Measurement of hydrolysis, polymerization and complexation in dilute aluminum solutions

by

George Norman White, Jr.

Dissertation submitted to the Faculty of the
Virginia Polytechnic Institute and State University
in partial fulfillment of the requirements for the degree of
Doctor of Philosophy
in
Agronomy

APPROVED:

Lucian W. Zelazny, Chairman

D. C. Martens   J. C. Baker

J. C. Parker   W. R. Knocke

March, 1987
Blacksburg, Virginia
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(ABSTRACT)

The nature of chemical reactions taking place during the titration of dilute Al solutions in the presence of either chloride or sulfate were examined by refining the apparent Al hydrolysis products assuming the presence of solution species with n (OH/Al mole ratio) equal to 1, 2, 2.5, 3 and 4. The second and third hydrolysis products for Al were refined by comparison of calculated titration patterns to those observed for 10^-3, 10^-4 and 10^-5 M Al in 1M, 0.1M and 0.01M KCl. A large degree of polynuclear character of Al solutions was found even at Al concentrations as low as 10^-5 M. The n value and size of the polynuclear complexes are affected by Al concentration. The concentration constant, \( pQ_{13} \), is found to be at least 17.4-17.7. It is concluded that the mononuclear Al(OH)\(_2\) species is never significant. Use of statistical analysis of the data and graphical methods did not result in consistent data for polymer size determinations.

The lower pQ values for mononuclear Al hydrolysis are explained by the structural instability of the mononuclear complexes. The bondstrengths required for the bonds in the second and third hydrolysis complexes are often larger than those allowed for octahedral coordination. For that reason, the pQ values would be lower than calculated by extrapolation between the stable first and fourth hydrolysis constants.

A new polynuclear complexation mechanism for Al is proposed to account for the high concentration of high n value polynuclear species in the titration refinements. The proposed linear double chain structure has a structure consistent with boehmite and diaspore. This structure differs from the linear single chain and ring based polynuclear structures by the presence of rows of three coordinated oxygens in the bond central chain and rows of two and one coordinated oxygens along the plane edges. A rearrangement of internal charge in this structure is proposed in which part of the charge is removed from the three coordinated oxygens to result in an uncharged hydroxyl with
the charge shifted to the one coordinated site neutralizing the hydroxyl. This results in a general formula for the polynuclear structure of \((\text{Al(OH})_3)_x(\text{Al(OH})_2)_y]^z+\). This structure results in a higher \(n\) value for a lower number of \(\text{Al}\) than does the other polynuclear complexation schemes and therefore explains the presence of high \(n\) value polymers in unaged \(\text{Al}\) solutions which would have required polymers of greater than a hundred \(\text{Al}\) cations.

The observed presence of a second \(\text{Al}\) plateau on titration patterns with \(\text{Al}\) concentrations greater than \(5 \times 10^{-4}\)M could not be the result of the onset of precipitation as earlier proposed. It is proposed that at a \(\text{pH}\) in the 6 to 7 range, a change of some of the one coordinated sites on the edge of the larger polynuclear and precipitant structures from water to hydroxyls results in a change in net edge charge from net positive to net negative which causes an increased rate of crystal growth due to the unlike charge between the edges and the smaller polynuclear and mononuclear complexes.

The refinement of \(\text{Al}\) titration data in \(\text{K}_2\text{SO}_4\) provide \(\text{pQ}\) values one to three \(\text{pQ}\) units lower than those obtained from equivalent \(\text{KCl}\) solutions. A catalytic mechanism is proposed in which \(\text{Al}\) polymerization is facilitated by the formation of mononuclear \(\text{Al}\) hydroxy sulfate complexes which combine together to form nonsulfate containing polynuclear complexes. The increased hydrolyzed concentration and lower ionic charge resulting from these complexes would increase the rate of polymerization in these systems.

Evidence for the presence of mononuclear hydroxy sulfate complexes comes from the better fit for titration patterns in sulfate systems which would not have been observed for increased polymerization alone.
Acknowledgements

There are so many people I need to thank that I do not know where to start. First, I would like to thank Dr. L. W. Zelazny, my committee chairman, who has helped keep me in funds long after I should have been dropped and has always had time for me when I needed it. I would also like to thank Dr. Martens, a dynamic, creative individual whose professionalism and innovative approaches have been my model, and who has been around for me to talk with in the early morning since I started here. I also owe a great debt of gratitude to the other members of my committee, 

The assistance of Dr. G. V. Gibbs, who calculated the structure of Al(OH)$_3$(OH)$_2$ for me at great cost, is also gratefully acknowledged along with 

who explained the results to me. In addition, I feel that I need to give a special acknowledgements to 

and the early morning crew at the College Inn who have helped keep me sane. Kudos also go to
and countless unnamed others for the help that each in their own way gave to help me finish this work.
# Table of Contents

