

Solubility of Aluminum in the Presence of Hydroxide Fluoride, and Sulfate

GEOLOGICAL SURVEY WATER-SUPPLY PAPER 1827-C



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

CHEMISTRY OF ALUMINUM IN NATURAL WATER

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*The solubility of
gibbsite ($\text{Al}(\text{OH})_3$) and of
cryolite (Na_3AlF_6) in
water is evaluated*



UNITED STATES DEPARTMENT OF THE INTERIOR

WALTER J. HICKEL, *Secretary*

GEOLOGICAL SURVEY

William T. Pecora, *Director*

CONTENTS

	Page
Abstract.....	C1
Introduction.....	1
Acknowledgments.....	2
Solubility calculations.....	2
Solubility in a hydroxide system.....	4
Solubility in the presence of hydroxide, fluoride, and sulfate.....	7
Application to natural water.....	14
Experimental test of solubility calculations.....	16
Formation of fluoro-aluminum solids.....	21
Solubility of cryolite.....	21
Cryolite solubility diagrams.....	26
Formation of aluminum sulfate solids.....	27
Stability-solubility diagrams.....	30
Applications to natural systems.....	31
References.....	36

ILLUSTRATIONS

[All illustrations are graphs]

	Page
FIGURE 1. Solubility of microcrystalline gibbsite as a function of pH, at 25°C and 1 atmosphere total pressure.....	C5
2-5. Solubility of microcrystalline gibbsite as a function of fluoride concentration. Sulfate absent:	
2. Ionic strength 0.....	8
3. Ionic strength 0.01.....	10
4. Ionic strength 0.10.....	12
5. Ionic strength 0.71.....	14
6-8. Solubility of microcrystalline gibbsite as a function of fluoride concentration. Sulfate concentration 0.005 molal:	
6. Ionic strength 0.01.....	16
7. Ionic strength 0.10.....	17
8. Ionic strength 0.71.....	18
9, 10. Solubility of microcrystalline gibbsite as a function of fluoride concentration. Sulfate concentration 0.05 molal:	
9. Ionic strength 0.10.....	19
10. Ionic strength 0.71.....	20

FIGURE		Page
11.	Solubility of microcrystalline gibbsite as a function of sulfate concentration. Fluoride absent. Ionic strength 0.10.....	C22
12.	Solubility of microcrystalline gibbsite as a function of sulfate concentration. Total fluoride concentration 10^{-4} molal. Ionic strength 0.10.....	24
13, 14.	Solubility of cryolite as a function of total fluoride concentration, for sodium concentrations 10^0 molal to 10^{-3} molal. OH species negligible:	
13.	Ionic strength 0.10.....	28
14.	Ionic strength 0.71.....	29
15-18.	Stability fields for cryolite and microcrystalline gibbsite and their solubilities in relation to pH and $[F^-]$:	
15.	Ionic strength 0.00 (N_a) = 0.001 molal.....	32
16.	Ionic strength 0.01 (N_a) = 0.01 molal.....	33
17.	Ionic strength 0.10 (N_a) = 0.10 molal.....	34
18.	Ionic strength 0.71 (N_a) = 1.0 molal.....	35

TABLES

TABLE		Page
1.	Equations used for calculations, for 25°C and 1 atmosphere total pressure.....	C3
2.	Individual ion activity coefficients at 25°C for dissolved species at ionic strengths 0.50 and 0.71.....	5
3.	Solubility of aluminum measured in precipitation experiments compared to predicted solubility of gibbsite. Complexing ligands: F^{-1} and OH^{-1}	18
4.	Solubility of aluminum measured in precipitation experiments compared to predicted solubility of gibbsite. Complexing ligands: SO_4^{-2} and OH^{-1}	19
5.	Analytical data used for calculating activity product, K_{s0} for solubility of cryolite. $K_{s0} = [Na^{+1}]^3[Al^{+3}][F^{-1}]^6$ at 25°C and 1 atmosphere total pressure.....	22

CHEMISTRY OF ALUMINUM IN NATURAL WATER

SOLUBILITY OF ALUMINUM IN THE PRESENCE OF HYDROXIDE, FLUORIDE, AND SULFATE

BY C. E. ROBERSON AND J. D. HEM

ABSTRACT

The total concentration of aqueous dissolved species of aluminum that will be present in equilibrium with microcrystalline gibbsite at various levels of complexing ligand concentration are shown graphically. The graphs can be used to estimate aluminum solubility, at 25°C and 1 atmosphere total pressure, when the pH of the solution, its ionic strength, and the total sulfate and fluoride concentrations are known. The standard free energy of formation of cryolite calculated from solubility experiments is -745.4 ± 1.0 kcal per mole at 25°C. Diagrams are included showing the solubility of cryolite in terms of aluminum, fluoride, and sodium concentrations. The stability fields of cryolite and microcrystalline gibbsite and their solubilities also are shown on pH-[F] diagrams.

INTRODUCTION

Hem and Roberson (1967) prepared and identified several forms of solid $\text{Al}(\text{OH})_3$ and calculated their standard free energies of formation (ΔG°_f) at 25° from solubility measurements. In aqueous aluminum solutions, there may be many dissolved aluminum species involved. Hem (1967) has determined the predominant species under various conditions and has derived methods for evaluating the ratio $[\text{Al}^{+3}]/C_{\text{Al}}$ where $[\text{Al}^{+3}]$ denotes the activity of free aluminum ion and C_{Al} represents the total concentration of all species of dissolved aluminum. Hem evaluated the ratios in solutions containing the ligands F^{-1} , SO_4^{-2} , and OH^{-1} . At the higher concentrations of ligands, the range of aluminum concentration permissible may be limited by precipitation. Hem's treatment was concerned only with interactions involving solute species.

Solubility effects are important in understanding the chemistry of aluminum in natural water, this report presents, graphically, calculations of gibbsite solubility in the presence of the same ligands, F^{-1} , SO_4^{-2} , and OH^{-1} . The results of the calculations were tested experimentally. The activity product of cryolite (Na_3AlF_6) was determined

by experiment. Conditions controlling the formation of cryolite and of aluminum-sodium-hydroxy fluoride, analogous to ralstonite, were established. Finally, solubility-phase transition diagrams were computed for equilibria involving gibbsite and cryolite.

The relationships are valid for systems low in dissolved silica. The solubility of aluminum in natural systems may be controlled by alumino-silicate minerals. Polzer and Hem (1965) showed that the solubility of aluminum was depressed by silica in the presence of kaolinite, and work has been continuing with the aim to evaluate the interactions of aluminum and silica in detail. Results of this work will be given in a later report.

ACKNOWLEDGMENTS

We wish to thank our colleagues of the U.S. Geological Survey, C. L. Christ, who contributed toward making the diagrams more applicable to natural water, and B. F. Jones, who reviewed the manuscript and made many helpful suggestions.

SOLUBILITY CALCULATIONS

Considered in this report are aqueous systems containing dissolved aluminum in equilibrium with one or two solids and containing the complexing ligands OH^{-1} , F^{-1} , and SO_4^{-2} . The selection of ions chosen to represent complexes of these ligands with aluminum and the choice of thermodynamic data for the species involved are discussed by Hem (1967). In brief, the ligands, OH^{-1} , F^{-1} , and SO_4^{-2} were chosen because they are present in natural water and because thermodynamic data are available for the formation of their complexes with aluminum. Although there are indications that orthophosphate (PO_4^{-3}) may influence aluminum behavior (Hsu, 1967), phosphate concentrations and species in natural water are not sufficiently known or understood to permit an adequate consideration here. The lack of data for the formation of aluminum complexes with other anions may suggest the unimportance of these anions in coordinating with aluminum.

The equations used for all the sets of calculations are included in table 1. For purposes of this report, the following definitions are made:

- [*i*] Molal activity of a dissolved constituent *i*, where *i* may be a charged species such as Al^{+3} , AlOH^{+2} , AlF_6^{-3} , or an uncharged species like AlF_3^0 .
- γ_i Activity coefficient of a dissolved species, *i*.
- (*i*) Molal concentrations of a dissolved species which may be charged or uncharged; [*i*] = $\gamma_i(i)$.

- C_i Sum of molal concentrations of all species of a given element. For example,
 $C_{Al} = [Al^{+3}] + [AlF^{+2}] + [AlOH^{+2}] + \dots$ etc.
- I Ionic strength of solution.
- ΔG_f° Standard free energy of formation at 25°C.

Equations 1 and 2 in table 1 represent activity products for microcrystalline gibbsite and for cryolite, respectively. Equation 3 is

TABLE 1.—Equations used for calculations for 25°C and 1 atmosphere total pressure

<i>Mass Action Equations</i>	<i>Reference for constant used</i>
(1) $[Al^{+3}][OH^{-1}]^3 = 10^{-32.65}$ -----	Hem and Roberson (1967, p. 46).
(2) $[Na^{+1}]^3[Al^{+3}][F^{-1}]^6 = 10^{-33.84}$ -----	This report.
(3) $\frac{[Na^{+1}]^3[F^{-1}]^6}{[OH^{-1}]^3} = 10^{-1.84}$ -----	This report.
(4) $[H^{+1}][OH^{-1}] = 10^{-14.00}$ -----	Harned and Harner (1933, p. 2198).
(5) $[HF^0] = 10^{3.17}[H^{+1}][F^{-1}]$ -----	Butler (1964, p. 113).
(6) $[AlOH^{+2}] = 10^{9.23}[Al^{+3}][OH^{-1}]$ -----	Hem (1968, p. B8).
(7) $[Al(OH)_4^{-1}] = 10^{33.96}[Al^{+3}][OH^{-1}]^4$ -----	Do.
(8) $[AlF^{+2}] = 10^{7.01}[Al^{+3}][F^{-1}]$ -----	Do.
(9) $[AlF^{2+1}] = 10^{12.75}[Al^{+3}][F^{-1}]^2$ -----	Do.
(10) $[AlF_3^0] = 10^{17.02}[Al^{+3}][F^{-1}]^3$ -----	Do.
(11) $[AlF_4^{-1}] = 10^{19.72}[Al^{+3}][F^{-1}]^4$ -----	Do.
(12) $[AlF_5^{-2}] = 10^{20.91}[Al^{+3}][F^{-1}]^5$ -----	Do.
(13) $[AlF_6^{-3}] = 10^{20.86}[Al^{+3}][F^{-1}]^6$ -----	Do.
(14) $[AlSO_4^{+1}] = 10^{3.2}[Al^{+3}][SO_4^{-2}]$ -----	Behr and Wendt (1962).
(15) $[Al(SO_4)_2^{-1}] = 10^{5.1}[Al^{+3}][SO_4^{-2}]^2$ -----	Do.

Mass Balance Equations

$$(16) C_{Al} = \frac{[Al^{+3}]}{\gamma_{Al^{+3}}} + \frac{[AlOH^{+2}]}{\gamma_{AlOH^{+2}}} + \frac{[Al(OH)_4^{-1}]}{\gamma_{Al(OH)_4^{-1}}} + \frac{[AlF^{+2}]}{\gamma_{AlF^{+2}}} + \frac{[AlF_2^{+1}]}{\gamma_{AlF_2^{+1}}} \\ + \frac{[AlF_3^0]}{\gamma_{AlF_3^0}} + \frac{[AlF_4^{-1}]}{\gamma_{AlF_4^{-1}}} + \frac{[AlF_5^{-2}]}{\gamma_{AlF_5^{-2}}} + \frac{[AlF_6^{-3}]}{\gamma_{AlF_6^{-3}}} + \frac{[AlSO_4^{+1}]}{\gamma_{AlSO_4^{+1}}} + \frac{[Al(SO_4)_2^{-1}]}{\gamma_{Al(SO_4)_2^{-1}}}$$

$$(17) C_F = \frac{[F^{-1}]}{\gamma_{F^{-1}}} + \frac{[HF^0]}{\gamma_{HF^0}} + \frac{[AlF^{+2}]}{\gamma_{AlF^{+2}}} + \frac{2[AlF_2^{+1}]}{\gamma_{AlF_2^{+1}}} + \frac{3[AlF_3^0]}{\gamma_{AlF_3^0}} \\ + \frac{4[AlF_4^{-1}]}{\gamma_{AlF_4^{-1}}} + \frac{5[AlF_5^{-2}]}{\gamma_{AlF_5^{-2}}} + \frac{6[AlF_6^{-3}]}{\gamma_{AlF_6^{-3}}}$$

$$(18) C_{SO_4} = \frac{[SO_4^{-2}]}{\gamma_{SO_4^{-2}}} + \frac{[Al(SO_4)^{+1}]}{\gamma_{Al(SO_4)^{+1}}} + \frac{2[Al(SO_4)_2^{-1}]}{\gamma_{Al(SO_4)_2^{-1}}}$$

$$(19) C_H = \frac{[H^{+1}]}{\gamma_{H^{+1}}} + \frac{[HF^0]}{\gamma_{HF^0}}$$

$$(20) C_{OH} = \frac{[OH^{-1}]}{\gamma_{OH^{-1}}} + \frac{[AlOH^{+2}]}{\gamma_{AlOH^{+2}}} + \frac{4[Al(OH)_4^{-1}]}{\gamma_{Al(OH)_4^{-1}}}$$

derived from 1 and 2 and represents conditions in a system where both solids are present at equilibrium. Equations 4 and 5 are for dissociations of water and hydrofluoric acid, respectively, and are taken from the published literature. Complexing equations for aluminum with hydroxide, equations 6 and 7, were taken from a previous work in this general study. The complexing equations for aluminum with fluoride and sulfate, equations 8-15, were calculated from data in the literature. The reference sources and computed values for ΔG_f° for the complex ions are shown in Hem (1968). Equations 16-20 are summations relating activities of dissolved species to stoichiometric concentrations.

For use with the equations of table 1, the individual ion-activity coefficients (γ_i), which are for 25°C and which correspond to given ionic strengths, were obtained as follows. For $I \leq 0.10$, tables shown in Butler (1964, p. 435) or a graph in Hem (1961, p. C5) were used to obtain γ_i values. Both Butler and Hem used the relation

$$-\log \gamma_i = \frac{Az^2\sqrt{I}}{1+a_iB\sqrt{I}}$$

for calculating γ_i . This is a well-known form of the Debye-Hückel equation, and the meaning and values for the different parameters are given in Garrels and Christ (1965, p. 61-62). The parameter a_i for ions not given in table 27 of Garrels and Christ (p. 62) was assumed to be 9×10^{-8} for trivalent ions and 4×10^{-8} for divalent and univalent ions.

For uncharged species, γ_i was taken as unity (Butler, 1964, p. 439) for $I \leq 0.10$.

For ionic strengths 0.50 and 0.71, the values for the activity coefficients for 25°C and their sources are shown in table 2.

SOLUBILITY IN A HYDROXIDE SYSTEM

The solid specified in the case of aluminum hydroxide was identified by X-ray diffraction to be gibbsite (Hem and Roberson, 1967, p. 26 and 46). Hem and Roberson found by electron microscopy that this material consisted of crystals 0.10 micron or less in diameter (their p. 34) and that the particles did not increase in size sufficiently to decrease the solubility to a significant extent for several months (their p. 48).

