlF}^{+2}]}{[\mathrm{Al}^{+3}]}=10^{7.01}[\mathrm{F}^{-}].$$

Therefore

$$[\mathrm{F}^{-}]=\frac{1}{2\times 10^{7.01}}=10^{-7.31}.$$

This represents the intersection of the 0.5 line with the diagonal.

The curved part of this line can be plotted by drawing other diagonals for different ratios of sulfate to fluoride complex activity and repeating the calculations to determine the intersection of these diagonals with the 0.5 line.

Figure 15 represents a system at zero ionic strength where activity coefficients all have a value of unity. Computations for systems having higher ionic strength require appropriate activity coefficients and modification of equilibrium constants.

An approximate indication of the effects at higher ionic strength can be obtained by combining appropriate graphs from figures 3–7 and 10–14. For example, figure 16 was prepared for solutions of ionic strength 0.10 from figures 6 and 13 by extending the lines for equal values of the ratio $[\mathrm{Al}^{+3}]/\Sigma\mathrm{Al}$ to their point of intersection. The dashed line connecting these intersections should represent equal total concentrations of aluminum species. This relationship is not the same as the one used for the diagonal line in figure 15, and no exact computation of the location of curved parts of the ratio lines in figure 16 was made.

A graphical evaluation of the competing effects of fluoride and hydroxide is given in figure 17. This diagram was prepared by techniques similar to those used in preparing figure 15. However, the line separating the areas of dominance of F and OH species takes into account all the significant forms. Below a pH of 5.00 only AlOH^{+2} and AlF^{+2} are considered. Above a pH of 6.00 the $\mathrm{Al(OH)}_4{}^{-}$ form is the only significant hydroxide complex, but several of the fluoride species must be considered at a time. The location of the dividing line was determined by plotting its intercept with integral pH values.

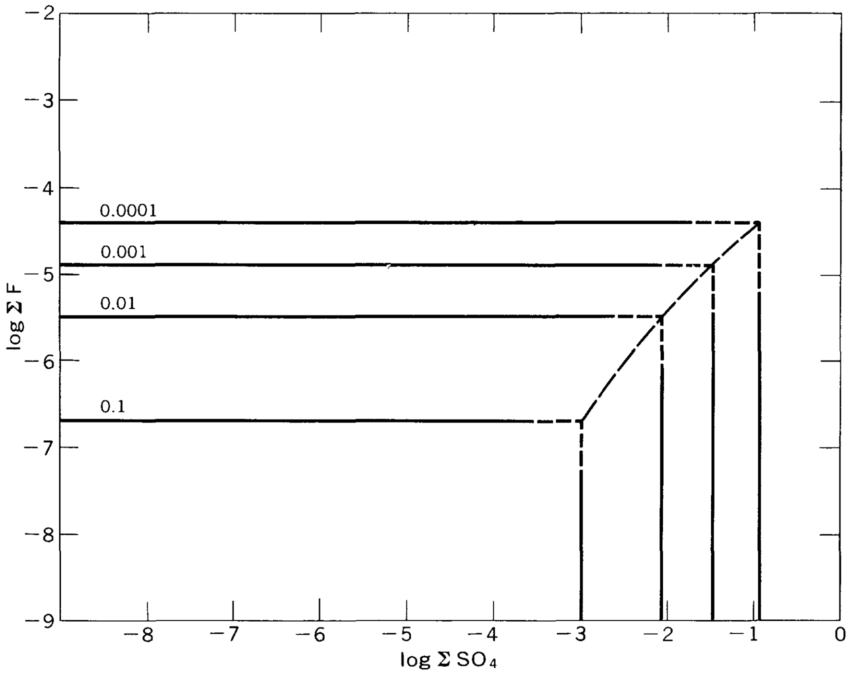

FIGURE 16.—Ratio of free aluminum activity to total dissolved aluminum as a function of the two competing ligands, fluoride and sulfate. (Ionic strength 0.1.)