Introduction .................................................................................................................. 1

Definitions ..................................................................................................................... 5

Theory .............................................................................................................................. 7
- Effects of Polymerization ............................................................................................ 9
- Effects of Soluble Ligands ......................................................................................... 11
- Effects of Precipitation ............................................................................................. 12

Titration Analysis and the Determination of Aluminum Hydrolysis ....................... 17

Literature Review .......................................................................................................... 24
- Aluminum Hydrolysis Constants .............................................................................. 24
  - Methods Used To Determine Hydrolysis Constants ................................................ 25
    - The dilution method ............................................................................................. 25
    - Potentiometry .................................................................................................... 26
    - Solubility methods .............................................................................................. 26
    - Equilibrium centrifugation .................................................................................. 27

Table of Contents vi
List of Illustrations

Figure 1. Calculated titration curves showing the effects of changes in the first pK on the shape of a titration curve. ............................................. 19

Figure 2. Calculated titration curves showing the effects of changes in the second pK on the shape of a titration curve. ............................................. 20

Figure 3. Calculated titration curves showing the effects of changes in the third pK on the shape of a titration curve. ............................................. 21

Figure 4. Calculated titration curves showing the effects of polynuclear complex formation. 22

Figure 5. Calculated titration curves for precipitation of amorphous Al(OH)₃ (b), gibbsite (c) and no precipitation (a). ............................................. 23

Figure 6. Inflection point method for determining total Al and activity coefficient for hydronium from potentiometric titration curves 44

Figure 7. Observed potentiometric titration curves for KCl solutions. 47

Figure 8. Observed potentiometric titration curves for K₂SO₄ solutions. 48

Figure 9. A plot of the observed n bar - pH relationship for Al in 1M KCl solutions. 49

Figure 10. A plot of the observed n bar - pH relationship for Al in 0.1M KCl solutions. 50

Figure 11. A plot of the observed n bar - pH relationship for Al in 0.01M KCl solutions. 51

Figure 12. A plot of the observed n bar - pH relationship for Al in 0.5 M IS K₂SO₄ solutions. 52

Figure 13. A plot of the observed n bar - pH relationship for Al in 0.05 M IS K₂SO₄ solutions. 53

Figure 14. A plot of the observed n bar - pH relationship for Al in 0.005 M IS K₂SO₄ solutions. 54

Figure 15. A plot of scaled standard deviations of the calculated n = 2 polynuclear species in KCl sorted by IS and total Al. 61

Figure 16. A plot of scaled standard deviations of the calculated n = 2 polynuclear species sorted by IS and total Al (sulfate). 69

List of Illustrations ix
List of Tables

Table 1. Sources for mononuclear hydrolysis constants of Al and the methods used for their determination. ................................................. 18

Table 2. Sources of polynuclear hydrolysis constants of Al. .......................... 31

Table 3. Sources for Al sulfate complexation products. ............................. 33

Table 4. Calculated concentration constants for Al hydrolysis in KCl solutions assuming no n = 2.5 species. ................................................. 56

Table 5. Calculated concentration constants along with standard deviations for Al hydrolysis in KCl solutions. ............................................... 57

Table 6. Significance level (F) for Al concentration on polynuclear complex pQ values in KCl solutions. ...................................................... 59

Table 7. Calculated Al polynuclear complex pQ values along with standard deviations in KCl solutions. .................................................... 60

Table 8. Observed concentration constants for the solubility of basaluminite in sulfate solutions during potentiometric titrations. ................. 64

Table 9. Residual sum of squares (and r^2) for fits of observed data to theoretical titration patterns. ......................................................... 65

Table 10. Calculated concentration constants for Al hydrolysis in K_2SO_4 solutions. .......................... 66

Table 11. Significance level (F) for ionic strength and Al concentration on polynuclear complex pQ values in K_2SO_4 solutions. ................. 68

Table 12. Effects of time on pH, titratable H, and Al adsorbed from a 0.001 M Al solution with added gibbsite. .......................... 81
Introduction

Only O and Si exceed Al in abundance among the elements of the outer part of the earth's crust (Hem and Roberson, 1967). Despite making up 8.13% of the crust by weight (Mason, 1966), Al rarely occurs in much higher concentrations but is instead fairly uniformly dispersed (Mason, 1966). Aluminum can be found as a tetrahedral cation (ionic radius = 0.046 nm) or as an octahedral cation (ionic radius = 0.061 nm) in coordination with oxygen (Frye, 1979). As a tetrahedral ion, it is present as an essential constituent in the feldspar group, the most common of all minerals, which can be represented by the general formula of WA1(Al,Si)Si2O8 where W can be Na, K, Ca, Ba, and NH4 with the variable (Al,Si) balanced by variation in the uni- and bivalent compounds. The tetrahedral aluminate ion is also found in alkaline solutions, in tetrahedral sites in clay minerals, and in some high temperature silicates and oxides. Octahedral Al is present in large quantities as a solution cation and in clay minerals and in many oxide and hydroxides.