Figure 1 shows the calculated solubility of aluminum at 25°C as a function of pH for a water solution in equilibrium with microcrystalline gibbsite. This graph is valid for solutions containing only OH^{-1} as a complexing ligand. The presence of other anions such as Cl^{-1} or ClO_4^{-1} , which do not form complexes with aluminum, is permissible,

TABLE 2.—Individual ion activity coefficients at 25° C for dissolved species at ionic strengths 0.50 and 0.71

Dissolved Species	γ_i for $I=0.50$	Source	γ_i for $I=0.71$	Source
Al ⁺³ -----	0. 03	(1)	0. 03	(2)
AlOH ⁺² -----	. 24	(1)	. 24	(2)
Al(OH) ₄ ⁻¹ -----	. 69	(1)	. 68	(3)
AlF ⁺² -----	. 24	(1)	. 12	(4)
AlF ₂ ⁺¹ -----	. 69	(1)	. 68	(3)
AlF ₃ ⁰ -----	1. 11	(5)	1. 13	(6)
AlF ₄ ⁻¹ -----	. 69	(1)	. 68	(3)
AlF ₅ ⁻² -----	. 24	(1)	. 12	(4)
AlF ₆ ⁻² -----	. 03	(1)	. 03	(2)
AlSO ₄ ⁺¹ -----	. 69	(1)	. 68	(3)
Al(SO ₄) ₂ ⁻¹ -----	. 69	(1)	. 68	(3)
Na ⁺¹ -----	. 69	(1)	. 76	(6)
F ⁻¹ -----	. 69	(1)	. 69	(2)
HF ⁰ -----	1. 11	(5)	1. 13	(5)
SO ₄ ⁻² -----	. 24	(1)	. 12	(6)

¹ Nomograph based on Davies' equation in Butler (1964, p. 438).

² Assumed to be the same as for $I=0.50$. (See Butler, 1964, p. 438.)

³ Garrels and Thompson (1962, p. 61) used this value for all the univalent complex ions which they considered.

⁴ Assumed to be the same as the ion-activity coefficient for SO₄⁻² (see footnote 6).

⁵ Assumed to be the same as for H₂CO₃ in NaCl solution (Garrels, and Christ, 1965, p. 69).

⁶ Garrels and Thompson (1962, p. 61).

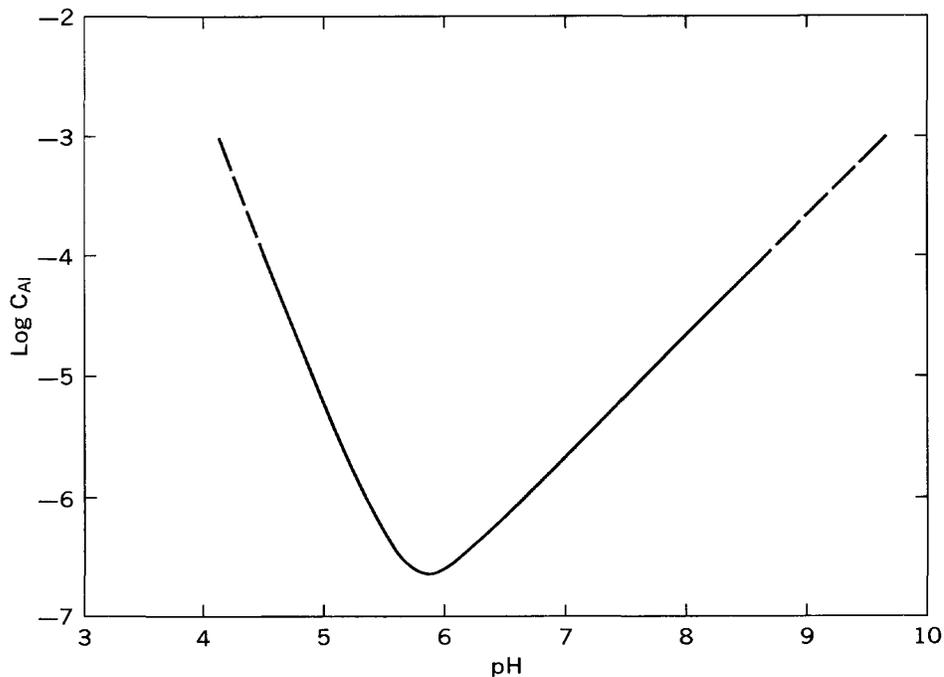


FIGURE 1.—Solubility of microcrystalline gibbsite as a function of pH, at 25°C and 1 atmosphere total pressure.

providing they are taken into account as far as their contribution to ionic strength is concerned. In this connection, the ordinate of figure 1 shows the total dissolved aluminum concentration when the ionic strength (I) is zero. Obviously, such solutions do not exist, but up to $I=10^{-4}$ the error in using figure 1 is probably within the limits imposed by uncertainties in thermodynamic data, analytical error, and a person's ability to read the graph. For use with solutions having higher ionic strengths, appropriate graphs may be prepared as discussed later.

In figure 1 and in the other graphs presented, we have attempted to show only those parts of solubility curves which are expected to be reasonably applicable to natural water solutions that have ionic strengths within a specified range. Because of the large number of variables involved, however, it has been necessary to be quite arbitrary in indicating regions of lesser applicability (dashed lines) and non-applicability (no lines). For example, in figure 1 and in the other graphs to be presented, the segments of curves considered to be applicable to natural water are represented by solid lines. The lines are discontinued when either of the plotted variables reaches a concentration equal to the ionic strength for which the particular diagram is recommended. This somewhat arbitrary cutoff implies that all the dissolved species in the water are univalent because ionic strength is given by

$$I = \frac{1}{2} \sum m_i z_i^2 \quad (\text{Lewis and Randall, 1961, p. 338}),$$

where m_i is the molality of ion i and z_i is the charge on the ion.

It is evident that the implication of univalency for all dissolved species is not always valid. From figure 1, $C_{Al}=10^{-4}$ at a pH of 4.5, and more than half the aluminum is present as trivalent Al^{+3} ; the ionic strength of a solution represented by this point on the curve could not be as low as 10^{-4} . Along the alkaline limb of the curve, however, the main species is monovalent $Al(OH)_4^{-1}$, and if the anions also have unit charges, then $C_{Al}=10^{-4}=I$. Notwithstanding such possible differences in charges on species in different regions of the graphs, we have discontinued the solid line segments when the C_{Al} (or C_F or C_{SO_4} for certain graphs) reaches a level equal to the ionic strength recommended. In all graphs, the curves have been dashed-in for concentrations up to one order of magnitude higher than the recommended level.

Another complication which arises when the concentration of either of the plotted master variables becomes large in a natural water is the difficulty of determining a true value for ionic strength of the natural solution. A process of reiteration must sometimes be employed because much of the ionic strength-determining ion(s) may be in-

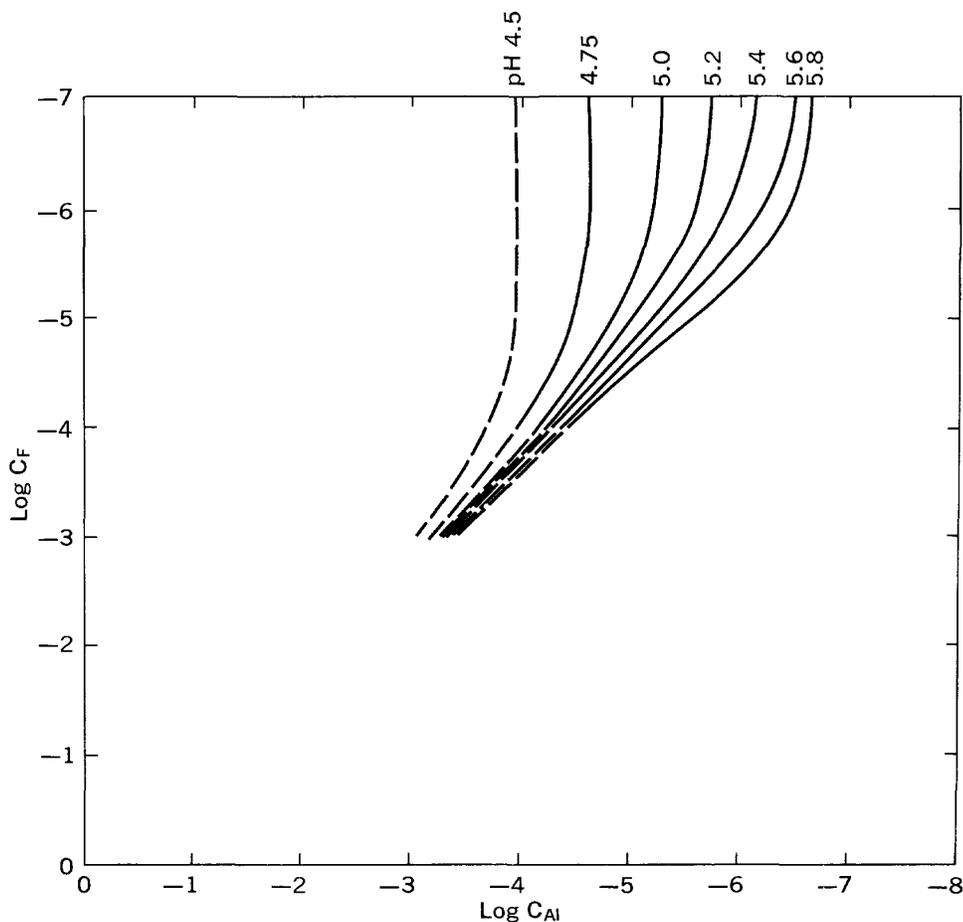
volved in complexes, a situation which alters the ion's contribution to ionic strength from what it would be in the absence of complexing. Fortunately, in most natural water at ionic strengths up to and including sea water, the ions which mainly determine ionic strength are those which are present in such abundance that their contribution to ionic strength is little affected by complexing. Aluminum, which is largely complexed in most natural solutions, is very low in concentration relative to other dissolved species, and hence has little effect on I . When C_{Al} is high, however, suggested by dashed segments of curves, one must exercise care in applying the solubility calculations to natural solutions. Obviously, it is not possible to prepare simple two-dimensional diagrams which are equally valid for all concentration levels.

To prepare the diagram of figure 1, equations 1, 4, 6, 7, 16 and 20 (table 1) were used. Because F^{-1} and SO_4^{-2} are absent in this system, only the first three terms of equation 16 are needed. If ionic strength is specified, there are seven variables— $[Al^{+3}]$, $[AlOH^{+2}]$, $[Al(OH)_4^{-1}]$, $[OH^{-1}]$, $[H^{+1}]$, C_{OH} , and C_{Al} —in six equations. This means that if one assigns a value to one variable, the amounts of the other six are fixed. For figure 1, values for $[H^{+1}]$, which are by definition equal to 10^{-pH} were assigned. One could just as readily plot the independent variable, pH, against any one of the other six dependent variables. The total dissolved aluminum concentration (C_{Al}) was chosen because it permits one to evaluate a solution, such as a natural water, with respect to possible equilibrium with gibbsite, even though one has only a minimum amount of analytical data at hand.

Figure 1 represents a system that is too simple to be applied directly to many natural waters. In natural water, F^{-1} and SO_4^{-2} are present, and these ions compete with the OH^{-1} in complexing Al^{+3} . Such competition may be significant at low pH values, but above about pH 7 it is generally quite unimportant. Figure 1 is valid only for very dilute solutions, but graphs for other ionic strengths can readily be prepared. The solubility of aluminum is increased by increasing the ionic strength. The minimum solubility shown in figure 1 is about 0.006 ppm as Al.

SOLUBILITY IN THE PRESENCE OF HYDROXIDE, FLUORIDE, AND SULFATE

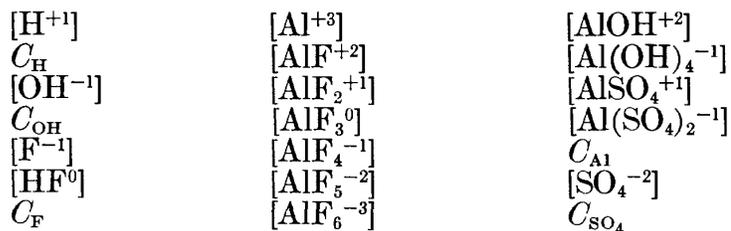
Most natural water contains ligands other than OH^{-1} that form complexes with aluminum. Probably the most significant of these are F^{-1} and SO_4^{-2} . Figures 2-12 were prepared to show the effects on the solubility of gibbsite of varying concentrations of the ligands OH^{-1} , F^{-1} , and SO_4^{-2} . For each of the diagrams, the solution described is assumed to be in equilibrium with microcrystalline gibbsite. To calculate data for these graphs, equations 1 and 4-20 (table 1) were used.



A

FIGURE 2.—Solubility of microcrystalline gibbsite as a function of fluoride total pressure. A, pH

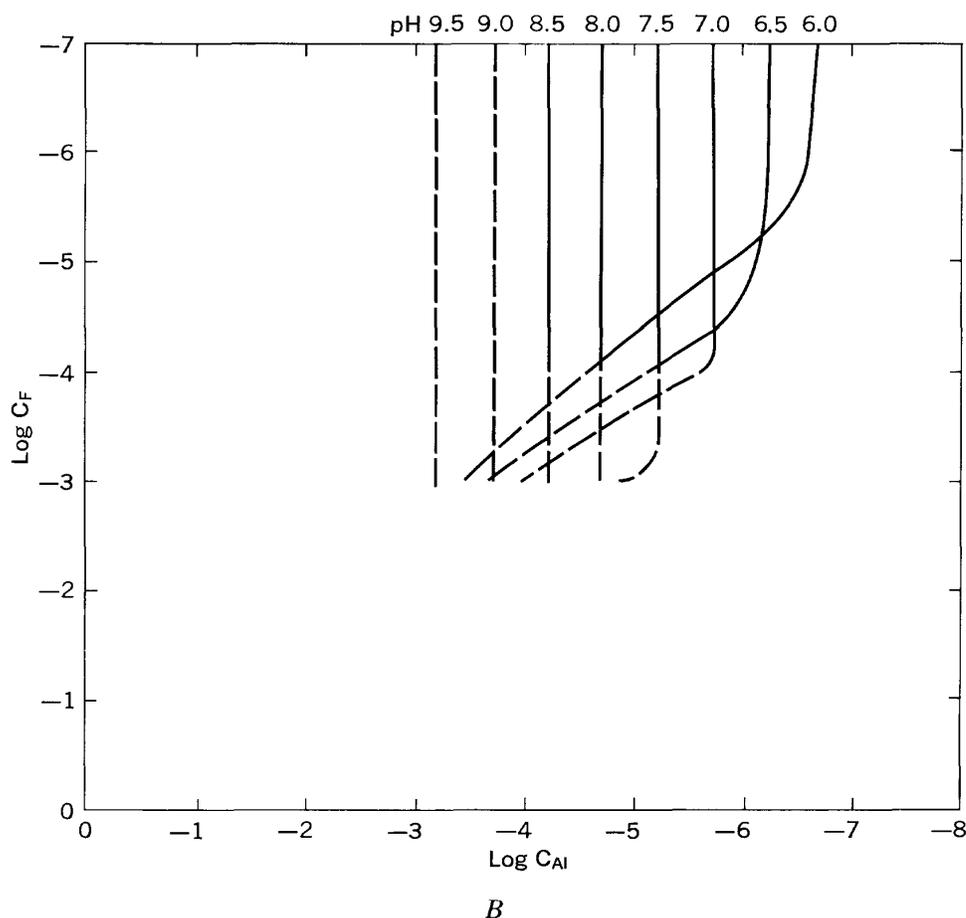
These are the 21 variables involved for any given ionic strength:



