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ALUMINUM IONS IN AQUEOUS SOLUTIONS

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ABSTRACT. The free energy of formation (ΔG^0_f) of $Al(OH)_4^-$ and $Al(OH)_2^+$ were estimated as −311.3 and −216.1 kcal/mole, respectively, from aqueous solubility data of high-alumina and aluminum silicate clay minerals. The $p{*}Ks_4$ and pKs_2 for boehmite are 14.4 and 15.0 respectively, yielding an isoelectric point at pH of 6.70. Electrophoretic migration of aluminum ions at various values of pH indicate that the relative effective charge on the anionic forms of aluminum ions between pH 10.0 and 12.5 are approximately equal and opposite to the cationic forms between pH 4.07 and 2.85. A marked three-fold increase in distance of migration occurred between pH 2.85 and 1.0, indicating that a probable three-fold increase in effective charge, $Al(OH)_2^+$ to Al^{3+}, had occurred within this range in pH.

INTRODUCTION

During a study of the dissolution of rock-forming minerals in which the solubility product constants (Ks) and standard free energies of formation (ΔG^0_f) of high alumina and aluminum silicate minerals were calculated, the published values of the ΔG^0_f for the supposed aluminum ions and the ranges in pH over which the ions were reported to be stable did not seem to fit the analytical data. The behavior of aluminum ions in solution is being reevaluated in this paper by the following means:

1. electrophoresis of aluminum ions at various values of pH,
2. reevaluating previously determined solubility constants,
3. using the analytical data of Reesman and Keller (1968) to develop a consistent and workable hypothesis as to the nature of the aluminum ions in aqueous solution and to approximate the ΔG^0_f for these ions.

GENERAL DISCUSSION OF ALUMINUM IN SOLUTION

Two divergent views concerning the nature of aluminum ions in solution have been proposed: one, that aluminum ions exist in solution as monomers, the other, that the aluminum ions are polymerized. The differing results may be related to the manner by which the aluminum ions were studied. Evidence of the importance of polynuclear-aluminum ions has been obtained from rather concentrated solutions of aluminum ions mainly by titration of acidic aluminum solutions with bases. Dissolution experiments with high alumina compounds in slightly buffered solutions have yielded solubility data that can usually be explained without supposing the formation of polynuclear complexes of aluminum ions. An excellent summary of previous work on aluminum in solution can be found in Hem and Roberson (1967).

Both conclusions may have some validity. Under certain conditions most aluminum ions are polymerized, and under other conditions the monomeric aluminum species predominate. Polymers could be formed when hydroxyl is added at a fairly rapid rate to solutions of aluminum

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*** Geology Department, University of Missouri, Columbia, Missouri 65201 ions of various concentrations, whereas monomers would be produced by slow dissolution from a solid phase.

The degree of polymerization of aqueous aluminum ions may be a significant factor in the formation of the large number of hydroxyl-containing high alumina compounds. In addition to amorphous aluminum hydroxide, there are at least five hydroxyl-containing high alumina minerals, for example, gibbsite, bayerite, norstrandite, boehmite, and diaspore, each of which can apparently form at or near room temperature. All these substances occur in nature and thus must have a certain amount of geologic stability—especially since only one of these phases should persist in the presence of water. The other five phases should tend to proceed toward the most stable phase through one of two routes: either by dissolution, nucleation, and crystal growth, or by the rearrangement of mineral surfaces into the most stable aluminous mineral. Rearrangement of mineral surfaces may be accompanied by the slow structural reorganization of the metastable interior, but such changes would tend to be inhibited because of the stabilizing and protective influence of the surface of the particles.

The occurrence in nature of six hydroxyl-containing high alumina compounds indicates that rates of formation are probably very important in the chemistry of highly aluminous mineral systems and also in those of the simple aluminum-silicates, for example, kaolin group minerals. Rates of reaction are important in controlling the availability or activity of aluminum in solution. The most stable mineral forms at the lowest activity of aluminum. Diaspore, probably the most stable phase, is a very dense solid having an extremely low entropy (King and Weller, 1961). Such a phase might grow very slowly by the process of addition of single aluminum ions. Slow growth from monomers would favor the location of the incorporated ions into positions of minimum potential energy and would produce the very good ordering, two conditions that are necessary for a compound to have low entropy. The remaining five aluminous phases (other than diaspore) are less dense, less well organized, and probably more amenable to more rapid growth, and perhaps to the incorporation of polymerized ions than is diaspore. Supersaturation in excess of that which is required for sustained crystal growth must be reached before any of the less stable phases can form from solution. If supersaturation is very high, amorphous aluminum hydroxide, the least stable phase, can form. Formation of amorphous aluminum hydroxide occurs very rapidly by the neutralization of concentrated aluminum solutions. This material, amorphous to X-rays, may form because of the rapid incorporation in a haphazard manner of various groups of polymerized aquated aluminum ions.