Despite its importance, little is known about the solution chemistry of Al. Aluminum represents the best known example of metal ion hydrolysis but at the same time, there is little agreement in the literature as to the species that are formed, and even less as to the hydrolysis constants for the complexes (Raupach, 1963a). This lack of knowledge causes difficulties for environmental chemists as the pH range for most soils and other important environments (pH 4 to 9) includes the zone of precipitation of Al(OH)3 as well as the acid and alkaline region on either side.
of the precipitation region (Raupach, 1963a). For that reason, it is essential that a quantitative understanding of the aqueous geochemistry of Al minerals and the speciation of Al in natural waters is obtained (May et al., 1979; Driscoll, 1984).

The environmental geochemistry of Al is important because elevated levels of Al have been reported for acidic waters receiving elevated inputs of acid deposition (Driscoll, 1984). Whether the increased levels of Al are due to the decreased pH associated with acid deposition, to the increased level of inorganic complexes such as sulfate (Driscoll, 1984) or to the increased levels of soluble organics released is not clear at this time. The elevated levels of Al in dilute acid waters are of importance because Al is an important pH buffer, it may affect the cycling of other important elements such as phosphate and organic C, and Al is potentially toxic to aquatic and terrestrial organisms (Driscoll, 1984).

Application of equilibrium chemistry models in studies of aqueous geochemistry of metallic elements with low solubilities involve many difficulties (Barnes, 1975). This is especially true for Al because of some serious experimental difficulties (Hem and Roberson, 1967). Hem and Roberson (1967) outlined the most serious problems as 1) slow kinetics for Al hydrolysis at 25°C; 2) the presence of metastable species which cause slow approaches to equilibrium; 3) the presence of a number of chemically similar Al oxides and hydroxides which differ only in solubility; 4) the fact that experimental conditions (temperature, Al concentration and even the rate of addition of the reactants) strongly influence the results; 5) poor analytical accuracy for Al at low concentrations; and 6) that Al(OH)$_3$ tends to form colloidal or subcolloidal suspensions that are difficult to describe thermodynamically.

Of the four hydrolysis reactions occurring at pH values commonly encountered in soils, only the first and fourth are considered well established (Baes and Mesmer, 1976, p.115). The presently assumed values for the second and third reactions are partially the result of one colorimetric study and partially the result of linear extrapolation between the first and fourth hydrolysis products. The extrapolation method is questionable because of a change in coordination number from six to four accompanies the fourth reaction (Baes and Mesmer, 1976) but the colorimetric method of Nazarenko and Nevskaya (1969) is considered worse due to the indirect method used and the as-
sumptions required for data analysis. For that reason, Baes and Mesmer (1976) advise redetermination of the second and third hydrolysis products. Their low opinion of the Al hydrolysis products is echoed by Lindsay (1979), who believed that all the hydrolysis products were in need of further investigation.

Very little may be known about the hydrolysis reactions themselves, but nothing is known about the effects of hydrolysis on Al complexation. Studies of Al complexation by sulfate, such as that of Behr and Wendt (1962), Nanda and Aditya (1962) and Izatt et al. (1969), are purposefully performed at a sufficiently acid pH to suppress the hydrolysis of the Al ion. As a result, only unhydrolyzed complexes have been found. Studies using the unhydrolyzed sulfate complexes along with the uncomplexed hydrolysis species often show poor correspondence between calculated and observed titration patterns for solutions with high complex concentrations (for example, Shah Singh, 1969). On the other hand, studies of Al hydrolysis in solutions high in sulfate show results which appear to indicate that sulfate ions do not form significant complexes of Al (Volokhov et al., 1971; Raupach, 1963b, 1963d; Nishide and Tsuchiya, 1965). Either there is a common error in all these studies, which is not apparent from their data, or the solution chemistry of Al is more complex than is commonly believed.

The void in knowledge of Al hydroxy sulfate complexes makes predictions on mineral solubility, acid precipitation effects, and agricultural fertilizer reactions open to large errors. Any data obtained on these unstudied reactions would be of enormous applicability to the modeling of these and other processes.