There are 18 equations relating to these variables; if values are assigned to three of the variables, all the others will be fixed.¹

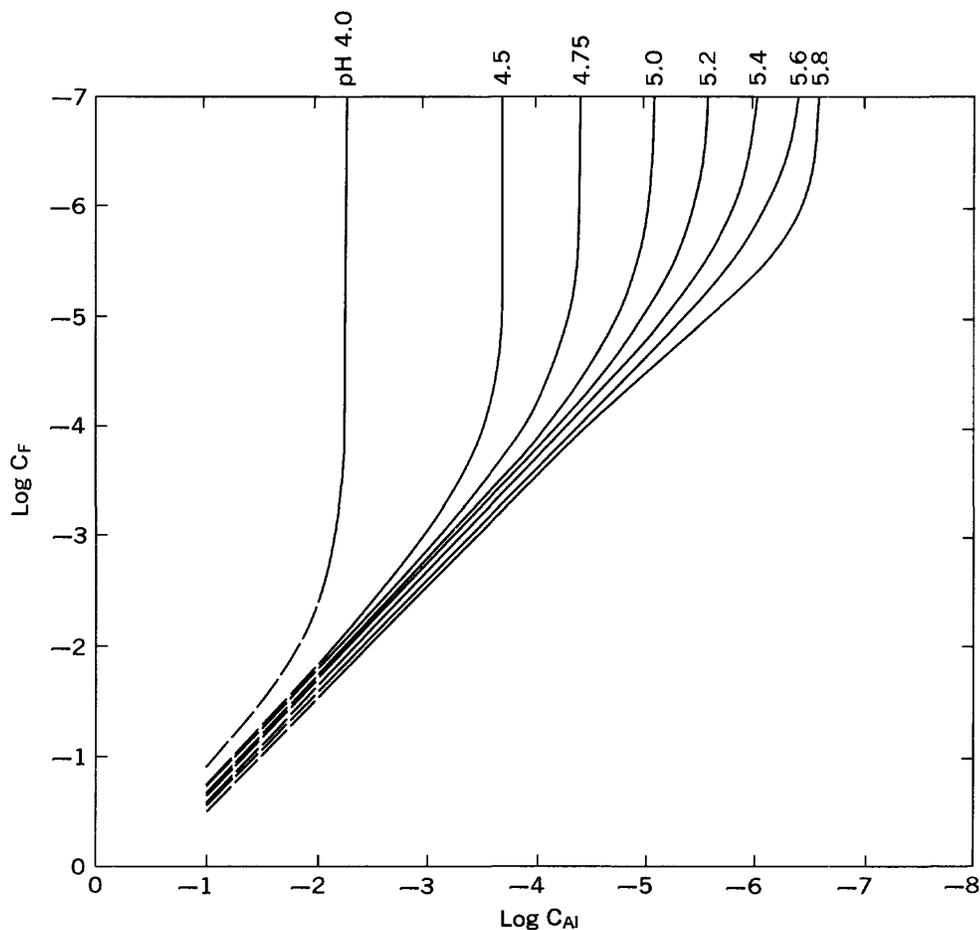
The four variables that can be measured in a water analysis are $[H^{+1}]$, C_{Al} , C_F , and C_{SO_4} . The set of equations permits calculation of any one of these variables if the other three are assigned specified

¹ Polynomial equations involving unknowns to as high as the 6th power were solved by successive approximations.



concentration. Sulfate absent. Ionic strength 0. For 25° C and 1 atmosphere 4.50–5.80. B, pH 6.00–9.50.

values. In figures 2–12, $\text{log } C_{Al}$ is plotted on one axis and either $\text{log } C_F$ or $\text{log } C_{SO_4}$ is plotted on the other. One of the master concentration variables is assigned a fixed value, which can be zero. The pH for equilibrium can be shown by contour lines on the graph. To avoid overlap, two graphs are required, one for pH below the point of minimum solubility and one for pH above that point. The resulting graph is valid only for the ionic strength assumed. To cover a range of concentrations, the calculations are repeated for other values of ionic strength. The calculations, while not difficult, are rather onerous if done by hand. They are readily programmed for calculation by an electronic computer. This method makes the preparation of graphs easy by calculating many possible combinations of variables, and it is also easy to test each individual water solution having a specific ionic composition. The diagrams in this report cover a rather wide range of conditions and should be approximately applicable to many



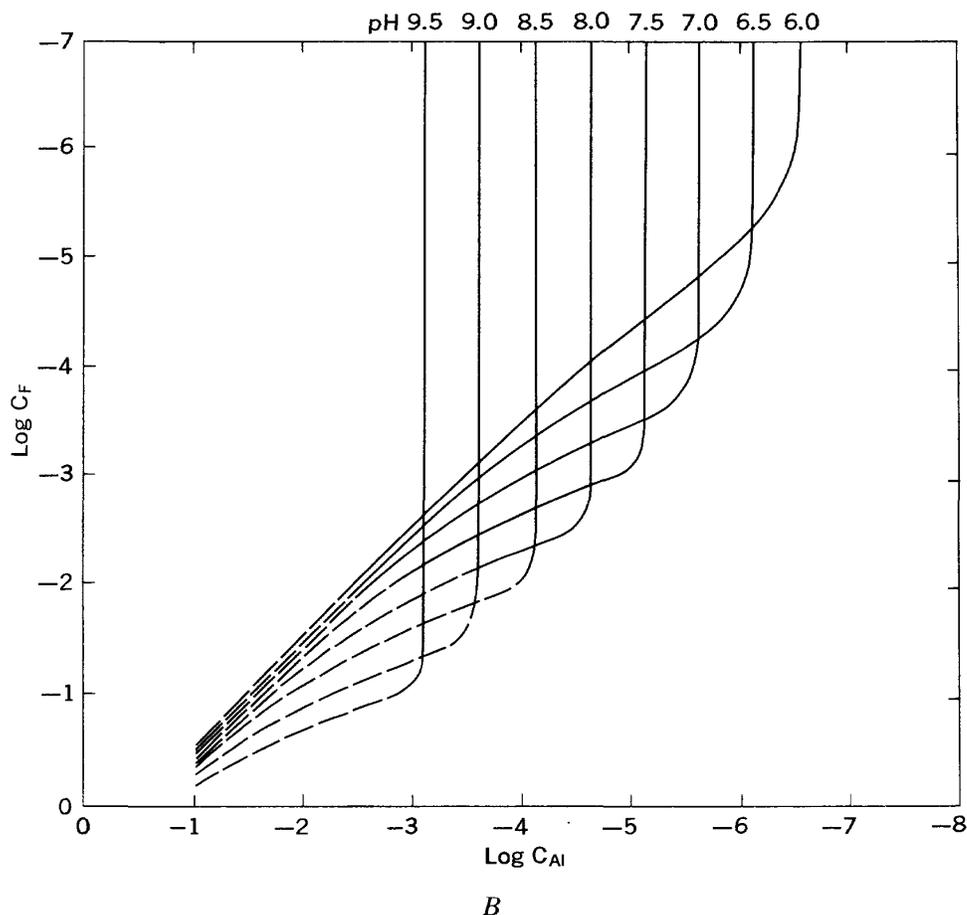
A

FIGURE 3.—Solubility of microcrystalline gibbsite as a function of fluoride total pressure. A, pH 4.00–5.80. B, pH 6.00–9.50. (See figure 6 for sulfate of sulfate up to 0.05 molal had negligible effect at pH 6.00–9.50, so the graph

natural solutions having ionic strengths between near zero and that of sea water (about 0.71).

Figures 2–10 show plots of C_{Al} against C_F at selected pH values, C_{SO_4} values, and ionic strengths. The graphs are presented in pairs, one for pH below the point of minimum solubility (around pH 6) and one for pH values above the point of minimum solubility. Because of the amphoteric nature of aluminum, the curves prepared for pH values below the minimum solubility point look quite different from those prepared for higher pH values.

Plotting C_{Al} against C_{SO_4} at selected C_F , pH, and ionic strengths, results in the curves shown in figures 11–12. Again, all graphs are based on the assumption that the solution is in equilibrium with solid microcrystalline gibbsite at 25°C.



concentration. Sulfate absent, Ionic strength 0.01. For 25°C and 1 atmosphere concentration 0.005 molal. Ionic strength 0.01. pH 3.50–5.80. Concentrations given here in figure 3B represents satisfactorily the solubility in this pH range.)

Some aspects of gibbsite solubility inferred from the diagrams are as follows:

1. The vertical parts of the pH lines in the graphs suggest regions where the main variable (C_F in figs. 2–10; C_{SO_4} in figs. 11–12) has a relatively negligible effect in increasing the solubility of gibbsite. For example, in figure 4A, the solubility of gibbsite is high ($C_{Al} = 10^{-1.8}$ or Al=428 mg/l) at a pH of 4.00; therefore the C_F must be as large as 10^{-2} (190 mg/l) to cause an appreciable increase in gibbsite solubility. An increase of fluoride complexing is suggested when the vertical lines, which are fixed by the invariant OH^{-1} (for a fixed pH) bend toward higher concentrations of C_{Al} . At a pH of 5.8 (fig.4A), the concentration of aluminum is low, and $C_F = 10^{-4.9}$ (F=0.23 mg/l) causes a 10-fold increase in C_{Al} over that expected in the absence of fluoride.

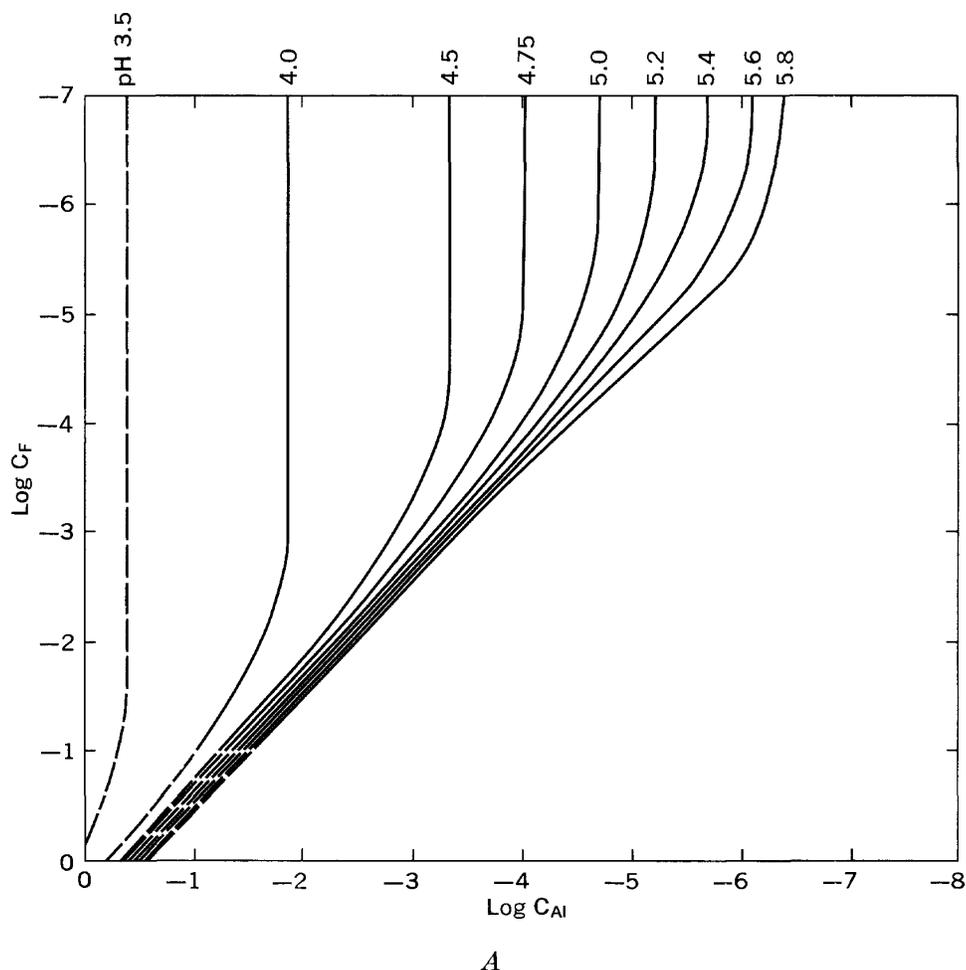
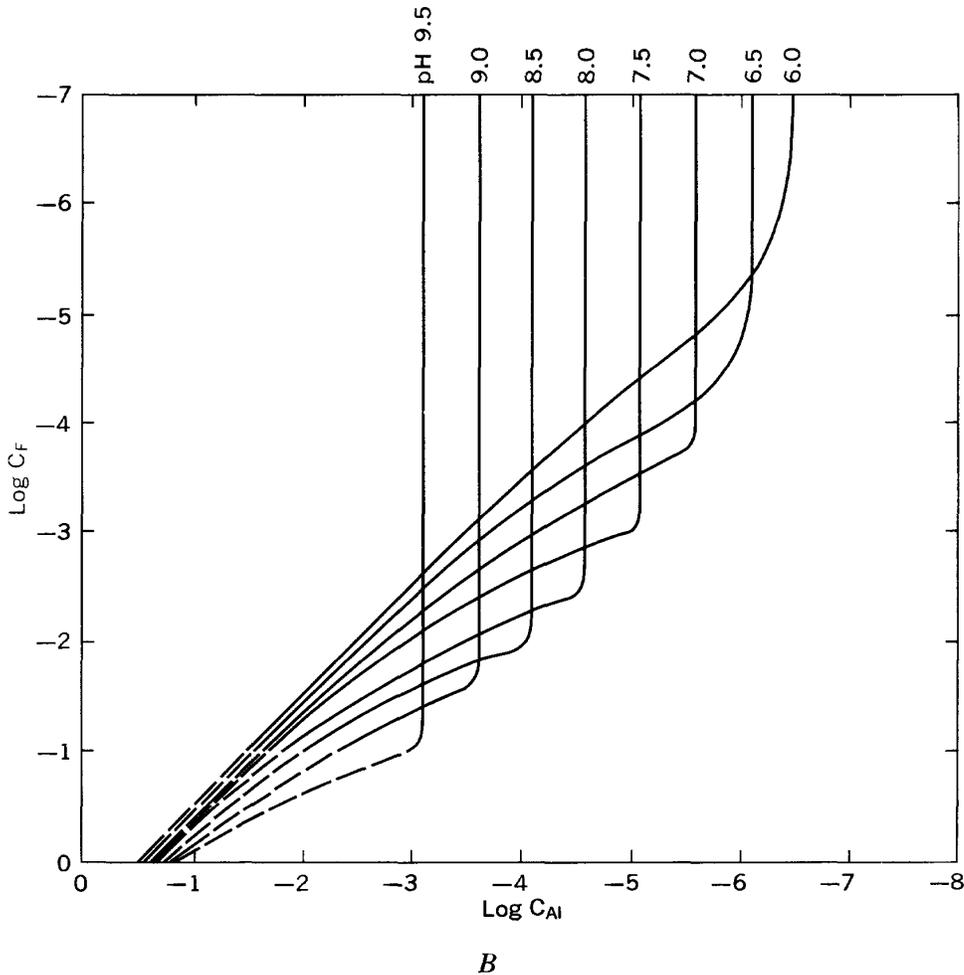


FIGURE 4.—Solubility of microcrystalline gibbsite as a function of fluoride total pressure. *A*, pH 3.50–5.80. *B*, pH 6.00–9.50. (See figs. 7 and 9 for 3.50–5.80. Concentrations of sulfate up to 0.05 molal had negligible effect at solubility in this pH range.)