The ratio of activity of free Al^{+3} to $Al(OH)_4^-$ was determined for the selected pH from the cumulative constant β_4 and the activity of OH^- for that pH. The ratio of free Al^{+3} to the total concentration of fluoride complexes (α_0) was calculated by means of equations developed previously for computation of complexing effects. By a procedure of successive approximation, a value for uncomplexed F^- was determined which gave $\alpha_0=[Al^{+3}]/[Al(OH)_4^-]$. This value for $[F^-]$ then represents the other coordinate fixing the point through the line separating fluoride from hydroxide domains passes. The computation is repeated for as many pH values as are required to locate the curved line.

Figure 17 represents a system at zero ionic strength: activity coefficients all are equal to 1. It would be possible to express the relationship for other ionic strengths with appropriate modifications in the stability constants. However, because pH measurements are direct measurements of hydrogen and hydroxide activities, there is less reason for using concentration values for these variables.

The proportion of free to complexed aluminum again can be expressed by means of contours drawn on the graph. The values shown in figure 17 were taken from the area of figure 3 where fluoride was

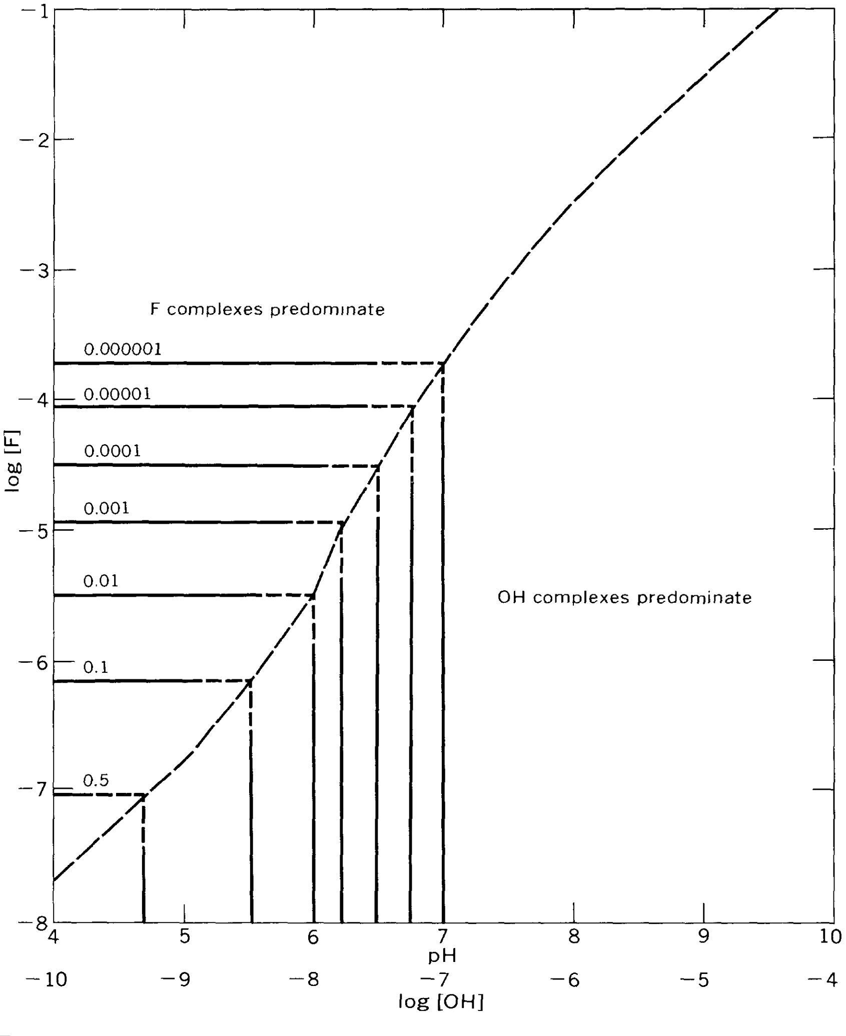

FIGURE 17.—Ratio of free aluminum activity to total dissolved aluminum as a function of fluoride and pH. (Ionic strength 0.00.)

present in excess. The values shown in figure 17 therefore are valid only where the total fluoride exceeds total aluminum by more than an order of magnitude. Under these conditions, total concentration of fluoride is approximately equal to the concentration of uncomplexed F^-.