The chemistry of Al in solids and solution is becoming one of the largest unknowns in the modeling of environmental processes. Better knowledge of its solution chemistry would be very advantageous to those making decisions on acid precipitation control regulations.

The objectives of this study are to determine the applicability of the mathematical analysis of titration patterns as a method for refinement of the second and third hydrolysis products and to search for significant Al hydroxy sulfate complexation. To perform these objectives, the hydrolysis products of Al are refined from titration patterns using a rigorous chemical model which allows for but does not require the presence of mononuclear complexes with 1 to 4 hydroxyls per Al.
polynuclear complexes with 1, 2, 2.5, 3, and 4 hydroxyls per Al and precipitants with 1, 2, 2.5, and 3 hydroxyls per Al. These results will be interpreted to give a more complete view of the solution chemistry of Al in the environment.
Definitions

For ease in understanding, it is felt important for some heavily used terms to be defined at this time. In this way the user of this work will not have to search through the dissertation for the first usage of a term.

One term which will be heavily used in this work is \( n \) and its specialty form \( \bar{n} \). Both terms will be used to describe the degree of hydrolysis of Al in solution. The general definition of \( n \) is

\[
n = \frac{[\text{OH}^-]}{[\text{Al}_{\text{tot}}]} \tag{1}
\]

where \([\text{OH}^-]\) and \([\text{Al}_{\text{tot}}]\) are the molar quantities of \(\text{OH}^-\) and Al. For the purposes of this work, \( n \) will be assumed to be the degree of hydrolysis of individual Al species while \( \bar{n} \) will be assumed to be the degree of hydrolysis of the solution as a whole (the average \( n \) for all titratable Al species).

Another grouping of terms which require definition are those describing the equations which are to be fitted. In this work, the terms \( K_{x,y} \) and \( Q_{x,y} \) will be defined as the activity and concentration products, respectively, describing the equation

\[
x\text{Al}^{3+} + xy\text{H}_2\text{O} \rightarrow \text{Al}_x(\text{OH})_{xy}^{3x-xy} + xy\text{H}^+ \tag{2}
\]
where \( x \) represents the number of Al in the species with an \( n \) value of \( y \). One reason that the results will not be corrected to form activity constants is that the resulting values would have to be recalculated by users preferring a different form of activity correction. Another reason for the lack of corrections is that the size parameter for polynuclear species is not known and so the only equations which may be used are those with no corrections. The general form of the Debye Huckel equation is

\[
\log \gamma = |Z_{\text{cation}} Z_{\text{anion}}| \left( \frac{-0.509 \sqrt{I}}{1 + \sqrt{I}} - 0.3I \right)
\]  

[3]

where \( \gamma \) is the activity coefficient for the species and \( I \) is the ionic strength. For any given equation, the only variable in this equation is \( Z_{\text{cation}} \) as everything else is constant. If this activity correction equation is applied to equation 2, no correction results. For that reason, no attempt was made at correcting concentration constants to activity constants.

In a manner similar to the case for hydrolysis and polymerization, \( K_{x,y,z} \) and \( Q_{x,y,z} \) will refer to the activity and concentration constants, respectively, for the equation

\[
xAl^{3+} + xyH_2O + zL^{y-} \rightarrow Al_x(OH)_{xy}L_z^{3x-xy-zy} + xyH^+
\]  

[4]

where \( L \) represents the ligand and \( z \) represents the amount of ligand needed for the stoichiometric complex.
The performance of potentiometric titration patterns involves the addition of acid or base to an aqueous solution with the pH resulting from the acid or base addition measured. In the potentiometric titration of dilute Al solutions with bases, the pH measured is lower than it would be in the absence of Al as a result of buffering by the hydrolysis of Al. The hydrolysis reactions of Al include the following monomeric reactions:

\[
\begin{align*}
\text{Al}^{3+} + \text{H}_2\text{O} &\rightarrow \text{Al(OH)}^{2+} + \text{H}^+ \quad [5] \\
\text{Al}^{3+} + 2\text{H}_2\text{O} &\rightarrow \text{Al(OH)}_2^+ + 2\text{H}^+ \quad [6] \\
\text{Al}^{3+} + 3\text{H}_2\text{O} &\rightarrow \text{Al(OH)}_3^0 + 3\text{H}^+ \quad [7] \\
\text{Al}^{3+} + 4\text{H}_2\text{O} &\rightarrow \text{Al(OH)}_4^- + 4\text{H}^+ \quad [8]
\end{align*}
\]

along with a plethora of polymeric hydrolysis reactions which can be generalized by:

\[
x\text{Al}^{3+} + xy\text{H}_2\text{O} \rightarrow \text{Al}_x\text{OH}_{xy}^{3x-xy} + xy\text{H}^+ \quad [9]
\]

where \(x\) is the number of Al ions and \(y\) is the number of OH ions per Al in the polynuclear hydrolysis species.
The amount of base neutralized by the Al hydrolysis reactions can be calculated using the equation:

\[
[\text{OH}^-_{\text{neutralized}}] = [\text{AlOH}^2^+] + 2[\text{Al(OH)}_2^+] + 3[\text{Al(OH)}_3^-] + 4[\text{Al(OH)}_4^-] + y[\text{Al}_x(\text{OH})_{xy}]^{3x-xy}.
\] [10]