2. At very low fluoride levels, 10^{-7} – 10^{-6} (0.002–0.02 mg/l) the effect of increasing ionic strength from 0 to 0.71 (that of sea water) is to increase the solubility of aluminum from gibbsite by about a factor of 25 at pH 4.5 and by a factor of 4 at pH 5.8 (figs. 2–5). The increase at pH 8 amounts to only a factor of 2 (figs. 2*B*, 5*B*).

3. The effect of fluoride complexing is much less important at pH values above neutrality. At a pH of 7, C_F must be greater than 10^{-4} molal (1.9 mg/l) to cause a significant increase in solubility of aluminum (fig. 2*B*). At a pH of 9.5 (fig. 4*B*), C_F must be about 10^{-1} molal (1,900 mg/l) to increase the solubility over that expected in systems with no fluoride present. As discussed later, however, at $C_F=10^{-1}$, gibbsite may not control the solubility, and other solid phases must be considered.



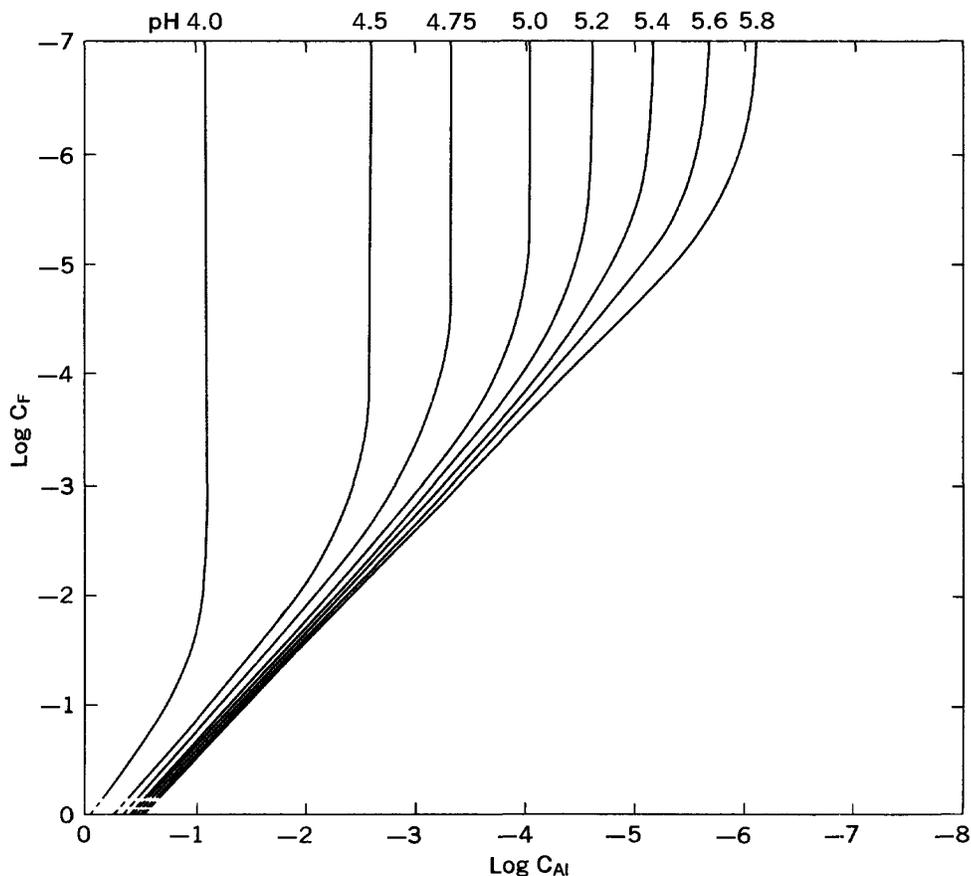
concentration. Sulfate absent, Ionic strength 0.10. For 25°C and 1 atmosphere sulfate concentrations 0.005 molal and 0.05 molal. Ionic strength 0.10. pH 6.00–9.50, so the graph given here in fig. 4B represents satisfactorily the

4. At pH values below the minimum solubility, which occurs near pH 5.9 under conditions suggested by figure 1, the effect of fluoride complexing becomes more important. At a pH of 5.8, the effect of as little as 10^{-6} molal fluoride (0.02 mg/l) is seen to have considerable relative effect on increasing gibbsite solubility (fig. 2A).

5. The effect of sulfate complexing at $\text{pH} \geq 7$ is negligible (figs. 11–12).

6. However, at pH values between 4.0 and 5.5, sulfate concentrations of about 10^{-2} molal (960 mg/l) become significant enough to increase the solubility (fig. 11A). Sulfate complexing at low pH (< 4.0) is, again, less important relatively, because of the much greater solubility of gibbsite in this region.

From the diagrams, it is possible to make certain inferences about natural water solutions.



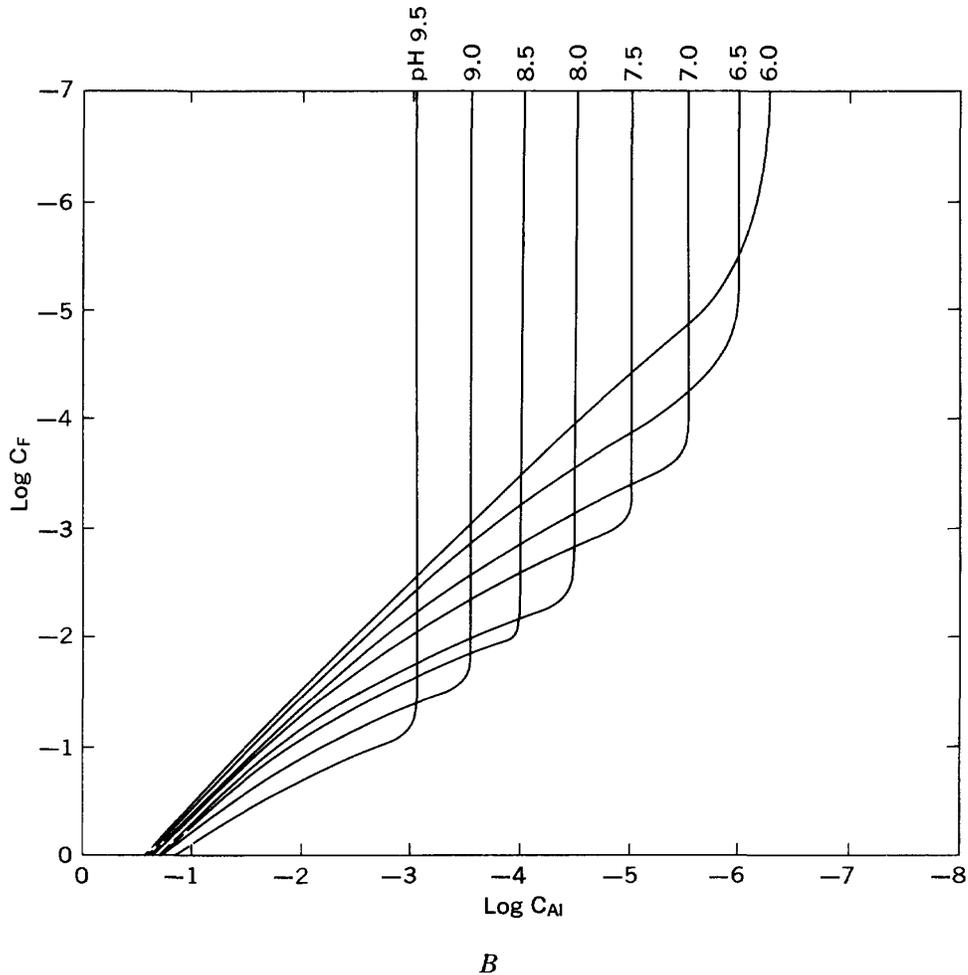
A

FIGURE 5.—Solubility of microcrystalline gibbsite as a function of fluoride total pressure. *A*, pH 4.00–5.80. *B*, pH 6.00–9.50. (See figs. 8 and 10 for 4.00–5.80. Concentrations of sulfate up to 0.05 molal had negligible effect at solubility in this pH range.)

APPLICATION TO NATURAL WATER

Published values for aluminum in natural water are difficult to evaluate quantitatively. The readiness with which aluminum polymerizes, its ubiquitous presence in suspended matter (some of the matter may consist of particles in the order of 0.10μ in diameter), and analytical interferences have not always been recognized by investigators. As a result, many of the aluminum values reported are probably too high. However, for water having near neutral pH, analytical values for aluminum are usually less than 0.02 mg/l Al. This is the value predicted by figure 2*B* if a water has a pH of 6.0, has a very low ionic strength ($I \leq 0.0001$), and is in equilibrium with gibbsite.

One can, however, expect gibbsite to control the amount of aluminum in water from certain environments. For example, in tropical



concentration. Sulfate absent, Ionic strength 0.71. For 25°C and 1 atmosphere sulfate concentrations 0.005 molal and 0.05 molal. Ionic strength 0.71. pH 6.00–9.50, so the graph given here in fig. 5B represents satisfactorily the

climates and certain temperate climates, the principal end products in the weathering of silicates are the oxides and hydroxides of aluminum and iron. Meager data (Patterson and Roberson, 1961) from one such area (Hawaii) suggests that even there the tendency is for the water to contain less aluminum than would be predicted from the theoretical values of gibbsite solubility. The evidence is far from conclusive, however, because of uncertainties involved with sampling and analysis; for example, the water samples came from auger holes that were for the most part deeper than the layer enriched in gibbsite (Patterson and Roberson, 1961, p. 196). More specifically oriented sampling and analyses might have shown results favorable to control by gibbsite.

Mine drainage samples commonly contain considerable dissolved aluminum resulting from relatively high hydrogen-ion concentrations.

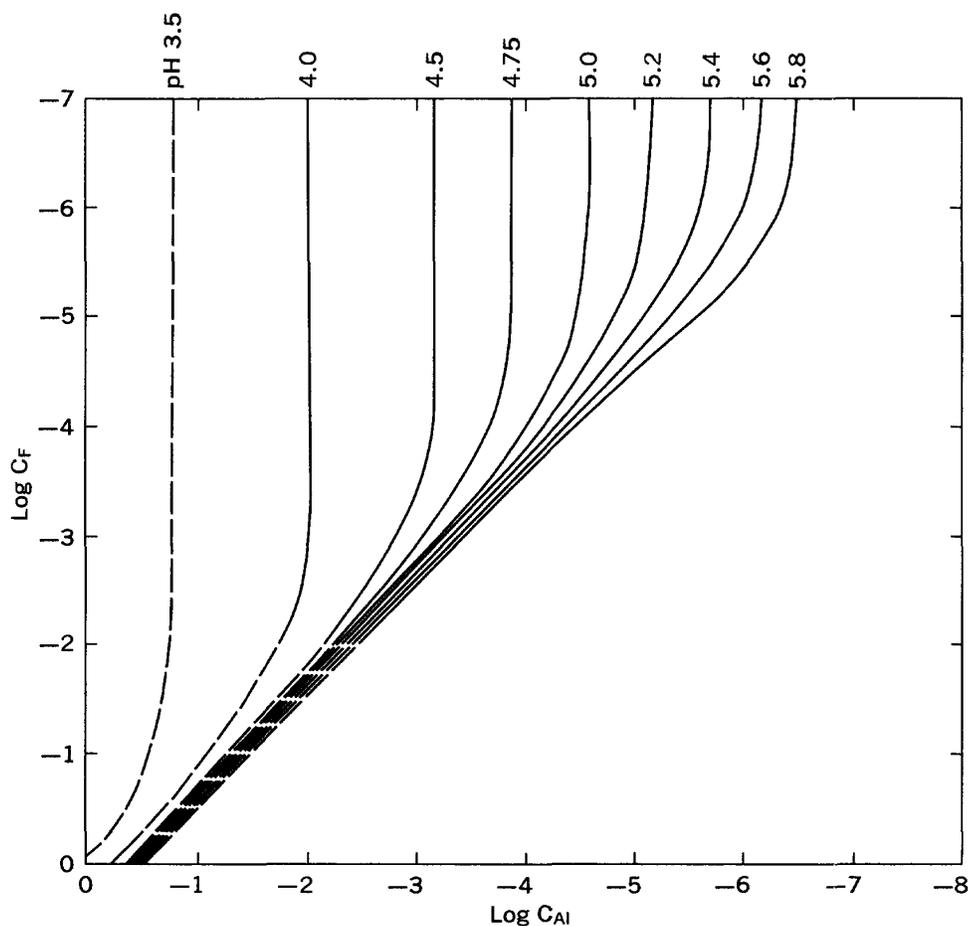


FIGURE 6.—Solubility of microcrystalline gibbsite as a function of fluoride concentration. Sulfate concentration 0.005 molal. Ionic strength 0.01. pH 3.50–5.80. (See fig. 3 for pH 6.00–9.50.) For 25°C and 1 atmosphere total pressure.

With regard to this type of sample, published data are presumably more reliable, because sampling and analytical errors should be less significant when C_{Al} and H^{+1} concentrations are high. Studies are under way to test some of the analytical data from literature with the gibbsite model as well as to test for equilibrium with aluminosilicates. Preliminary calculations on a few data again suggest equilibrium with a phase that is less soluble than gibbsite.

EXPERIMENTAL TEST OF SOLUBILITY CALCULATIONS

The solubility diagrams (figs. 2–12) are based on theoretical considerations that have made use of assumed equilibrium of solutions with freshly precipitated gibbsite. Experiments were performed in the laboratory to test the validity of the diagrams.