MIGRATION OF ALUMINUM IONS BY ELECTROPHORESIS

Electrophoresis was used in an attempt to determine the relative effective charge on the aluminum ions as a function of pH. This study was conducted in a 30-cm electrophoresis unit (E-C Apparatus Company), using buffered chromatographic paper strips as the transport medium. Buffered electrolyte solutions at various pH values were prepared with an ionic strength of 0.1, in which acetic acid, sodium hydroxide, and perchloric acid were used to adjust pH and ionic strength.

Following electrophoresis, the paper strips were removed and sprayed with a 0.2 percent solution of 8-hydroxyquinoline (oxine) buffered to a pH of 8.5. The buffered oxine solution formed a fluorescent (in ultraviolet light) complex with that portion of the aluminum that was complexable, which probably includes at least some freshly precipitated aluminum hydroxide. Inasmuch as the background fluorescence of the paper was too strong when the paper strips were dried, all measurements of migration were made while the paper was still moist. The sensitivity limit for detection of the complexed aluminum was less than 0.005 micrograms per square millimeter on the paper strips.

Results of the electrophoresis of aluminum are summarized in table 1. Electrophoresis runs at pH 5.5 and 7.4 are not shown because precipitation of aluminum hydroxide occurred at the origin, and the migration of aluminum ions was at such low concentration that only faint fluorescence was noted. This faint fluorescence decreased in intensity away from the origin, but no band or front was detectable.

Electrophoresis runs listed in table 1 with the same number were made simultaneously but differed in initial concentration of aluminum or in pH of the aluminum solution used for spotting. Concentrations of aluminum used were 1000 ppm, 100 ppm, and 10 ppm with an aliquot size of either 50 or 25 microliters. Care was used in trying to distribute the sample solutions evenly across the buffer-moistened paper strips.

The initial pH of the sample solution was important because the buffer capacity of the carrier electrolyte was slight. If the sample pH was not very different from the pH of the buffer solution, there was at least a general indication of the migration distance or the species or group of species of aluminum ions in equilibrium with the buffer. Runs seven, eight, and nine showed a main band at about 13 cm, but if the initial spotting pH was lower than the buffered electrolyte, there was a leading fluorescence along one edge of the paper strip. Run seven, which had an initial pH of 1.0 for the sample solution, had a main band head at 14.2 and 15.0 cm and also a leading edge fluorescence as far as 24 cm. Run eleven showed a band head at 10.8 cm the same as run 11B, but run 11 also had a leading fluorescence that ran into the buffer reservoir (about 17 cm).

The distance of migration during electrophoresis is a direct function of the applied voltage, the time interval of the run, and the effective charge on the ion as shown in the following:

$$d = \frac{VQt}{knrl} \qquad (1)$$

where d is the distance of migration, V is the applied voltage, Q is the charge on the ion, t is the time of the run, k is a constant related to the

TABLE 1

Electrophoresis of aluminum ions

Run	pH of Buffer	pH of Al ion	ug Al used	Applied voltage	Time of run	Distance of migration	Distance in (800V)(hr)	Effective charge	Comments
1	10.5	12.5	2.5	400	2 hr	11.0 cm (mean of 2)	11.0 cm	-0.8	$Al(OH)_4^-$ assumed present
2	12.5	12.5	2.5	800	1 hr	11.1 cm (mean of 3)	11.1 cm	-0.8	
3	1.0	1.0	2.5	800	30 min	21.0 cm	42.0 cm	3.0	$Al(H_2O)_6^{3+}$ assumed present, faint band at 14.5 cm;
3A	1.0	1.0	0.25	800	30 min	18.5 cm (mean of 2)	37.0 cm	2.6	2.5 cm wide band head
4	1.0	1.0	25.0	400	35 min	12.4 cm (mean of 2)	42.5 cm	3.0	7.7 cm band width
5	2.0	1.9	5.0	800	1 hr	22.3 cm (mean of 2)	22.3 cm	1.6	6 cm band width
5A	2.0	1.9	0.5	800	1 hr	18.5 cm	18.5 cm	1.25	6 cm band width
6	2.3	1.9	5.0	800	1 hr	21.8 cm (mean of 2)	21.8 cm	1.5	6.5 cm band width
6A	2.3	1.9	0.5	800	1 hr	20.2 cm	20.2 cm	1.4	3 cm tear shaped band
7	2.6	1.0	50.0	800	1 hr	14.2 cm	14.2 cm	1.0	fluorescence from band head to the origin;
7A	2.6	1.0	25.0	800	1 hr	15.0 cm	15.0 cm	1.1	migration on edge of paper to 21.5 cm, main band extends to origin;
7B	2.6	1.9	2.5	800	1 hr	15.0 cm	15.0 cm	1.1	edge migration to 19.5 cm, main band 9 cm wide;
8	2.85	2.5	2.5	800	1 hr	13.0 cm (mean of 2)	13.0 cm	0.9	leading edge fluorescence to 15.5
8A	2.85	1.9	2.5	800	1 hr	17.6 cm	17.6 cm	1.25	all migration along edge only
9	2.85	1.0	25.0	800	1 hr	13.0 cm	13.0 cm	0.9	band extends to origin, edge migration to 17.7 cm;
9A	2.85	1.0	50.0	800	1 hr	21.0 cm	21.0 cm	1.5	main band 13 cm wide smudge with a strong 1.5 cm band 14 cm from origin;
10	2.85	2.5	5.0	800	1 hr	13.5 cm (mean of 3)	13.5 cm	0.95	1.5 cm wide band
11	4.07	1.0	25.0	800	50 min	10.8 cm	13.0 cm	0.9	sharp band at 10.8 cm with edge fluorescence to 18 cm;
11A	4.07	1.9	2.5	800	50 min	11.3 cm	13.4 cm	0.95	faint band 4 cm wide
11B	4.07	2.5	2.5	800	50 min	10.8 cm	13.0 cm	0.9	faint fluorescence back to origin