Substituting the concentration constants for each of the species yields:

\[
[\text{OH}^-_{\text{neutralized}}] = Q_{11} \frac{[\text{Al}^{3+}]}{[\text{H}^+]} + 2Q_{12} \frac{[\text{Al}^{3+}]}{[\text{H}^+]^2} + 3Q_{13} \frac{[\text{Al}^{3+}]}{[\text{H}^+]^3} + 4Q_{14} \frac{[\text{Al}^{3+}]}{[\text{H}^+]^4} + yQ_{x,xy} \frac{[\text{Al}^{3+}]^x}{[\text{H}^+]^{xy}}.
\] [11]

where \( Q_{x,xy} \) is the concentration constant for the hydrolysis reaction resulting in a species with \( x \) \( \text{Al}^{3+} \) and \( xy \) \( \text{OH} \) ions. To solve each of these equations requires knowledge as to the concentration of \( \text{Al}^{3+} \) in solution. The concentration of \( \text{Al}^{3+} \) in solution can be calculated from the equation:

\[
[\text{Al}^{3+}] = \frac{[\text{Al}_{\text{tot}}]}{\left( \sum_{x=1}^{n} \frac{n}{\sum_{y=1}^{n} xQ_{x,xy} \frac{[\text{Al}^{3+}]^x}{[\text{H}^+]^{xy}} - 1 \right)}
\] [12]

where the summation includes all positive integer values for the number of \( \text{Al} \) and \( \text{OH} \) ions in the hydrolyzed species. Equation 12 is not directly solvable for \( \text{Al}^{3+} \) because of its presence on both sides of the equation. For that reason, a simplification of monomeric hydrolysis only will be introduced to ease calculations.

For the case of monomeric hydrolysis species, equation 11 simplifies to:

\[
[\text{OH}^-_{\text{neutralized}}] = Q_{11} \frac{[\text{Al}^{3+}]}{[\text{H}^+]} + 2Q_{12} \frac{[\text{Al}^{3+}]}{[\text{H}^+]^2} + 3Q_{13} \frac{[\text{Al}^{3+}]}{[\text{H}^+]^3} + 4Q_{14} \frac{[\text{Al}^{3+}]}{[\text{H}^+]^4}.
\] [13]

In a like manner, equation 12 simplifies to:
\[
[\text{Al}^{3+}] = \frac{[\text{Al}_{\text{tot}}]}{\left( \sum_{y=1}^{4} \frac{Q_{1y}}{[\text{H}^+]^y} \right)}
\]  

which can be solved for directly. The solution for equation 12 is not direct because of the \([\text{Al}^{3+}]\) term in the denominator. For that reason, the initial determination of the hydrolysis products for Al assumes no polynuclear species are present.

To solve for the hydrolysis concentration products, a FORTRAN computer program, TIFIT, was developed which compares the results obtained by solving equations 13 and 14 for ranges of \(Q_{xy}\) to observed data.

**Effects of Polymerization**

One of the significant problems with titration analysis is how to consider the effects of polynuclear species on potentiometric titration patterns of dilute Al solutions. The effects of polynuclear species are not as self evident on individual potentiometric titration patterns as they are when the results of several titration patterns are compared. To use more than one titration pattern in a refinement scheme to determine hydrolysis species is theoretically possible but not practical due to large iteration time and subsequent refinement costs.

A practical way to determine the polynuclear contribution to potentiometric titration patterns is to refine the titration patterns as mononuclear species only and then to separate the mononuclear and polynuclear Al contributions to a hydrolysis species numerically calculated from these results.

In this refinement, the first assumption made is that only one polynuclear species is present or as stated mathematically:

\[
[\text{Al(OH)}_y_{\text{obs}}] = [\text{Al(OH)}_y] + x[\text{Al}_x(\text{OH})_{xy}].
\]  

Theory
Substituting in the equilibrium constants yields:

\[ Q_{obs} \left( \frac{[Al^{3+}]}{[H^+]^y} \right) = Q_{1y} \left( \frac{[Al^{3+}]}{[H^+]^y} \right) + xQ_{x,xy} \left( \frac{[Al^{3+}]}{[H^+]^y} \right)^x \]  \hspace{1cm} [16]

with one equation of this type resulting from each titration pattern.