The method used previously for locating the ratio lines near the intersections of the fluoride and hydroxide domains is not readily applicable where more than two species at a time must be considered; therefore, no attempt was made to refine the diagram in that area.

Figure 17 demonstrates the importance of the pH effects on aluminum solute complexes. Above neutral pH only solutions containing more than 2×10^{-4} moles per liter of fluoride (about 3.8 ppm) will contain more fluoride-complexed aluminum than the hydroxide complex ($Al(OH)_4^-$).

Figure 18 is a representation of competing effects between sulfate and hydroxide complexes and was prepared by a method analogous to that used for figure 17. It is evident that sulfate complexes of aluminum will predominate only in acid solutions because even in brines concentrations of sulfate will be unlikely to exceed 1 molar.

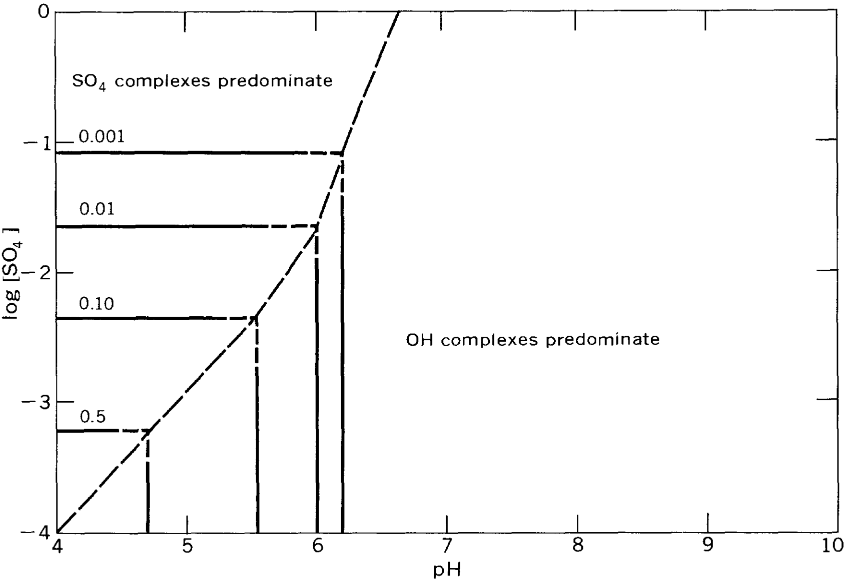

FIGURE 18.—Ratio of free aluminum activity to total dissolved aluminum as a function of sulfate and pH. (Ionic strength 0.00.)

ALUMINUM SOLUBILITY

The effects of precipitation reactions were not considered when preparing the illustrations for this paper. The graphs show which species might be expected to be predominant in solution; they also show proportions of one species to others over certain concentration ranges. The total concentration of aluminum which could be present in solution at equilibrium, however, cannot be determined without taking precipitation reactions and solid species into account.

For pH's above neutrality, a consideration of hydroxide solubility is essential. Basic aluminum sulfates may be precipitated from some solutions. Johansson (1963) reported obtaining crystals of a material having the composition $13Al_2O_3 \cdot 6SO_3 \cdot xH_2O$ (where $x \approx 79$) from solutions 0.01 molar in aluminum and 0.03 molar in sulfate. The pH was not indicated but probably was in the vicinity of 4.5. The mineral alunite, $KAl_3(OH)_6(SO_4)_2$, occurs naturally. When aluminum and fluoride activities become high, in solutions which contain sodium ions, cryolite (Na_3AlF_6) can be precipitated (C. E. Roberson, 1966, oral commun.).