Table 3 shows measured aluminum concentrations from precipitation experiments compared with values for solubility of gibbsite

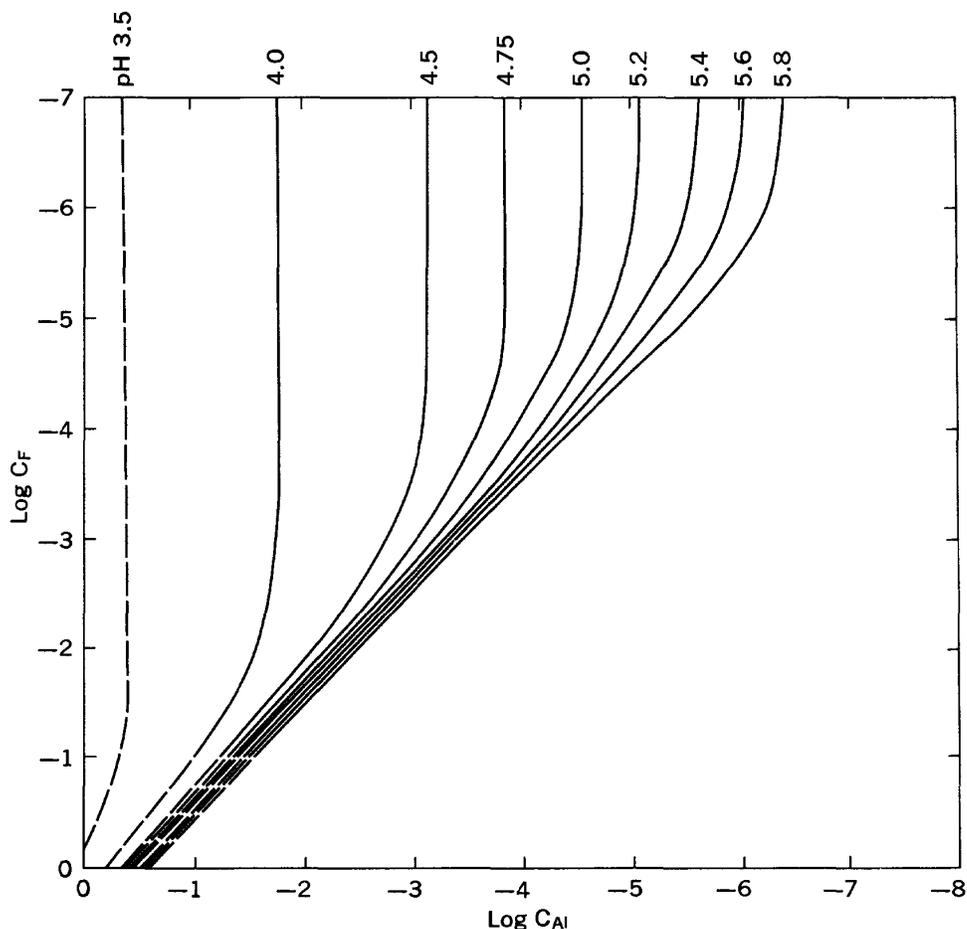


FIGURE 7.—Solubility of microcrystalline gibbsite as a function of fluoride concentration. Sulfate concentration 0.005 molal. Ionic strength 0.10. pH 3.50–5.80. (See fig. 4 for pH 6.00–9.50.) For 25°C and 1 atmosphere total pressure.

predicted from the diagrams in this report. In all solutions a solid phase was present. The precipitation was performed in each test by adding base to an aluminum solution in the presence of fluoride. The agreement between measured and predicted C_{Al} values when concentrations of fluoride did not exceed $10^{-2.00}$ was reasonably good (experiments 1–3, 7–9, table 3). In two of the solutions which contained 10^{-1} moles per liter of fluoride, a reasonably good agreement also was obtained. Those were the solutions having the lowest pH (a little less than 5). In the other solutions high in fluoride, the dissolved aluminum was much less than the amount predicted by the diagrams.

A second series of solubility experiments was carried out using sulfate instead of fluoride. The results are given in table 4. The aluminum concentrations measured were less than the calculated

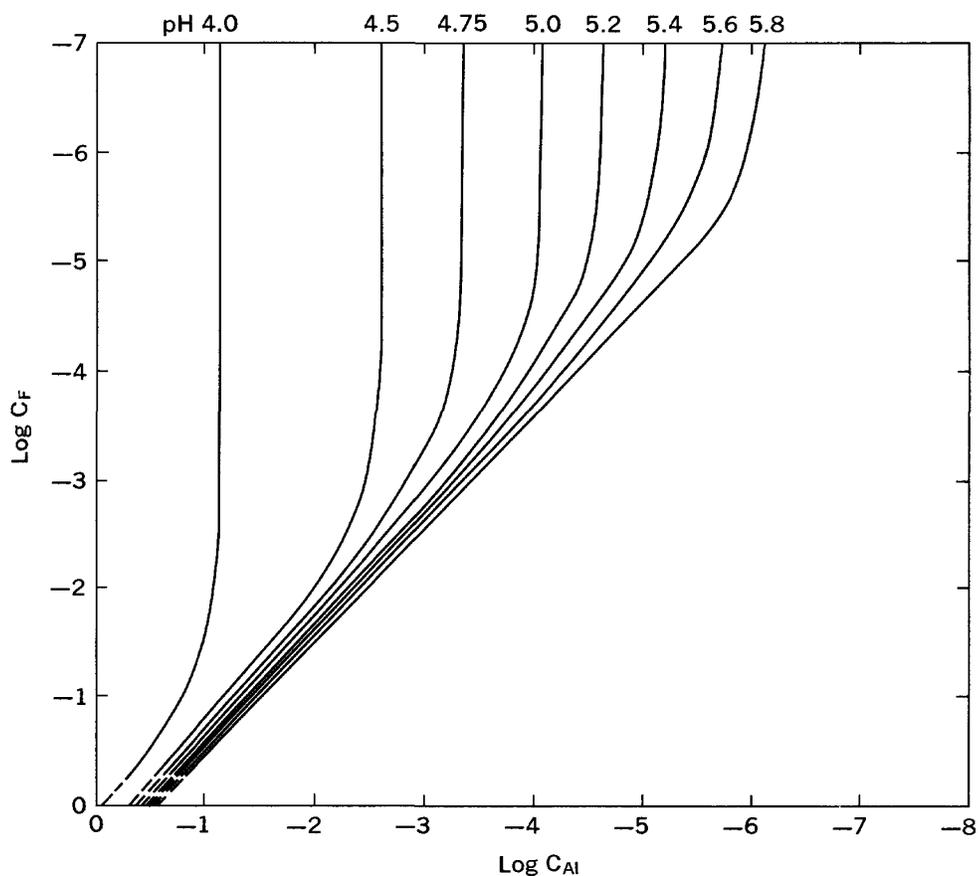


FIGURE 8.—Solubility of microcrystalline gibbsite as a function of fluoride concentration. Sulfate concentration 0.005 molal. Ionic strength 0.71. pH 4.00–5.80. (See fig. 5 for pH 6.00–9.50.) For 25°C and 1 atmosphere total pressure.

TABLE 3.—Solubility of aluminum measured in precipitation experiments compared with predicted solubility of gibbsite
[Complexing ligands: F^{-1} and OH^{-1}]

Experiment	Log C_F	pH	Log C_{Al}	
			Measured	Gibbsite Theoretical (see figure)
1	-2.00	7.94	-3.49	-3.13 (3B)
2	-2.00	8.67	-3.59	-3.85 (3B)
3	-2.00	8.77	-3.51	-3.75 (3B)
4	-.30	8.82	-3.09	-1.10 (5B)
5	-1.01	9.29	-3.23	-2.65 (4B)
6	-1.31	8.88	-3.78	-2.75 (4B)
7	-2.01	8.49	-4.05	-4.00 (3B)
8	-2.31	8.75	-3.81	-3.85 (3B)
9	-3.31	8.83	-3.93	-3.8 (3B)
10	-1.00	4.91	-1.44	-1.3 (4A)
11	-1.00	4.84	-1.52	-1.3 (4A)
12	-1.00	5.46	-1.67	-1.4 (4A)
13	-1.00	5.51	-1.73	-1.4 (4A)
14	-1.00	5.79	-1.99	-1.5 (4A)
15	-1.00	6.40	-2.89	-1.5 (4B)
16	-1.00	7.43	-3.90	-1.6 (4B)
17	-1.00	8.73	-4.13	-1.9 (4B)

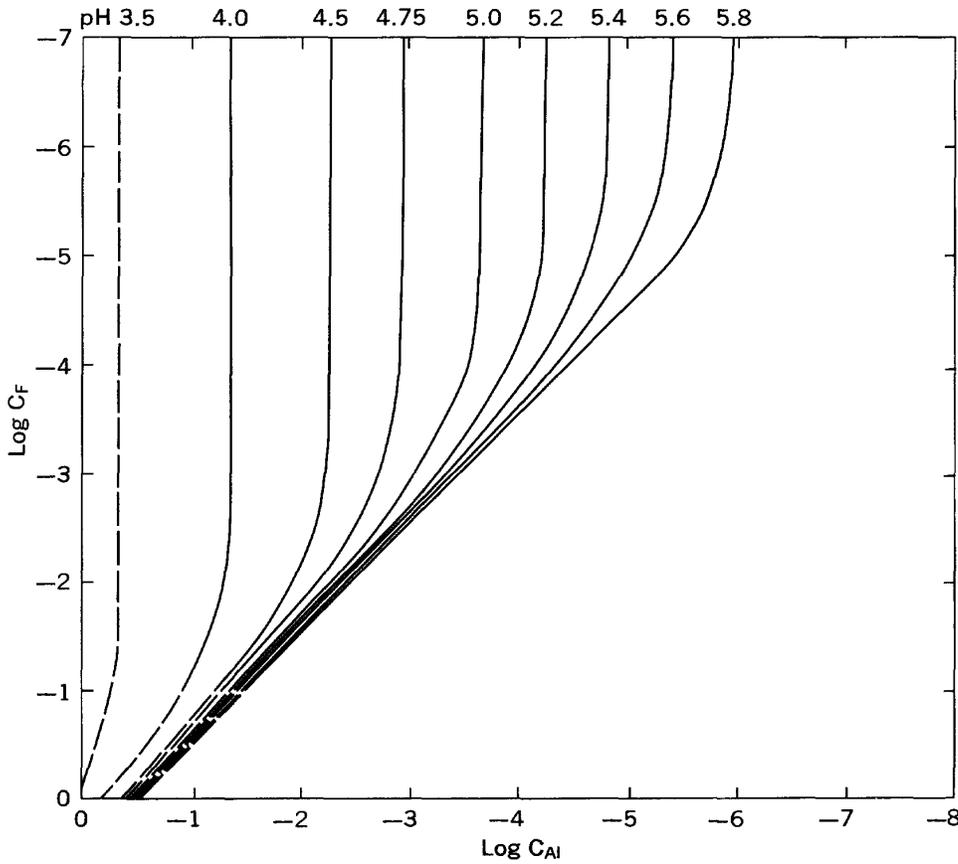


FIGURE 9.—Solubility of microcrystalline gibbsite as a function of fluoride concentration. Sulfate concentration 0.05 molal. Ionic strength 0.10. pH 3.50–5.80. (See fig. 4 for pH 6.00–9.50.) For 25°C and 1 atmosphere total pressure.

TABLE 4.—Solubility of aluminum measured in precipitation experiments compared to predicted solubility of gibbsite

[Complexing ligands: SO_4^{2-} and OH^-]

Experiment	Log C_{SO_4}	pH	Log C_{Al}	
			Measured	Theoretical for gibbsite (see figure 11A)
1	-2.00	4.50	-3.44	-3.0
2	-2.00	4.67	-3.80	-3.5
3	-2.00	5.19	-4.95	-4.8
4	-2.00	5.46	-5.43	-5.6
5	-2.00	4.67	-3.64	-3.4
6	-2.00	4.80	-4.03	-3.8
7	-1.00	4.63	-2.95	-2.2
8	-1.00	4.89	-3.59	-2.9
9	-1.00	5.31	-4.52	-4.1
10	-1.00	5.17	-4.26	-3.6

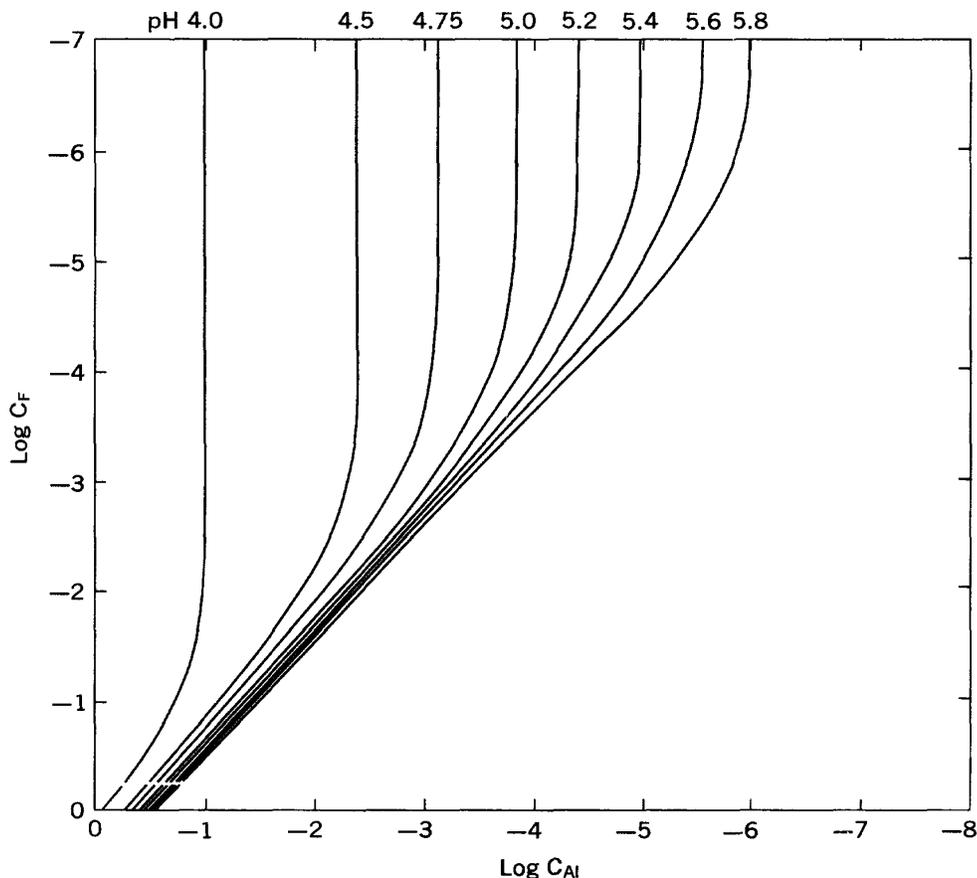


FIGURE 10.—Solubility of microcrystalline gibbsite as a function of fluoride concentration. Sulfate concentration 0.05 molal. Ionic strength 0.71. pH 4.00–5.80. (See fig. 5 for pH 6.00–9.50.) For 25°C and 1 atmosphere total pressure.

amount in all but one of the solutions however, the difference was not large in some. No experiments were made with sulfate above a pH of 5.46.

The most likely explanations for these departures of observed from predicted values are:

1. Equilibrium was not attained or
2. A solid of lower solubility than microcrystalline gibbsite was obtained.

The first explanation seems the less probable because the solutions were aged at 25°C for more than a month, and aluminum determinations showed no significant increases in concentration with longer aging.

Solid species of aluminum containing both hydroxide and another anion are known and further investigations of the solids formed in the presence of fluoride and sulfate were undertaken.