Dividing each side of equation 16 by \( \left( \frac{[Al^{3+}]}{[H^+]^y} \right) \) results in:

\[ Q_{obs} = Q_{1y} + xQ_{x,xy} \left( \frac{[Al^{3+}]}{[H^+]^y} \right)^{x-1} \]  \hspace{1cm} [17]

and combining \( Q_{obs} \) and \( Q_{x,xy} \) to obtain:

\[ Q_{obs} - Q_{1y} = xQ_{x,xy} \left( \frac{[Al^{3+}]}{[H^+]^y} \right)^{x-1} \]  \hspace{1cm} [18]

Considering that only the Q values and x are unknowns, this equation can be solved. A plot of the log of equation 18 would yield a slope from which the number of Al ions in the polynuclear species can be determined. With this knowledge, the rest of the parameters can be calculated.

The actual pQ for a polynuclear species is much easier to derive from the observed mononuclear species value if there is no equivalent mononuclear species present, such as in the case of polynuclear species with nonintegral OH/Al ratios. In these cases, equation 17 is simplified to:

\[ Q_{obs \times,xy} = xQ_{x,xy} \left( \frac{[Al^{3+}]}{[H^+]^y} \right)^{x-1} \]  \hspace{1cm} [19]

If the log \( Q_{obs \times,xy} \) is plotted against log Al\(^{3+}\) then the slope could be equated to the number of Al ions in the polynuclear species and equation 19 can be solved for \( Q_{xy} \).
Effects of Soluble Ligands

Aluminum in solution can be considered either as an uncomplexed or a complexed hydrolyzed species or stated mathematically:

\[ [\text{Al}_{\text{tot}}] = \sum x[\text{Al}(\text{OH})_{xy}^{3x-xy}] + \sum a[\text{Al}(\text{OH})_bL_z^{2a-b-vz}] \]  

where \( L \) represents the ligand of charge \( v^- \) or in the general case where \( z \) can equal zero:

\[ [\text{Al}_{\text{tot}}] = \sum x[\text{Al}(\text{OH})_{xy}^{3x-xy-vz}] \]

for the generalized chemical equation:

\[ x\text{Al}^{3+} + xy\text{H}_2\text{O} + zL^- \rightarrow \text{Al}(\text{OH})_{xy}L_z^{3x-xy-vz} + xy\text{H}^+ \]

with an equilibrium constant, \( K_{x,xy,z} \).

The effects of an Al complex on a titration pattern is the same as the uncomplexed species of the same degree of hydrolysis. For that reason, an apparently larger concentration of that hydrolysis species is observed being equal to the concentration of the complexed and uncomplexed species. Substituting for the two species:

\[ [\text{Al}(\text{OH})_{xy}]_{\text{obs}} = Q_{x,xy} [\text{Al}^{3+}]^x [\text{H}^+]^{xy} + xQ_{x,xy,z} [\text{Al}^{3+}]^x [L^-]^{2y} [\text{H}^+]^{xy} \]

and rearranging results in:

\[ [\text{Al}(\text{OH})_{xy}]_{\text{obs}} = \frac{[\text{Al}^{3+}]^x [\text{H}^+]^{xy}}{[\text{H}^+]^{xy}} (Q_{x,xy} + xQ_{x,xy,z}[L^-]^{2y}) \]

which allows for the calculation of \( Q_{x,xy,z} \). Log \( Q_{x,xy,z} \) can be calculated in a manner similar to that used for the hydrolyzed uncomplexed species.
The only significant complexation known to occur in the solutions used in this study was the Al sulfate complexes, $\text{AlSO}_4^+$ and $\text{Al(SO}_4)_2^-$ whose presence was detected by Izatt et al. (1969) and Behr and Wendt (1962) among others. These complexes were included in the computer TIFIT by changing the $[\text{Al}^{3+}]$ term to $(1 + 10^{3.2}[\text{SO}_4^{2-}]) + 10^{6.1}[\text{SO}_4^{2-}]^2[\text{Al}^{3+}]$ in accordance with the results of Behr and Wendt (1962). Neither of the studies of Behr and Wendt (1962) or Izatt et al. (1969) noted any Al hydroxy sulfate complexes because they carried out their experiments at low concentrations to reduce any complications due to hydrolysis.