geometry of the ion, n is the viscosity of the solution, r is the effective radius of the ion, and l is the length of the paper strip from one buffer reservoir to the other (Lederer, 1955). For ease of comparison all runs were made either for one hour at 800 volts or were standardized to an hour at 800 volts by simple multiplication of relative time and voltage. Thus, two hours at 400 volts is roughly equivalent to one hour at 800 volts, and the distance migrated after 30 minutes at 800 volts is multiplied by two to get the equivalent distance at the end of an hour.

The column labeled "charge" in table 1 is based upon the assumption that the major ionic form of aluminum in solution at a pH of 1.0 is Al^{3+} or its hydrated equivalent, $Al(H_2O)_6{}^{3+}$. The equivalent distance of migration per hour for Al^{3+} with a potential of 800 volts across a 30 cm plate was about 42 cm. From equation (1) it can be seen that the distance of migration is directly proportional to the effective charge on the ion. Thus, a distance of migration of 14 cm should be expected from a singly charged ion if all other factors in equation (1) are held constant.

The almost identical rates of ion migration between the anionic species of aluminum at pH 10.0 and 12.5 and the cationic species between pH 4.07 and 2.85 would indicate that the ionic forms are equal but opposite in effective charge. If $Al\ (OH)_4{}^-$ is the anonic form of aluminum, a singly charged cationic form, presumably $Al(OH)_2{}^+$, would most reasonably explain the aluminum migration at pH values down to less than 3.0.

No evidence was found from distances of migration of aluminum ions that would confirm the previously reported equilibrium constant $^*K_1$ with a value of about $10^{-5.0}$. If valid, this constant would give the pH (in this about 5.0) at which the species $Al(H_2O)_6{}^{3+}$ and $Al(H_2O)_5$-$(OH)^{2+}$ are in equilibrium. If $Al(H_2O)^{3+}$ was stable up to a pH of 5.0, the marked three-fold increase in distance of aluminum migration between pH 2.85 and 1.0 would not be expected.

Results from the electrophoresis experiment should be classified as semi-quantitative. Assumptions that constants k and r in equation (1) remain fixed at various values of pH is questionable, as slight changes in these values could result from differing degrees of OH coordination with aluminum. Solutions of aluminum ions used in the electrophoresis experiment were introduced along with chloride ions. Hem (1968) showed the importance of both sulfate and fluoride complexes with aluminum. Similar complexes could exist with chlorides thereby reducing the effective charge per aluminum ion.

REFINEMENT OF AQUEOUS SOLUBILITY DATA OF ALUMINUM IONS

Experimental data from Reesman and Keller (1968) on aqueous dissolution of high-alumina and clay minerals were used to reevaluate the state of ions of aluminum in aqueous solution and to approximate the ΔG^0_f of these aluminum ions. The analytical data of Reesman and Keller

(1968) have been placed in the American Documention Institute (A.D.I.)[1], as they are too extensive for the Journal. Readers, who desire to make a critical evaluation of this section of the paper, will find it necessary to use either the data from the A.D.I. or from Reesman (ms).

Solutions that were equilibrated with high alumina or aluminum silicate minerals were centrifuged to optical clarity and analyzed as follows:

1. Aluminum was determined fluorometrically as the 8-hydroxyquinoline complex extracted in chloroform (Goon, 1953).
2. Silicon in solution was determined by the reduced silico-molybdate procedure of Shapiro and Brannock (1956).
3. The activity of the hydrogen ion was determined by glass electrode.
4. Other cations were determined by flame photometry (Na and K) or by atomic absorption (Ca and Mg).

Activities of the ions were determined on a computer by the Debye-Hückel method.