FORMATION OF FLUORO-ALUMINUM SOLIDS

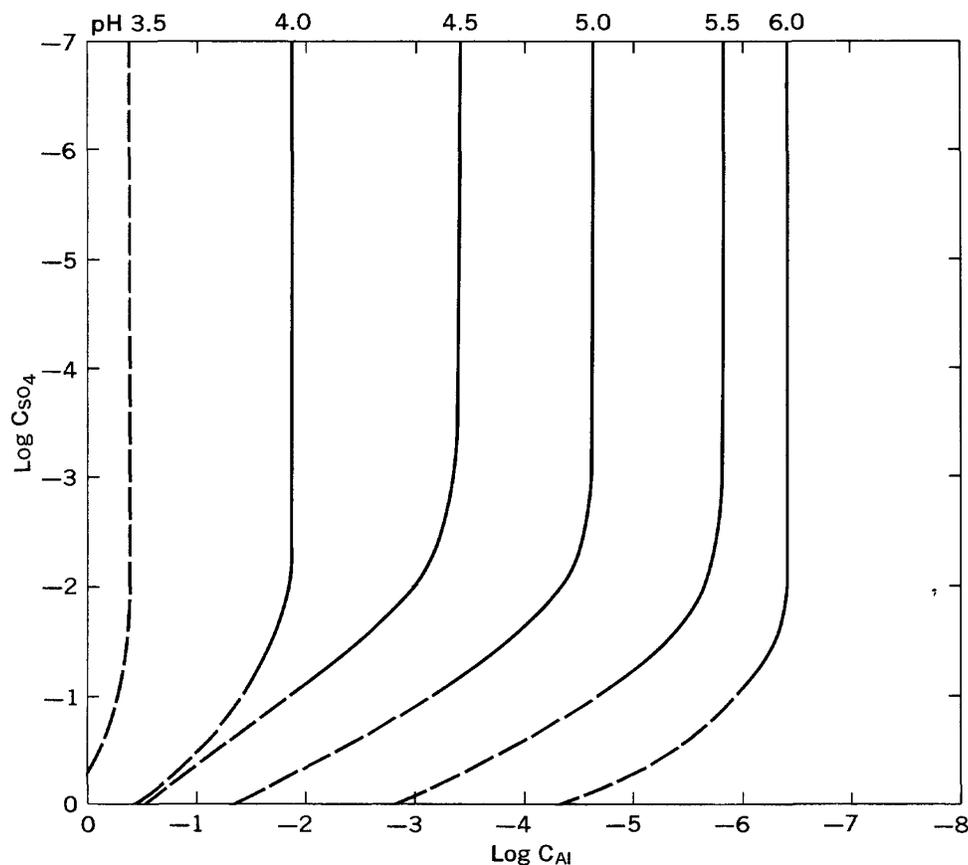
Some of the solid phases obtained from mixed solutions were examined by X-ray diffraction. Portions of a solution having pH 2.1, which was 0.035 molar with respect to $\text{Al}(\text{ClO}_4)_3$ and 0.1 molar with NaF , were adjusted to various pH values with 0.148 *N* NaOH . The pH was measured with a glass electrode. The total aluminum and fluoride concentrations in the system were held constant by adding an amount (equal to the NaOH volume) of a third solution which was 0.070 molar with $\text{Al}(\text{ClO}_4)_3$ and 0.2 molar with NaF . During preparation and aging, the solutions were at room temperature. The predominant cation in the final solution obviously was sodium.

The precipitates, which formed rapidly, were examined by X-ray diffraction. All contained well-crystallized cryolite when examined after aging periods ranging from 1 day to 9 months. Five of eight precipitates prepared, in addition to cryolite, contained ralstonite. The latter phase also was apparently stable. The precipitates were from solutions having pH values of 3.95, 4.58, 5.57, 5.72, and 6.78. Solutions at higher pH values, 6.82, 7.41, and 8.46, contained only cryolite as the crystalline solid.

The formula for cryolite is Na_3AlF_6 . Ralstonite is a name for a series of compounds having the two end members $\text{NaMgAl}(\text{F},\text{OH})_6 \cdot \text{H}_2\text{O}$ and $\text{Al}_2(\text{F},\text{OH})_6\text{H}_2\text{O}$ (Pauly, 1965, p. 1851). Because ralstonite was always accompanied by cryolite in our solutions, it could not be isolated for chemical analysis. Our solutions contained no magnesium as suggested by one of the ralstonite end members; therefore, it can be assumed that the ralstonite formed in our experiments differs in composition from cryolite primarily by OH^- replacing part of the fluoride. That this substitution occurs more readily at low pH than at high pH is at first surprising. Earlier work has shown (Hem and Roberson, 1967) that aluminum and hydroxide ions polymerize extensively in weakly acid solutions. It is likely that the F^- is able to replace part of the OH^- , which is present in the polymer in the form of OH-bridges. The replacement, however, of OH^- by F^- is incomplete because of the inaccessibility of part of the OH^- in the relatively larger polymer. Therefore, part of the OH^- remains in the resulting ralstonite structure. At high pH, probably, very little polymer small enough to react with F^- is present and the complexing reaction is between the ions F^- and $\text{Al}(\text{OH})_4^-$ rather than between F^- and a polymeric species. Apparently the ability of F^- to replace all the OH^- in the ion $\text{Al}(\text{OH})_4^-$, permits the formation of cryolite which contains no OH^- .

SOLUBILITY OF CRYOLITE

Five of the solutions described above were studied in detail for the purpose of estimating an activity product for the solubility of cryolite. The analytical results for the two solutions are shown in table 5.



A

FIGURE 11.—Solubility of microcrystalline gibbsite as a function of sulfate concentration and aluminum concentration at various pH values. A, pH

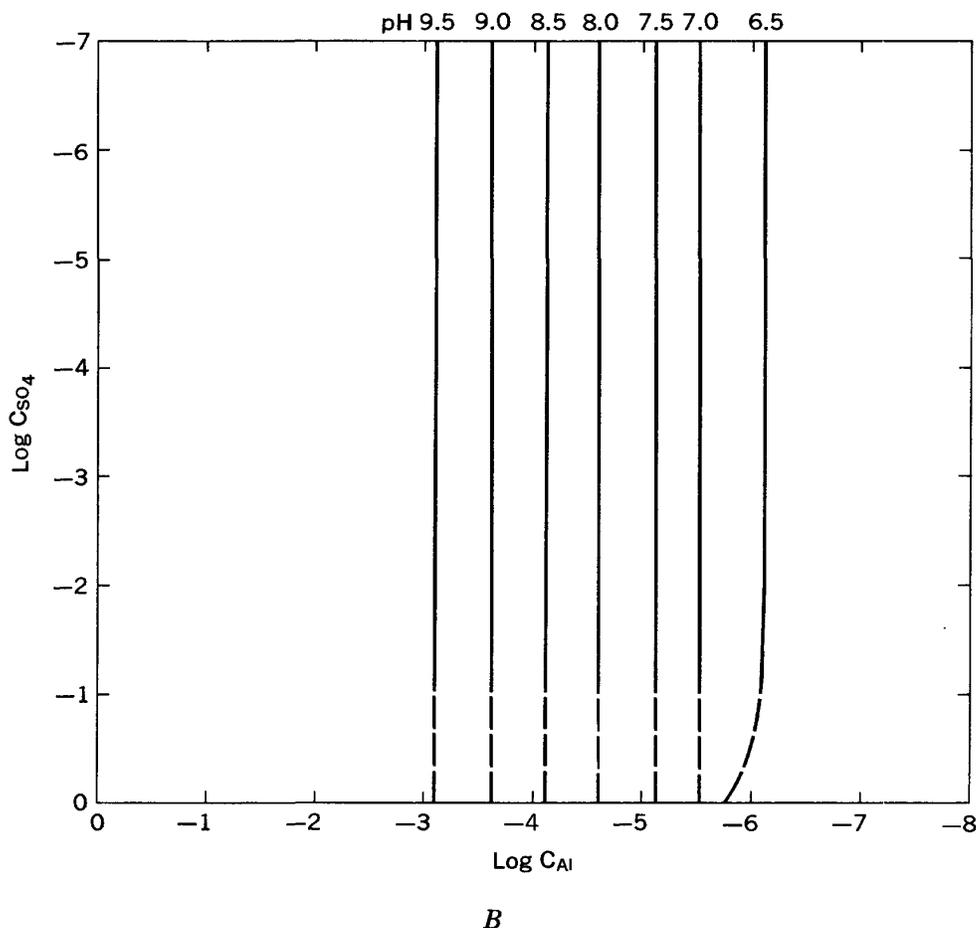
TABLE 5.—Analytical data used for calculating activity product, K_{s0} for solubility of cryolite

$$[K_{s0} = [Na^+]^3[Al^{+3}][F^{-1}]^6 \text{ at } 25^\circ\text{C and 1 atmosphere total pressure}]$$

Item measured	Solutions				
	I	II	III	IV	V
pH	5.57	4.58	8.46	7.41	3.95
C_{Al}	7.59×10^{-3}	2.72×10^{-2}	1.12×10^{-4}	1.11×10^{-5}	2.59×10^{-2}
C_F	2.60×10^{-2}	5.69×10^{-2}	8.21×10^{-3}	2.05×10^{-3}	6.65×10^{-2}
$[F^{-1}]$	2.14×10^{-4}	1.07×10^{-4}	5.0×10^{-3}	1.51×10^{-3}	1.04×10^{-4}
C_{Na}	1.04×10^{-1}	9.09×10^{-2}	1.11×10^{-1}	1.11×10^{-1}	9.74×10^{-2}
$[Na^{+1}]$	8.10×10^{-2}	7.58×10^{-2}	8.90×10^{-2}	8.90×10^{-2}	8.5×10^{-2}
C_{ClO_4}	1.05×10^{-1}	1.05×10^{-1}	1.05×10^{-1}	1.09×10^{-1}	1.09×10^{-1}

NOTES.—The term C_i denotes total molal concentration of all species (complexed and uncomplexed) of ion i . The symbol $[i]$ refers to molal activity of free ion i . The analytical methods used are as follows:

	Method
pH	Glass electrode.
$[Na^{+1}]$	Beckman 78178 sodium electrode.
$[F^{-1}]$	Orion 94-09 fluoride electrode.
C_{Al}	Atomic absorption.
C_{Na}	Atomic absorption.
C_F	Spectrophotometric (Rainwater and Thatcher, 1960, p.163).
C_{ClO_4}	Known amount added.



concentration. Fluoride absent. Ionic strength 0.10. For 25°C and 1 atmos-
3.50–6.00. *B*, pH 6.50 and 9.50.

The activity product for cryolite is represented by

$$[\text{Na}^{+1}]^3[\text{Al}^{+3}][\text{F}^{-1}]^6 = K_{s_0}.$$

The constant K_{s_0} has the same meaning as that given by Sil'én and Martell (1964, p. xiii). In calculating K_{s_0} from a solution in equilibrium with solid cryolite, it is necessary to evaluate the activity of Al^{+3} , Na^{+1} , and F^{-1} . The Na^{+1} and F^{-1} activities were measured directly by means of a Beckman glass sodium electrode (78178) and an Orion fluoride electrode (94-09). This left the more difficult problem of evaluating the activity of Al^{+3} . No electrode was available to us for doing this. There are, theoretically, nine different species of aluminum that exist in an aqueous solution containing the ligands F^{-1} and OH^{-1} . Many of them, including the Al^{+3} species, are sometimes present at concentrations that are too low to be analytically detected. Knowing the stability constants for all the species, however, one can calculate theoretical quantities of any or all of the nine species.

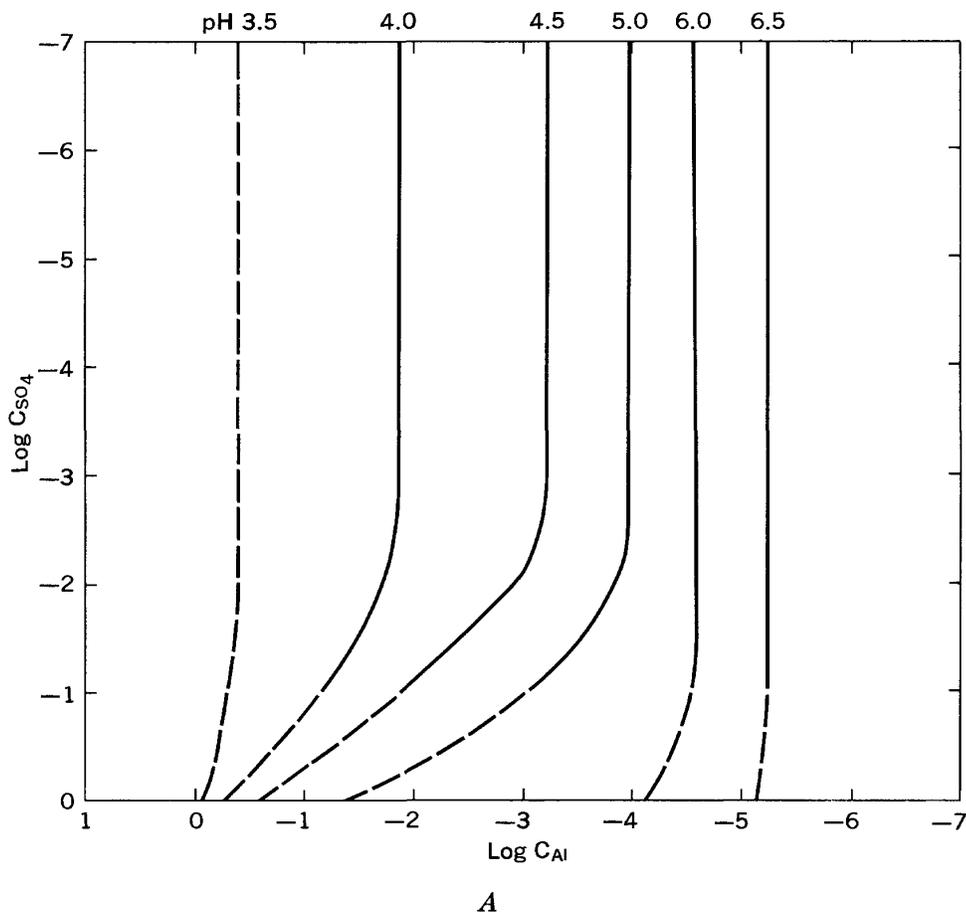
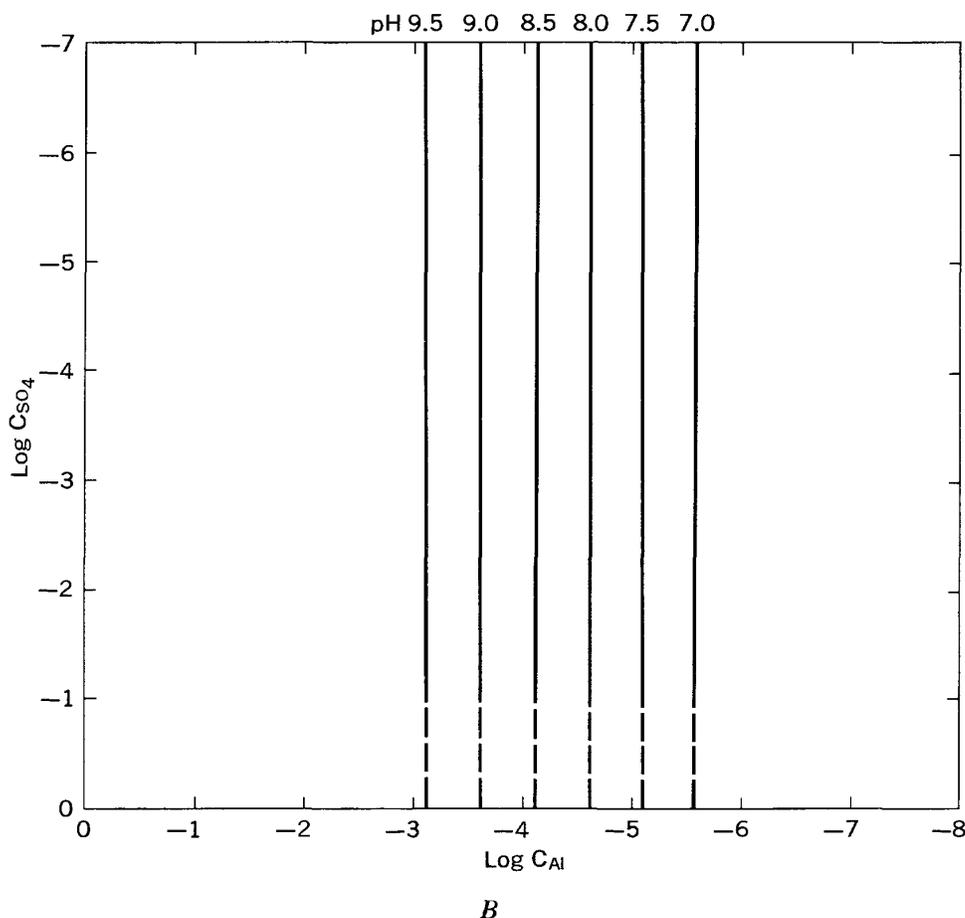


FIGURE 12.—Solubility of microcrystalline gibbsite as a function of sulfate
For 25°C and 1 atmosphere total pressure.