Laboratory and theoretical studies designed to explore the behavior of aluminum in mixed electrolyte solutions where complexes and various solids are formed will be described in later papers in this series.

In general, one would expect the solution complexes to increase the solubility of a given solid. In the simpler systems at least this expectation is realized and can be demonstrated in laboratory experiments. As the solutions increase in concentration and number of dissolved forms, however, some unexpected results can occur.

In mixed electrolyte solutions brought to supersaturation with one or more solids, the form that will be precipitated may depend more on reaction kinetics than on equilibrium status. Silica, which is present as H_4SiO_4 in all natural water, may depress the solubility of aluminum by forming co-polymer layer-type minerals, such as the clay minerals. Solid basic aluminum fluoride and other mixed species may be less soluble than simple hydroxides under some conditions.

APPLICATION TO NATURAL WATER

The graphs in this paper can be used directly for estimating the proportion of the total aluminum content comprised by uncomplexed Al and the most likely forms of aluminum in solution. The two analyses used here were published by White, Hem, and Waring (1963, p. F54) and represent samples collected in September 1957 from Mammoth Springs and Big Horn Spring in Wyoming. Computed values for the logarithms of the concentrations of fluoride, sulfate and aluminum and other pertinent data are given in table 3.

TABLE 3.—*Chemical analyses for two natural waters*

Source pH Ionic strength	Mammoth Spring 6.6 0.039			Big Horn Spring 6.2 0.057		
	ppm	moles per liter	log moles per liter	ppm	moles per liter	log moles per liter
Al	0.2	0.7×10^{-5}	−5.13	0.4	1.5×10^{-5}	−4.82
SO_4	501	5.2×10^{-3}	−2.28	726	7.6×10^{-3}	−2.12
F	2.4	1.3×10^{-4}	−3.89	3.5	1.8×10^{-4}	−3.74

From the concentrations of the complexing ligands and figures 15–18, it is evident that fluoride complexes of aluminum are the predominant aluminum species in these solutions. Because the water has an ionic strength considerably greater than zero these graphs cannot be used to compute $[Al^{+3}]$. Figure 6, however, provides a means of estimating this value. For both waters $[Al^{+3}]$ is indicated to be very nearly $10^{-5}\times$total Al, or in the vicinity of 10^{-10} moles per liter. Figure 2 indicates the predominant complex to be AlF_3^0.

Both of these waters contain moderate amounts of silica, and the low activity of free aluminum may be related to interactions between aluminum and silica.

SUMMARY

Despite limitations mentioned for use of the diagrams, several interesting implications for natural waters appear.

1. In a solution containing fluoride in excess of aluminum, nearly all the latter would be associated with one or more fluoride ions. This is true below neutral pH. Above neutral pH the hydroxy complex appears to be dominant.
2. Below neutral pH, except in water containing very high sulfate concentrations, fluoride, if present in excess of aluminum, is probably the most important ligand in tying up aluminum. This means that OH^- also is generally unimportant in this region and the effect of pH can be ignored, if one keeps in mind the fact that only aluminum in "true" solution is being considered.
3. A unique type of distribution graph has been introduced in this report. This graph permits one to estimate the activity of uncomplexed aluminum in an aqueous solution, given merely the stoichiometric analytical data. The activity so obtained should be useful in studies of the factors which control aluminum solubility.
4. The methods for preparing these diagrams, although not new, have involved some unique features. Calculations like these are not complicated but are laborious if done by hand because of the potentially large number of variables and species. Use of an electronic computer, however, permits a large number of calculations to be performed so that simple two-dimensional graphs, each applicable to a restricted set of conditions, may readily be prepared.

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