Effects of Precipitation

The effects of precipitation on Al reactions are too significant to be overlooked. For that reason, the possibility of precipitation was included in the FORTRAN program, TIFIT. The program was written in such a way to allow, at the users option, the refinement of a titration pattern as the result of precipitation processes in addition to hydrolysis reactions alone.

For all solutions except possibly those high in sulfate or silica, the solid most likely to precipitate is $\text{Al(OH)}_3$. This solid commonly occurs in three crystalline polymorphs and as a non-crystalline gel. The identification of the precipitating solid is not needed as the solubility can be calculated similarly regardless of identity. For the purposes of the refinement method used in TIFIT for titration patterns, only the hydroxyl to Al ratio of the precipitant is needed. This is fortuitous as there would not be sufficient precipitant in dilute solutions to identify.

For solutions in which $\text{Al(OH)}_3$ is precipitating, equation 10 becomes:

\[
[\text{OH}_{\text{neutralized}}^-] = [\text{AlOH}^{2+}] + 2[\text{Al(OH)}_2^+] + 3[\text{Al(OH)}_3^3] + 3[\text{Al(OH)}_3^3_{\text{ppr}}] + 4[\text{Al(OH)}_4^-] + y[\text{Al}_4(\text{OH})_{3y-x}^{3x-xy}].
\]

where $\text{Al(OH)}_3^3_{\text{ppr}}$ represents the precipitated solid. The pH at which precipitation commences corresponds to that pH when the $\text{Al(OH)}_3^3_{\text{ppr}}$ calculated by equation 25 is equal to zero.
The concentration of the precipitating solid can be calculated from the relation:

\[
[\text{Al(OH)}_3\text{ ppt.}] = [\text{Al}_{\text{total}}] - [\text{Al}^3^+] - [\text{AlOH}^2^+] - [\text{Al(OH)}^+] - [\text{Al(OH)}_2^-] - x[\text{Al}_x(\text{OH})_y] - [\text{Al(OH)}_4^-].
\]  

[26]

One simplification which makes this relationship easier to solve is that the Al concentrations for this system make the presence of polynuclear species very unlikely. This reduces equation 26 to:

\[
[\text{Al(OH)}_3\text{ ppt.}] = [\text{Al}_{\text{total}}] - [\text{Al}^3^+] - [\text{AlOH}^2^+] - [\text{Al(OH)}_2^+] - [\text{Al(OH)}_3^0] - [\text{Al(OH)}_4^-].
\]  

[27]

If one takes equation 27 and combines it with:

\[
[\text{OH}^-_{\text{neutralized}}] = [\text{AlOH}^2^+] + 2[\text{Al(OH)}_2^+] + 3[\text{Al(OH)}_3^0] + 4[\text{Al(OH)}_4^-] + 3[\text{Al(OH)}_3\text{ ppt.}],
\]  

[28]

one obtains the equation describing a titration pattern for a solution with Al(OH)$_3$ precipitating. After substituting for Al(OH)$_3$ precipitation, the relationship becomes:

\[
[\text{OH}^-_{\text{neutralized}}] = 3[\text{Al}_{\text{total}}] - 3[\text{Al}^3^+] - 2[\text{AlOH}^2^+] - [\text{Al(OH)}_2^+] - [\text{Al(OH)}_4^-].
\]  

[29]

Notice that this relationship is independent of the third pK as the Al(OH)$_3$ solution species does not appear in the equation.

The equations used to calculate species concentrations are different in the precipitation case than in the nonprecipitation case. This is not because equations 5 through 8 no longer describe the relevant hydrolysis equations but because [Al$^+$] cannot be described as the remainder in solution after the monomeric hydrolysis products are described as is implied by equation 12. Instead, the hydrolysis reactions are described by the general reaction:

\[
\text{Al(OH)}_3\text{ ppt} + x\text{H}^+ \rightarrow \text{Al(OH)}_3^x^- - x + x\text{H}_2\text{O}
\]  

[30]
which describe $\text{Al(OH)}_3 \text{ppt}$ as the source of Al for hydrolysis rather than $\text{Al}^{3+}$. The concentration constants for this equation is abbreviated $Q_{\text{SlY}}$ which can be related to the monomeric concentration constant $Q_{\text{LY}}$ by the relation:

$$Q_{\text{SlY}} = Q_{\text{So}} Q_{\text{Ly}} \quad [31]$$

where $Q_{\text{Sia}}$ is the concentration constant for the equation:

$$\text{Al(OH)}_3 \text{ppt} + 3\text{H}^+ \rightarrow \text{Al}^{3+} + 3\text{H}_2\text{O}. \quad [32]$$