The equations for evaluating the activity of free aluminum, $[Al^{+3}]$, in the solutions for which data are given in table 5, are included in table 1. Appropriate activity coefficients, measured $[H^{+1}]$, $[F^{-1}]$, C_{Al} , are used in connection with equations 4 and 6 through 13 to express the mass balance equation 16 in terms of the unknown $[Al^{+3}]$. The latter is then readily calculated.

The values for ionic strength of the solutions in table 5 are largely controlled by sodium and perchlorate ions. Reiteration calculations indicated that the effect of aluminum-fluoride species on ionic strength can be adequately taken into account by assuming an average ionic charge on all dissolved species of ± 1 . The values for ionic strength of all solutions (table 5) were close enough together ($I=0.112 \pm 0.003$) to permit use of the same activity coefficients for all solutions. The coefficients were calculated by the Debye-Hückel equation as discussed earlier in connection with table 2. The coefficients for uncharged species were taken as unity.



concentration. Total fluoride concentration 10^{-4} molal. Ionic strength 0.10. *A*, pH 3.50–6.50. *B*, pH 7.00–9.50.

After calculating $[Al^{+3}]$ as indicated above and using measured values for $[Na^{+1}]$ and $[F^{-1}]$ as shown in table 5, the activity products K_{s0} are as follows:

<i>Solution</i>	$K_{s0} = [Na^{+1}]^3 [Al^{+3}] [F^{-1}]^6$
I -----	2.57×10^{-34}
II -----	0.80×10^{-34}
III -----	$[14.10 \times 10^{-34}]$
IV -----	1.47×10^{-34}
V -----	1.00×10^{-34}

If K_{s0} for solution III is omitted, the average value is 1.46×10^{-34} . From this value, ΔG_r° for cryolite at $25^\circ C$ is -745.4 kcal mole $^{-1}$. This is identical with the value that is based on calorimetry (Robie, 1962, p. 7). We are assuming that the mean of solutions I, II, IV and V represents the true value of K_{s0} . However, the fact that K_{s0} for solution III is about an order of magnitude larger suggests a possible uncertainty in our value of 1 kcal mole $^{-1}$. This is also the uncertainty given for the calorimetric value (Robie, 1962, p. 7).

CRYOLITE SOLUBILITY DIAGRAMS

Solubility diagrams were prepared to illustrate the natural or laboratory conditions under which cryolite might be expected to form. Figures 13 and 14 were prepared from computer calculations and plots. The graphs show total dissolved aluminum as a function of total dissolved fluoride for selected sodium-concentration levels. The curves were generated using, from table 1, the cryolite solubility expression 2 and equations 8 through 13 and 17. In addition, equation 16 is used after removing the second, third, and last two terms. The calculations assume a low enough pH that hydroxide species can be ignored. Hydroxide would be important at certain pH levels and one should then use, in addition to the above-mentioned equations, equations 4 through 7, 19 and 20. In that case, equation 16 should include all terms except the last two.

Figure 13 represents a solution of 0.10 ionic strength. Cryolite precipitation is not likely to occur in solutions of ionic strength much below this value because when C_F and C_{Al} are low, C_{Na} is high (upper right-hand part of diagram) and when C_{Na} is relatively low, C_F and C_{Al} are high (lower left-hand side of diagram). Therefore, the ionic strength can never be less than 0.1 at $C_{Na}=0.1$. The results in figure 13 are not greatly different from those obtained at $I=0.71$ (fig. 14). In other words, the solubility relations are not extremely sensitive to ionic strength.

For each sodium concentration expressed in molality (C_{Na}), the curves are seen to go through a minimum with respect to the log of the fluoride concentration (C_F). For example, referring to figure 14, as representing a more realistic model than 13 for application to natural solutions, the minimum amount of fluoride required for precipitation of cryolite at 2.7 mg/l Al and $C_{Na}=0.1$ molar is about 30 mg/l F. At $C_{Na}=10^{-3}$, the minimum fluoride required is 7,500 mg/l F at 850 mg/l Al. Most natural water solutions do not contain Al^{+3} , Na^{+1} , and F^{-1} in appropriate concentrations to cause precipitation of cryolite. There are certain restricted environments, however, where cryolite might precipitate from natural solutions. It should, for example, be looked for in the mineral assemblages associated with volcanic fumaroles where HF is commonly quite abundant (White and Waring, 1963, p. K3).

Cryolite is rare in nature, the only commercially important deposit being at Ivigtut, Greenland. There it is found as a large intrusive mass in granite (Rankama and Sahama, 1950, p. 507). As far as we know, it has never been suggested that cryolite forms in nature by precipitation from aqueous solutions at temperatures as low as 25°C.

The further possibility, that silica, which is ever-present in nature, may prevent cryolite precipitation, should be considered.

One important limitation to figures 13 and 14 is that they are applicable only for pH values below about 7. Above that pH, OH^{-1} complexes begin to become important. Hem (1968, fig. 17) has presented a graph which permits one to estimate the relative importance of OH^{-1} and F^{-1} complexes in aluminum solutions as a function of pH. If the indication is that OH^{-1} complexes are important, then graphs similar to those of figures 13 and 14 (this report) can be prepared to show the relationship of pH to solubility.

FORMATION OF ALUMINUM SULFATE SOLIDS

In a manner analogous to the way in which basic aluminum fluoride (ralstonite) and cryolite form in solutions containing considerable fluoride, one would expect solids other than $\text{Al}(\text{OH})_3$ to form in solutions having high concentrations of aluminum and sulfate. In the experiments of table 4 which were performed to test the gibbsite-solubility diagrams, sodium sulfate was used as the source of sulfate. The precipitates were not analyzed by X-ray, but the solubility was generally lower than that predicted for equilibrium with gibbsite. It is likely that solid(s) other than gibbsite was present in the solutions.

Other solutions were prepared that were 0.1 molar with respect to sulfate and in which, in different solutions, potassium ranged from 0.17 to 0.27 molar. The solutions were aged at 25°C and the precipitate from one solution was examined after aging times of one day, six days, 3 months and 4 months. No crystallinity was noted by X-ray diffraction.

Johansson (1963) reported a basic aluminum sulfate having a formula $13\text{Al}_2\text{O}_3 \cdot 6\text{SO}_3 \cdot x\text{H}_2\text{O}$ ($x \approx 83$). This compound, which he identified by X-ray diffraction, was obtained in an aluminum chloride solution, which was adjusted to contain a molar ratio of OH^{-1} to Al of 2.5. Sodium sulfate was added to that solution and, after aging the solution for several weeks, Johansson obtained a crystalline product having the above composition. During the course of the experiment, the solution was heated for a short time at 80°C–90°C.

Hostetler and Hemley (written commun., 1967) were able to prepare alunite ($\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$) at 1 atm and 100°C within a week in aluminum solutions that were 0.1 molar and 0.02 molar, respectively, with reference to sulfate and potassium.

Our solutions contained about 10 times as much potassium as those of Hostetler and Hemley, but the lack of crystallization in our work probably was the result of the low temperature used (25°C).

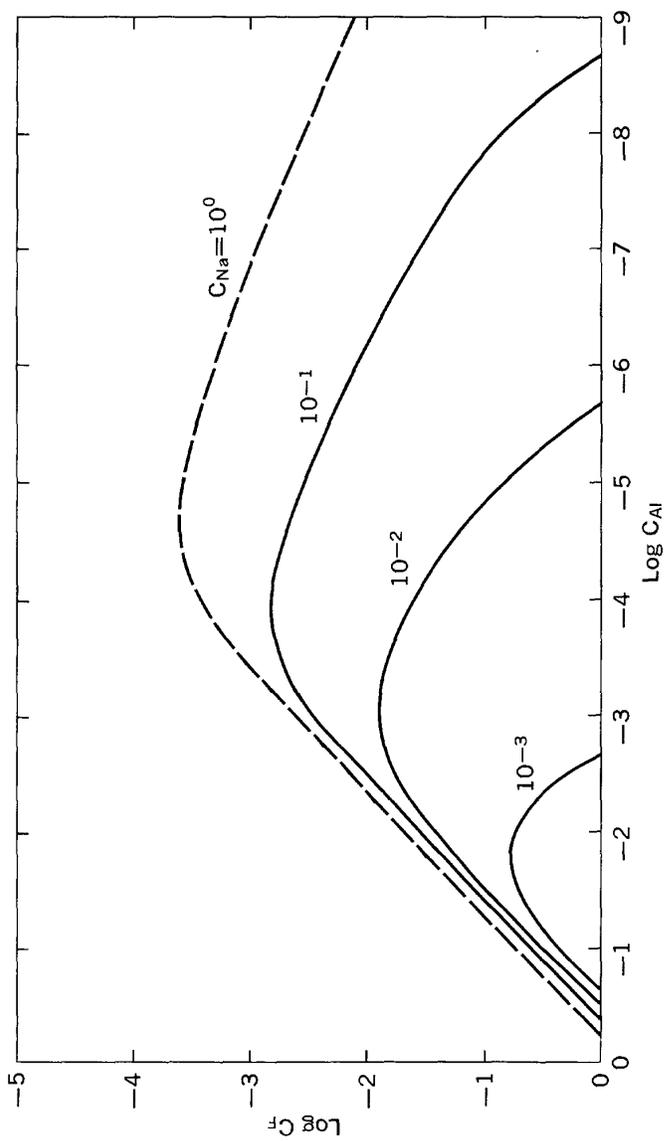


FIGURE 13.—Solubility of cryolite as a function of total fluoride concentration, for sodium concentrations 10^0 molal to 10^{-3} molal. OH species negligible. Ionic strength 0.10. For 25°C and 1 atmosphere total pressure.

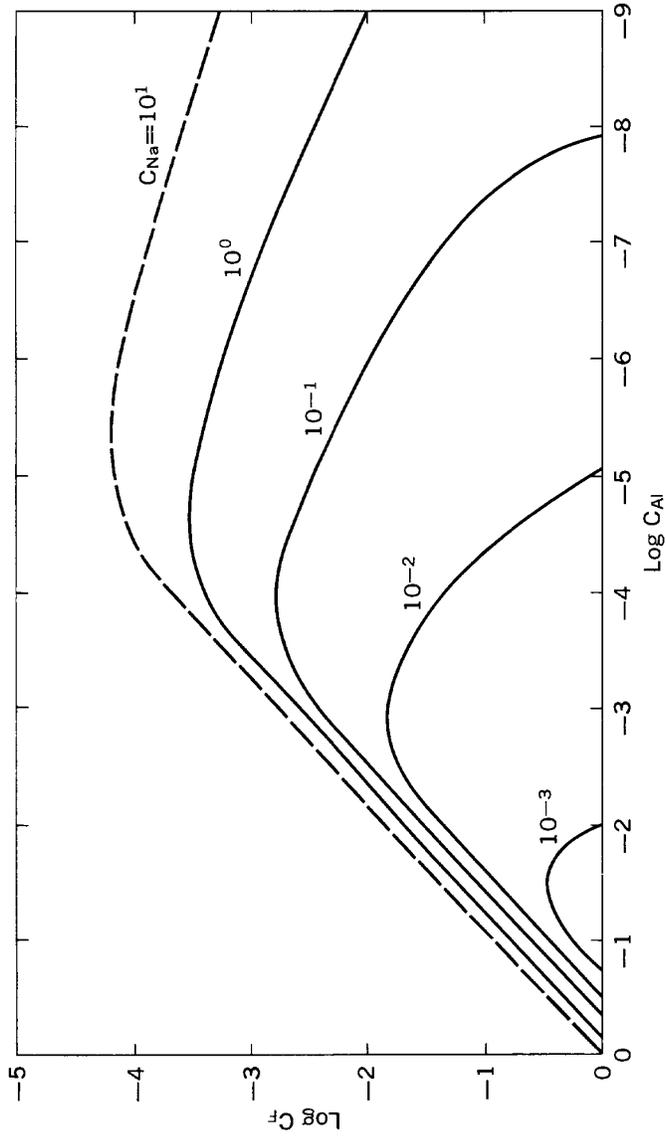


FIGURE 14.—Solubility of cryolite as a function of total fluoride concentration, for sodium concentrations 10⁰ molal to 10⁻³ molal. OH species negligible. Ionic strength 0.71. For 25°C and 1 atmosphere total pressure.

Our precipitates were probably amorphous basic aluminum sulfates, possibly amorphous alunite (or the amorphous sodium equivalent of alunite in those solutions where the sodium salt was present).² The presence of such a solid may explain why the aluminum concentrations were lower than those predicted from gibbsite solubility (table 4). The activity product for the precipitate could not be calculated, however, because its composition is not known.

STABILITY-SOLUBILITY DIAGRAMS

As noted in the foregoing discussion, several different solids containing aluminum can form from mixed solutions. If the free energy of formation of the solids is known, their stable conditions can be represented as an area on a two-dimensional plot, and the solubility of each solid can be shown by contours of aluminum concentration within their respective stability fields.

The solubility of aluminum and the stability relations between freshly precipitated aluminum hydroxide and cryolite are shown in figures 15–18. The axes of the graphs represent pH and the activity of uncomplexed fluoride. All complex species known to exist among ions of aluminum hydroxide, and fluoride are considered. The diagrams were prepared by computer for selected levels of sodium concentrations and ionic strengths. The straight diagonal line of each diagram represents the boundary between the stability fields of the two solids as determined by equation (3) of table 1. Contours to the right of the diagonal represent concentrations of aluminum determined by equilibrium of aqueous solution with aluminum hydroxide (equation (1), table 1). To the left of the diagonal, the solubility control is exercised by cryolite (equation (2) table 1). For each side of the diagonal, the concentrations of the species Al^{+3} , AlOH^{+2} , Al(OH)_4^{-1} , AlF^{+2} . . . AlF_6^{-3} were computed using appropriate equations found in table 1.