Equilibration times of the solutions varied from a minimum of 3 to more than 500 days with either high-alumina or aluminum-silicate mineral in excess. Evidence for equilibration is discussed in Reesman and Keller (1968).

Activities of dissolved ions were used to calculate solubility constants for the minerals. Because the solubility constants did not fit our preconceived ideas on the behavior of aluminum ions in aqueous solutions, as interpreted from the literature, a new tack was taken. Solubility constants for the minerals were calculated with respect to four charged ionic species of aluminum, that is, Al^{3+}, $Al(OH)^{2+}$, $Al(OH)_2^+$, and $Al(OH)_4^-$. These species were chosen on the basic assumption that the solubility data could be accounted for by monomeric aluminum ions. Reactions with aluminum hydroxide and solubility constants with respect to each of these four ionic forms of aluminum are as follows:

$$\begin{gathered} Al(OH)_3 = Al^{3+} + 3(OH)^- \\ Ks_0 = [Al^{3+}]\,[(OH)^-]^3 \end{gathered} \tag{2}$$

$$\begin{gathered} Al(OH)_3 = Al(OH)^{2+} + 2(OH)^- \\ Ks_1 = [Al(OH)^{2+}]\,[(OH)^-]^2 \end{gathered} \tag{3}$$

$$\begin{gathered} Al(OH)_3 = Al(OH)_2^+ + (OH)^- \\ Ks_2 = [Al(OH)_2^+]\,[(OH)^-] \end{gathered} \tag{4}$$

$$\begin{gathered} Al(OH)_3 + H_2O = Al(OH)_4^- + H^+ \\ {}^*Ks_4 = [Al(OH)_4^-]\,[H^+] \end{gathered} \tag{5}$$

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[1] Analytical data from 311 analyses have been deposited as Document No. 9818 with the American Documentation Institute, Auxiliary Publications Department, Photoduplication Service, Library of Congress, Washington, D.C. Copies may be obtained by submitting $1.25 in advance and citing the document number.

For a simple aluminum silicate mineral (kaolinite) the assumed reactions are:

$$Al_2Si_2O_5(OH)_4 + 5H_2O = 2Al^{3+} + 2H_4SiO_4 + 6(OH)^- \quad (6)$$
$$Ks_0 = [Al^{3+}]^2\ [H_4SiO_4]^2\ [(OH)^-]^6$$

$$Al_2Si_2O_5(OH)_4 + 5H_2O = 2Al(OH)^{2+} + 2H_4SiO_4 + 4(OH)^- \quad (7)$$
$$Ks_1 = [Al(OH)^{2+}]^2\ [H_4SiO_4]^2\ [(OH)^-]^4$$

$$Al_2Si_2O_5(OH)_4 + 5H_2O = 2Al(OH)_2{}^+ + 2H_4SiO_4 + 2(OH)^- \quad (8)$$
$$Ks_2 = [Al(OH)_2{}^+]^2\ [H_4SiO_4]^2\ [(OH)^-]^2$$

$$Al_2Si_2O_5(OH)_4 = 7H_2O = 2Al(OH)_4{}^- + 2H_4SiO_4 + 2H^+ \quad (9)$$
$$^*Ks_4 = [Al(OH)_4{}^-]^2\ [H_4SiO_4]^2\ [H^+]^2$$

In order to use solubility constants to define regions of ionic stability, it is necessary to know the effects that would result from the presence of the four ionic species of monomeric aluminum ions and the effects that would result as one ionic species becomes predominant over another. Figure 1 is a diagram showing the hypothetical relationship between aluminum in solution and the pH of the solution in equilibrium with a solid aluminous compound. The slope of the line at any point on the diagram is related to the effective charge on the ions at that particular pH.

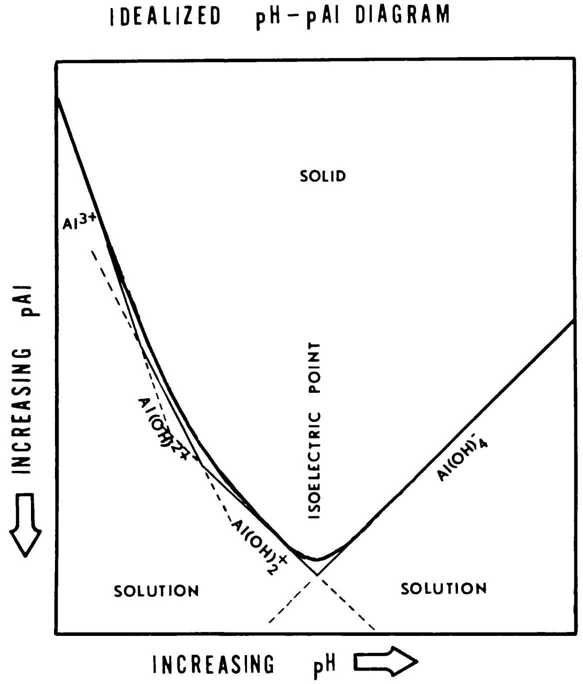

Fig. 1. Solubility diagram showing an idealized relationship between four ionic forms of aluminum in solution and the pH of the solution.