Because single ionic strength and sodium concentration must be specified, a single graph is valid only for a limited range of concentrations. The effect of changing ionic strength and sodium concentration is demonstrated by the four examples given in figures 15–18.

Because the abscissa of figures 15–18 represents the activity of uncomplexed fluoride, the diagrams are not exactly comparable with other illustrations that use total concentration of fluoride as the ordinate. The activity of uncomplexed fluoride, however, is directly measurable by means of the specific ion fluoride electrode, so the diagrams are readily usable.

² After the manuscript for this report was completed, X-ray diffraction examination of the precipitate, aged for 16 months, showed crystalline alunite.

Figure 15 is for a solution of near zero ionic strength and 10^{-3} molal in sodium ($\text{Na}=23$ mg/l). In such a solution, cryolite would be very unlikely to form because both high fluoride and high aluminum concentrations would be required. Strictly speaking, the diagram could only be applied to rather dilute water. Figure 16 is for an ionic strength of 0.10 and 10^{-2} molal sodium, and figures 17 and 18 are for more concentrated solutions.

The solubility of cryolite is very strongly affected by increased sodium concentrations. Figure 17 approximates the conditions in the solutions given in table 5.

APPLICATIONS TO NATURAL SYSTEMS

Aluminum is abundant in the upper crust of the earth and can be expected, therefore, to participate extensively in surficial alteration or weathering reactions. Its chemical reactions in water, at low temperatures and pressures, must be understood in order to understand and evaluate the importance of weathering processes in controlling the chemical composition of natural water. Aluminum readily reacts with certain anions found in natural water to form complex ions.

To evaluate the solubility of aluminum-bearing minerals thermodynamically, it is necessary to gain information about the nature of the different aluminum species and their distribution. It is not enough to have an analytical value for aluminum because such a value, depending on the ligands present, may be a gross value for dissolved aluminum representing several dissolved species.

Hem (1967) has presented diagrams that evaluate the distribution of dissolved aluminum species in the presence of the common ligands OH^{-1} , F^{-1} , and SO_4^{-2} . The present report contains graphs that represent the solubility of aluminum hydroxide precipitated in the presence of the same ligands and of cryolite precipitated in the presence of sodium and fluoride.

The activity product for solubility of cryolite was experimentally determined from solution studies, and solubility diagrams for cryolite have been prepared to represent solutions of different ionic strengths, and of different fluoride, and sodium concentrations.

By use of analytical data for a natural water sample, one can evaluate from the solubility graphs whether cryolite, aluminum hydroxide, or some other solid species is in control of solubility. The uniqueness of these diagrams rests on the fact that stoichiometric measurements of certain complex systems in which aluminum complexing becomes quite important may be evaluated without having to resort to laborious calculations.

Graphs (figs. 15–18) also show whether cryolite or aluminum hy-

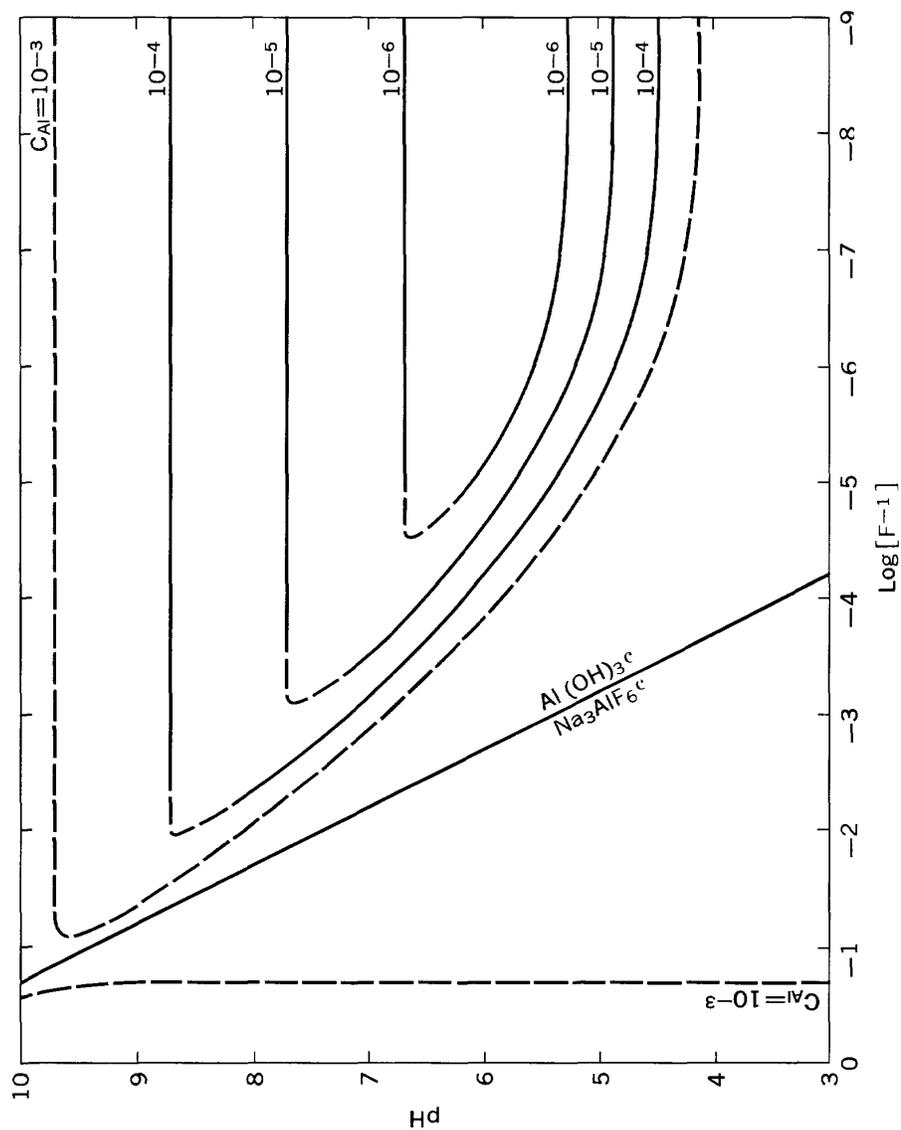


FIGURE 15.—Stability fields for cryolite and microcrystalline gibbsite and their solubilities in relation to pH and $[F^-]$. For 25°C and 1 atmosphere total pressure. Ionic strength 0.00 (Na) = 0.001 molal.

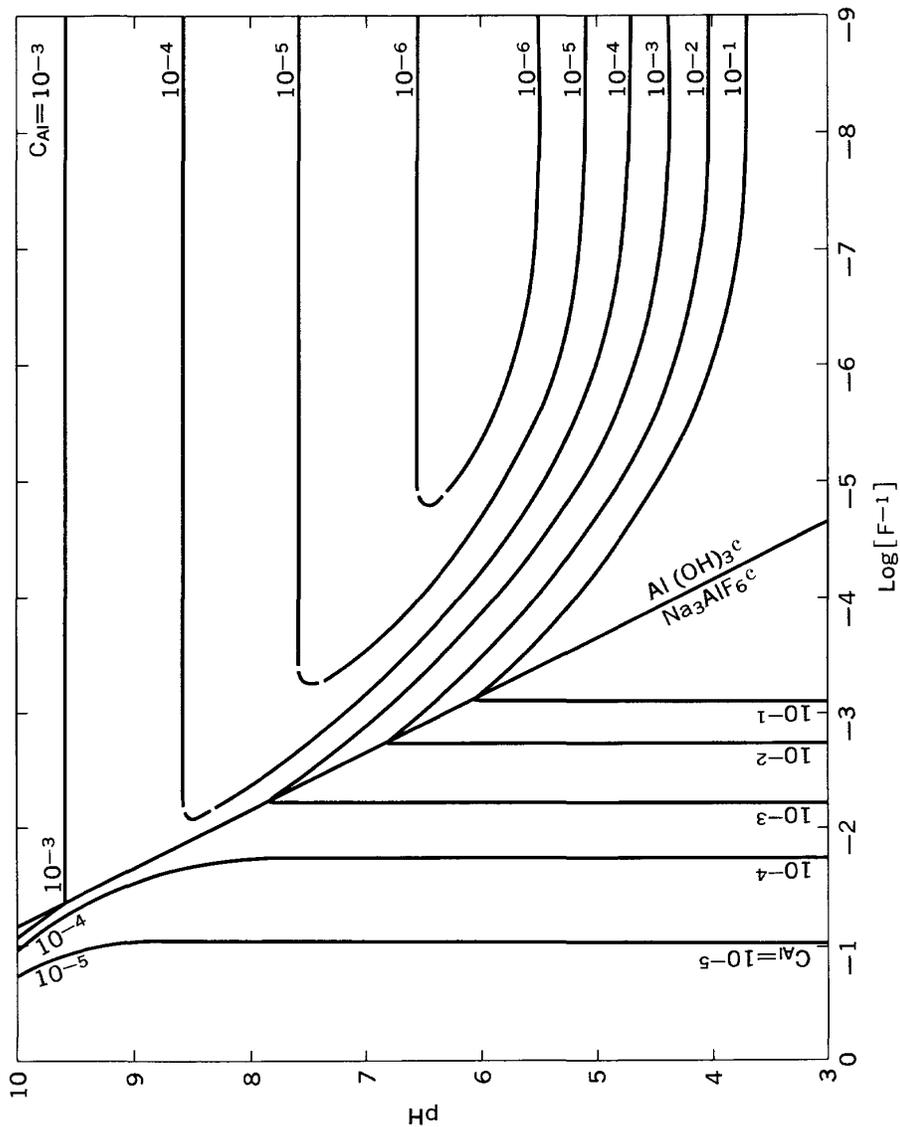


FIGURE 16.—Stability fields for cryolite and microcrystalline gibbsite and their solubilities in relation to pH and $[F^{-}]$. For 25° C and 1 atmosphere total pressure. Ionic strength 0.01 (Na) = 0.01 molal.

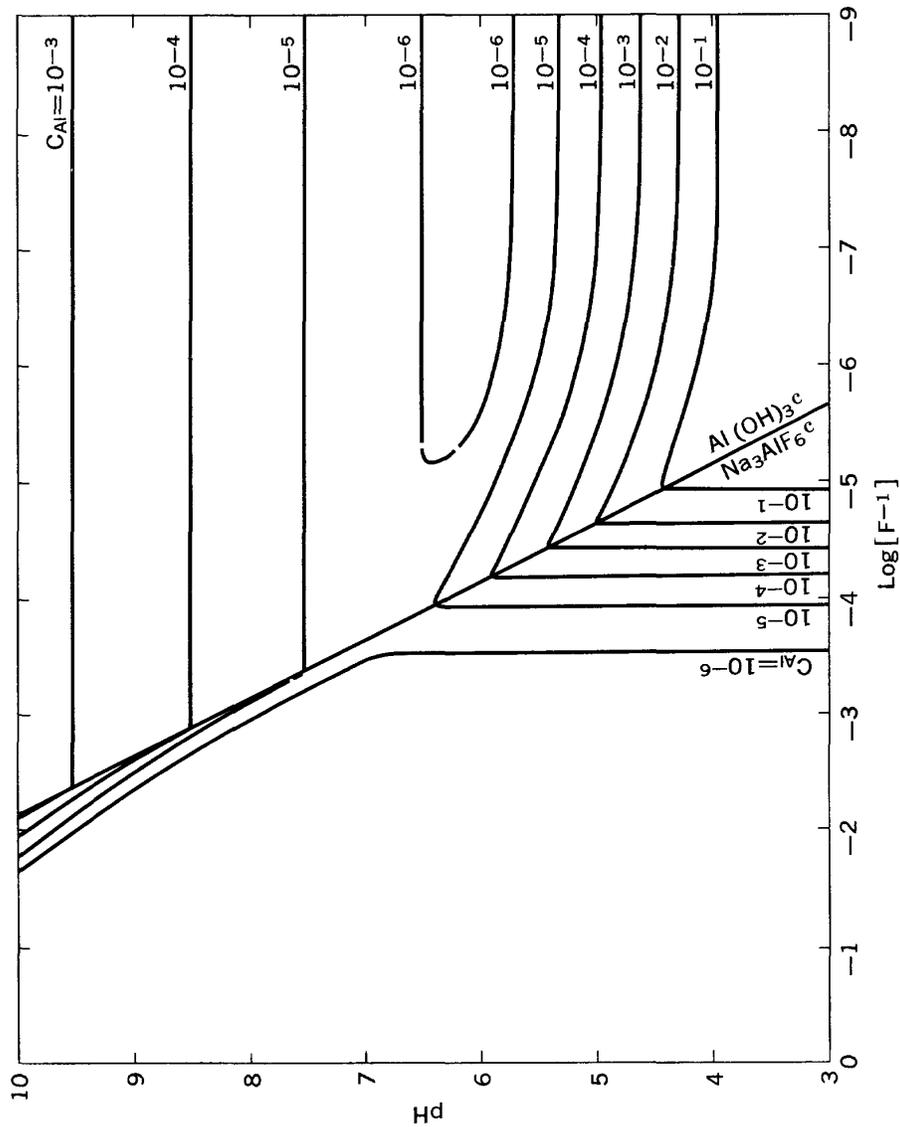


FIGURE 18.—Stability fields for cryolite and microcrystalline gibbsite and their solubilities in relation to pH and $[F^{-}]$. For 25° C and 1 atmosphere total pressure. Ionic strength 0.71 (Na) = 1.0 molal.

droxide is the more stable form in aqueous solutions, and they also show solubility relations with respect to each mineral in its own field of stability.

One factor important in controlling the solubility of aluminum in natural water has been omitted from consideration in the theoretical and experimental studies described in this report. This factor is the effect of aqueous silica. Interactions between aluminum and silicon species are being studied and will be described in future reports in this series. These reactions produce clay minerals, many of which are very stable.

The silicate-rock minerals include many species in which aluminum is an essential constituent. In a few of these, there are as many aluminum atoms as silicon atoms, but usually silicon is more abundant. The weathering of silicate minerals can therefore be expected to produce solutions containing both aluminum and silica. The aluminum and silica evidently have a strong tendency to combine to form clay minerals, characterized by layers of aluminum hydroxide polymer (gibbsite) alternating with layers of silica polymer. The residual solutions that result from silicate-rock weathering can thus be expected to contain aluminum and silica in proportions that reflect the influence of clay synthesis.

In some natural environments, silica is maintained at a low enough level that aluminum hydroxide reactions can reasonably be expected to control aluminum solubility. Regions of high rainfall, for example, may fit in this category.

The influence of fluoride may be strong enough in regions of volcanic activity to overshadow other effects and produce cryolite. Under most conditions of nature, however, the aluminosilicates probably exert a very important influence in controlling the concentration of dissolved aluminum. The results of studies of these materials are contained in another chapter of this report series.

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