Determination of the isoelectric point.—The easiest point to locate on figure 1 should be the isoelectric point or point of minimum solubility because (1) the solubility constants with respect to $Al(OH)_4^-$ should start to increase (become a smaller negative exponent) on the acid side of the isoelectric point, and (2) the solubility constant for $Al(OH)_2^+$ should start to increase on the basic side of the isoelectric point. Therefore, the isoelectric point should occur at the pH of intersection between the stabilities of $Al(OH)_2^+$ and $Al(OH)_4^-$.

The pH of the isoelectric point can be located most effectively from solubility data on those samples that showed a rather wide change in pH during the several analytical runs of the mineral and had crossed the isoelectric point one or more times. It was possible to show from a study of such solubility constants (Reesman, ms) that the isoelectric point probably lay between pH 6.2 and 7.2.

A more nearly accurate determination of the isoelectric point was made by a critical examination of the change in solubility constants of those minerals that showed a range in dissolution pH in the region of the isoelectric point (between pH values of 6.2 and 7.2). Twelve pairs of data (constants) were chosen from the analyses as the best available for determining the isoelectric point. To pick these pairs of data (one of the pair above and one below the isoelectric point) restrictions were imposed that the pH shift be such that the solubility constant with respect to $Al(OH)_2^+$ (Ks_2) be followed by a good solubility constant for $Al(OH)_4^-$ ($^*Ks_4$), or vice versa. Data were rejected if the range in pH over which dissolution of a particular mineral occurred was not great enough to reduce effects that resulted from the presence of both aluminum species or where the pH of the solutions was too high or low.

By using pairs of solubility constants on each side of the isoelectric point, assuming that the constants are reasonably valid, a line having a slope of plus one is constructed on a pKs-pH diagram (similar to fig. 1) for a valid p^*Ks_4, and a line of slope minus one is constructed for the solubility constant, which yielded a valid pKs_2. These two lines represent the extrapolation of the solubility constant as a function of pH. The intersection of these two lines can be calculated directly without graphical plotting by obtaining the difference in the logarithms of the two constants ($pKs_2 - p^*Ks_4$). At the isoelectric point the activity of aluminum, or aluminum and silicic acid, would work equally well for either constant, pKs_2 or p^*Ks_4, the only difference being the pH-pOH relationship between the two constants. If $pKs_2 - p^*Ks_4$ is positive, the isoelectric point is below; if negative, it is above a pH of 7.0. A shift in pH either above or below a pH of 7.0 causes the same degree of shift in pOH but in the opposite direction; thus, for each pH represented in the solubility constant the isoelectric point will be shifted by half the difference between the two constants or to formulate:

$$\text{Isoelectric point} = 7.0 - \frac{(pKs_2 - p^*Ks_4)}{2n} \tag{10}$$

where "n" is the number of moles of hydrogen or hydroxyl involved in the solubility constant for the particular mineral of interest.

Table 2 shows the data of Reesman and Keller (1968) that were used in the primary determination of the isoelectric point. Analytical data from each of the equilibrated solutions were used to calculate solu-

TABLE 2

Refinement of the isoelectric point by solubility intercept method

$$\text{Isoelectric point } 7-\left(\frac{pKs_2 - p^*Ks_4}{2n}\right)$$

Sample	Run	pKs_2	p^*Ks_4	pH	pKs_2-p^*Ks_4	2n	Isoelectric pH
Diaspore (Missouri)	1	12.46	12.86	7.20			
	2	13.56	11.76	6.10	0.70	2	6.65
Diaspore (Japan)	3	14.32	9.92	4.80			
	4	12.11	14.31	8.10	0.01	2	6.99
	5	14.89	12.07	5.59	0.58	2	6.71
Kaolinite (A.P.Green Missouri)	1	37.12	36.78	6.91			
	2	36.70	35.66	6.74			
	3	39.58	35.22	5.91	2.80	4	6.30
	4	38.42	30.58	5.04	1.64	4	6.59
Kaolinite (Dry Branch, Georgia)	6	38.10	32.50	5.60			
	7	35.42	35.90	7.12	2.20	4	6.45
Kaolinite (Georgia No. 2)	6	35.32	29.42	5.55			
	7	33.48	34.24	7.19	1.08	4	6.73
	8	34.34	34.82	7.12			
	9	36.32	33.96	6.41	1.50	4	6.62
Kaolinite (Zettlitz)	2	36.24	30.44	5.55			
	3	35.42	35.50	7.02	0.74	4	6.81
	6	36.30	33.70	6.40	0.80	4	6.80
Kaolinite (Keokuk, Iowa)							
(Fine fraction)		40.02	35.36	5.83			
(Intermediate fraction)		35.64	39.48	7.88	0.54	4	6.86
(Coarse fraction)		34.31	38.51	8.05	1.51	4	6.62
					Mean.of 12		6.68 ± .10

bility constants with respect to both the $Al(OH)_2^+$ and $Al(OH)_4^-$ forms of aluminum in solution. Values of the solubility constants for each solution are given as pKs_2 and p^*Ks_4 along with the pH of the solution. The slanting lines between the columns headed pKs_2 and p^*Ks_4 in table 2 indicate the pairs of solubility constants that were used in determining the isoelectric point. The mean value of the isoelectric point as calculated from the twelve separate pairs of data is 6.68 with a standard deviation of ± 0.10.

A second method, "equal-deviation" (or shift to equal deviation), was used to refine the isoelectric point. In this method, the solubility data from solution-equilibrations that yielded pH values very close to the previously determined value of 6.68 were used. The solubility constants were calculated with respect to both the cationic and anionic forms of aluminum ions for each of three or more analytical runs on a particular sample.

The equal-deviation method also assumes that at the isoelectric point, the analytical data for the aluminum in solution, or silicon and aluminum in solution, is applicable to the calculation of either the pKs_2 of p^*Ks_4. By using analytical data from three or more equilibrated solutions from the same mineral sample, mean values of pKs_2, p^*Ks_4, and pH could be determined. If the mean pH value is at the isoelectric point, the deviations from the mean pKs_2 and p^*Ks_4 should be nearly identical. If the deviation from the mean for pKs_2 is greater than for the p^*Ks_4, the isoelectric point should be above the mean pH value, because a shift toward the stability field of $^*Ks_4$ causes an increase in the hypothetical equilibrium constant with respect to Ks_2. The contribution of aluminum, or aluminum and silicon, is the same for each equilibrated solution with respect to Ks_2 and $^*Ks_4$, as compared for that analytical run. Although most of the deviation for each mean solubility constant may come from interconstant variation, the differences in the deviations from the means between the two sets of constants can only occur from the effects of pH variation from the mean pH value. Thus, the data for aluminum and silicon in solution need not be so precise as for the solubility constant intercept method, since the effects of analytical precision of these ions tend to balance.

The following formula was used for the equal deviation method:

$$\text{Isoelectric point} = \overline{pH} - \frac{({}_{s}pKs_2 - {}_{s}p^*Ks_4)}{2n} \qquad (11)$$

where ${}_{s}pKs_2$ is the deviation from the mean of the values of pKs_2, ${}_{s}p^*Ks_4$ is the deviation from the mean of the p^*Ks_4, $\overline{pH}$ is the mean value of the pH, and n is the number of moles of hydrogen or hydroxyl involved in the equation for the dissolution (n = 1 for high aluminum minerals and 2 for kaolin minerals).

Five samples gave information with three or more runs over the pH range of interest. The solubility constants and the calculated shifts for each of these samples are given in table 3. The mean value for the iso-

TABLE 3

Deviation shift method for refining the isoelectric point

Isoelectric point $= \overline{\text{pH}} - \left(\frac{\sigma pks_2 - \sigma p^*Ks_4}{2n}\right)$

Sample	pKs$_2$	p*Ks$_4$	pH	$\overline{\text{pH}} - \frac{(\sigma pKs_2 - \sigma p^*Ks_4)}{2n}$
Keokuk	40.42	38.82	6.80	
Kaolinite	39.60	38.20	6.65	
	39.58	38.50	6.73	$6.73 - \frac{(0.56 - 0.36)}{4} = 6.68$
	39.87	38.51	6.73	
	± 0.56	± 0.36	± 0.08	
Bueker	36.34	34.54	6.55	
Kaolinite	36.18	34.98	6.45	
Swiss, Mo.	36.42	35.14	6.68	
	37.80	36.90	6.78	$6.62 - \frac{(0.73 - 1.04)}{4} = 6.70$
	36.69	35.39	6.62	
	± 0.73	± 1.04	± 0.14	
Endellite	36.24	33.44	6.30	
Lawrence	35.88	34.88	6.75	
County, Ind.	36.36	34.76	6.60	
	36.56	34.76	6.55	$6.55 - \frac{(0.28 - 0.68)}{4} = 6.65$
	36.26	34.46	6.55	
	± 0.28	± 0.68	± 0.18	
Kaolinite	36.90	35.34	6.61	
Bland, Mo.	36.66	36.46	6.70	
	36.92	35.76	6.71	
	37.36	36.12	6.69	$6.68 - \frac{(0.36 - 0.48)}{4} = 6.71$
	37.21	35.92	6.68	
	± 0.36	± 0.48	± 0.04	
Edwin	35.04	33.76	6.68	
Kaolinite	34.16	34.24	7.02	
	36.12	34.44	6.58	
	36.22	35.90	6.92	$6.80 - \frac{(0.98 - 0.92)}{4} = 6.78$
	35.39	34.59	6.80	
	± 0.98	± 0.92	± 0.20	
				Mean of 5 6.70 ± 0.044

electric point is 6.70 ± 0.044, which is in very good agreement with the previously determined 6.68.

Determination of ΔG^0_f *of* $Al(OH)_4^-$.—If 6.70 is chosen as the isoelectric point for aluminum ions in solution, the determination of one of the solubility constants, either Ks_2 of $^*Ks_4$, should aid in determining the other. Six previous values for $^*Ks_2$ at 25°C were obtained from Sillén and Martell (1964). The range in values of these six constants was $10^{-12.19}$ to $10^{-12.61}$ for what is thought to be amorphous aluminum hydroxide. With the ΔG^0_f of amorphous aluminum hydroxide at −271.9 kcal/formula wt (Latimer, 1952) a value for the ΔG^0_f of $Al(OH)_4^-$ can be calculated as follows:

$$Al(OH)_3 + H_2O = Al(OH)_4^- + H^- \qquad (5)$$

$$^*Ks_4 = 10^{-12.6}$$

$$\Delta G^0_R = -1.364 \log {}^*Ks_4 = -1.364(-12.6)$$

$$= 17.20 \text{ kcal}$$

$$\Delta G^0_f \text{ reactants} = -271.9 + (-56.7) = -328.6 \text{ kcal}$$

$$\Delta G^0_f\ Al(OH)_4^- = (-328.6) + (17.2) = -311.4 \text{ kcal/mole}$$

The preceding value is above the −313.9 kcal/mole reported by Raupach (1963a), who used a value of $10^{-12.45}$ as the $^*Ks_4$ for "fresh" boehmite. This "fresh" boehmite might have been mainly boehmite, at least to X-ray diffraction, but if a small amount of material amorphous to X-rays remained in the sample, it would be dissolved in preference to the boehmite and would yield a larger solubility constant (smaller negative exponent). Boehmite has a ΔG^0_f of −435.0 kcal/formula wt (Latimer, 1952), which is equal to −274.2 kcal when expressed as $Al(OH)_3$ rather than $Al_2O_3.H_2O$. The difference in ΔG^0_f between amorphous $Al(OH)_3$ and boehmite is 2.3 kcal, or it is roughly equivalent to the difference between −313.9 and −311.4 kcal/mole.

Two samples rich in natural boehmite were used in this study, and the pH of their resultant solutions were consistently above the isoelectric point. It seemed likely that these natural "aged" boehmites might yield better results than "fresh" synthetic boehmites. The solubility constants for these samples with respect to boehmite were:

Ochesky boehmite = $10^{-14.34 \pm 0.08}$ (mean of 7 runs)
Israel boehmite = $10^{-14.44 \pm 10.5}$ (mean of 5 runs)

Assuming a ΔG^0_f for boehmite of −435.0 kcal/formula wt and a p^*Ks_4 of 14.40, the resulting ΔG^0_f for $Al(OH)_4^-$ would be −311.26 kcal/mole, or for AlO_2^- (used by Latimer 1952), −197.86. This value for the ΔG^0_f of $Al(OH)_4^-$ is in good agreement with the −311.69 kcal/mole reported by Hem and Roberson (1967). Using a value of −311.3 kcal/mole as the ΔG^0_f for $Al(OH)_4^-$, Reesman and Keller (1968) found that ΔG^0_f of minerals calculated from solubility constants were in good agreement with ΔG^0_f reported previously by other methods. If a ΔG^0_f of −313.9 kcal/mole for $Al(OH)_4^-$ had been used in calculating ΔG^0_f for these minerals, the resulting ΔG^0_f would be about 2.6 kcal/mole of aluminum lower than previous values for the minerals.

Determination of ΔG^0_f *of* $Al(OH)_2^+$.—Accepting −311.3 kcal/mole for $Al(OH)_4^-$, at least tentatively, and 14.40 for the p^*Ks_4 of boehmite, an approximate value of Ks_2 can be calculated. Replacement of the hydrogen ion activity at the isoelectric point ($10^{-6.70}$) with the corresponding hydroxyl activity ($10^{-7.30}$) yields a Ks_2 of $10^{-15.0}$ for boehmite and a $\Delta G^0{}_f$ of $Al(OH)_2{}^+$ as follows:

$$
\begin{array}{llll}
AlO(OH) + H_2O & = & Al(OH)_2{}^+ + (OH)^- & \quad (4) \\
(-217.5) \quad (-56.7) & & X \qquad (-37.6) & \\
pKs_2 = 15.00 & & \Delta G^0{}_R = 20.46 \text{ kcal} & \\
\Delta G^0{}_f \text{ reactants} & = & -274.2 \text{ kcal} & \\
\Delta G^0{}_f \text{ products} & = & X + (-37.6) & \\
\mathbf{\Delta G^0{}_f\ Al(OH)_2{}^+} & = & -274.2 - (-37.6) + (20.46) & \\
 & = & -216.14 \text{ kcal/mole} &
\end{array}
$$

The value of −216.1 kcal/mole for $Al(OH)_2{}^+$ is 1.0 kcal more stable than the −215.1 kcal reported by Raupach (1963a). Reesman and Keller (1968) found that $\Delta G^0{}_f$ for minerals calculated from solubility constants involving $Al(OH)_2{}^+$ agree with results of $\Delta G^0{}_f$ for those minerals that were determined by other methods.

If the preceding assumptions are correct, and $Al(OH)_4{}^-$ and $Al(OH)_2{}^+$ are valid species under dissolution conditions, the equilibrium fields of the other two possible mononuclear ions must be determined. Free energy data are available for Al^{3+} from Latimer (1952) and Plumb (1962), who have determined the $\Delta G^0{}_f$ to be −115.0 and −114.4 kcal, respectively. In addition to the free energy data, Ks_0 values have been determined by several workers (Sillén and Martell, 1964). These Ks_0 values show a rather wide range, which is probably related in part to the exact nature of the solid phase used for study. A constant, $^*K_1$, considered to relate equilibrium between Al^{3+} and $Al(OH)^{2+}$, has been determined by several investigators (Sillén and Martell, 1964). Hem and Roberson (1967) determined the value of $^*K_1$ to be $(1.8 \pm 1.0) \times 10^{-5}$ from reaction-rate data, and Raupach (1963b) determined the constant to be $10^{-5.0}$ from solubility, conductivity, and potentimetric data. These values are in agreement with the bulk of previously reported $^*K_1$ values from Sillén and Martell (1964).

Reesman (ms) made a critical evaluation of solubility data from 137 solutions from various minerals that underwent dissolution at pH values below 5.5. Several mineral samples developed more acid solutions with increasing time of dissolution, which might be related to the oxidation of iron sulfides. Solubility constants for these solutions were calculated with respect to Al^{3+}, $Al(OH)^{2+}$, and $Al(OH)_2{}^+$ for each of the solutions, and variations in these constants for a particular mineral were studied in relationship to the pH of dissolution.

No evidence from the evaluation of these solubility constants was found to indicate that a change in ionic stability fields of aluminum ions had occurred. Solutions that had a pH of 3.0 could be interpreted best by assuming an effective charge of 1.0 per aluminum. Hsu and Bates (1964) proposed that $Al_6(OH)_{12}{}^{6+}$ is the predominant ionic species through a pH range of about 4.0 to 6.0. If such a species is present in this region of pH, it would have an effective charge of one per aluminum and would remain undetected as a polymeric aluminum species.

Discussion.—Solubility data from aluminum bearing minerals with solution pH values as low as 3.0 can best be interpreted by assuming that the aluminum ions are singly charged when computing solubility constants. Thus, the solubility data tends to support the conclusions from the migration of aluminum ions by electrophoresis.

If one accepts –216.1 kcal/mole as the ΔG^0_f for $Al(OH)_2^+$ and –115.0 kcal/mole for Al^{3+}, these two species of aluminum ions (neglecting the possibility of $Al(OH)^{2+}$) should be in equilibrium at a pH of about 4.5. The failure to determine a stability region of either Al^{3+} or $Al(OH)^{2+}$ by dissolution techniques poses a problem for which there is no simple answer at this time. However, the recent paper by Hem (1968) that stresses the importance of sulfate complexes with aluminum ions and the fact that the ΔG^0_f of Al^{3+} was determined indirectly from data based upon the solution of cesium alum (Latimer and Greensfelder, 1928) may indicate that the ΔG^0_f of Al^{3+} needs reevaluation.

CONCLUSIONS

The following data for aluminum ions in aqueous solution were determined from dissolution experiment of minerals:

1. The isoelectric point or point of minimum aluminum solubility is at a pH of 6.70.
2. The p^*Ks_4 for boehmite is 14.40 with a resulting free energy of formation of –311.3 kcal/mole for $Al(OH)_4^-$, if the ΔG^0_f of boehmite is –435.0 kcal/formula wt.
3. The pKs_2 for boehmite is 15.0, and the resultant free energy of formation for $Al(OH)_2^+$ is –216.1 kcal/mole, if boehmite has a ΔG^0_f of –435.0 kcal/formula wt.
4. No other aluminum ions were determined to be present over the pH range from 3.0 to 9.0

As the analytical method for aluminum in solution would probably tend to break down all but the most complex polymerized aluminum species, evidence for or against the formation of polymeric aluminum species was not obtained. Attempts to improve the equilibrium constants of the minerals by assuming non-integer charges on the ionic aluminum did not improve the relationship between equilibrium constants and pH in a consistent manner.

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