The choices for the precipitating phase are much more complex in the sulfate containing solutions. In these solutions, there exists the possibility of several other precipitants: jurbanite ($\text{Al(OH)SO}_4\cdot5\text{H}_2\text{O}$) with a hydroxide to Al ratio of 1.0, alunite ($\text{KAl}_3(\text{OH})_6(\text{SO}_4)_2$) with a hydroxide to Al ratio of 2 and basalluminite ($\text{Al}_4(\text{OH})_10\text{SO}_4\cdot5\text{H}_2\text{O}$) with a hydroxide to Al ratio of 2.5. Each of these precipitants are considered possible precipitants in sulfate containing Al solutions and were therefore included as possible precipitating phases in the TIFIT program. The only difference in the treatment of the Al sulfate precipitants from the precipitation of gibbsite in TIFIT is that the sulfate portion of the solubility product for the sulfate precipitants is not included in the fitted solubility product. Because much more sulfate is present in solution than Al, sulfate is constant for any single titration pattern, and therefore its inclusion in the solubility product is not required. For solutions in which jurbanite is precipitating, equation 10 becomes (assuming no polynuclear complexes are present):

$$[\text{OH}^{-}_\text{neutralized}] = [\text{Al(OH)}^{2+}] + 2[\text{Al(OH)}_2^+] + 3[\text{Al(OH)}_3^0] + [\text{jurbanite}] + 4[\text{Al(OH)}_4^-] + y[\text{Al}_x\text{OH}_{3y-x}]^z. \quad [33]$$

where $[\text{jurbanite}]$ represents the precipitated solid. The pH at which precipitation commences corresponds to that pH where the concentration of jurbanite calculated by equation 33 is equal to zero.

The concentration of the precipitating solid can be calculated from the relation:
\[
\text{jurbanite} = [\text{Al}_\text{total}] - [\text{Al}^3^+] - [\text{Al(OH)}^2^+] - [\text{Al(OH)}_2^+] - [\text{Al(OH)}_3^-] - [\text{Al(OH)}_4^-].
\]

If one takes equation 34 and combines it with:

\[
[\text{OH}_{\text{neutralized}}^\text{−}] = [\text{Al(OH)}^2^+] + 2[\text{Al(OH)}_2^+] + 3[\text{Al(OH)}_3^+] + 4[\text{Al(OH)}_4^-] + [\text{jurbanite}],
\]

one obtains the equation describing a titration pattern for a solution with jurbanite precipitating. This relationship is:

\[
[\text{OH}_{\text{neutralized}}^\text{−}] = [\text{Al}_\text{total}] - [\text{Al}^3^+] - [\text{Al(OH)}^2^+] - 2[\text{Al(OH)}_2^+] + 3[\text{Al(OH)}_4^-].
\]

Notice that this relationship is independent of the first pK as the Al(OH) solution species does not appear in the equation.

The equations used to calculate species concentrations are different in the jurbanite precipitation case than in the case due to Al(OH)_3 precipitation or in the nonprecipitation case. Instead, the hydrolysis reactions are described by the general reaction:

\[
\text{Al(OH)SO}_4_{\text{jurbanite}} + x\text{H}^+ \rightarrow \text{Al(OH)}_2^{2+x} + x\text{H}_2\text{O} + \text{SO}_4^{2-}
\]

which describes jurbanite as the source of Al for hydrolysis rather than Al^{3+}.

In a similar manner, the precipitation of alunite and basaluminite can be described as a sink for Al.

The equations used to calculate species concentrations for alunite precipitation can be generalized as:

\[
K\text{Al}_3(\text{OH})_6(\text{SO}_4)_2 \text{alunite} + 3x\text{H}^+ \rightarrow K^+ + 3\text{Al(OH)}_2^{1+x} + 3x\text{H}_2\text{O} + 2\text{SO}_4^{2-}.
\]
In this form, however, the equation is third order with respect to Al. This makes the equation difficult to solve. Therefore, for ease of calculation, the equation was divided by 3 yielding:

\[(1/3)\text{KAl}_3(\text{OH})_6\text{SO}_4 \text{ alunite} + x\text{H}^+ \rightarrow (1/3)\text{K}^+ + \text{Al(OH)}_{2-\frac{x}{3}} + x\text{H}_2\text{O} + (2/3)\text{SO}_4^{2-}\]  \[39\]

which has the equilibrium concentration constant:

\[Q_{sly} = \frac{[\text{K}^+]^{1/3}[\text{Al(OH)}_{2-\frac{x}{3}}^+]}{[\text{H}^+]^x[\text{SO}_4^{2-}]^{2/3}} \]  \[40\]

The equations used to calculate species concentrations for basaluminite are like that of alunite in that the stoichiometric formula has more than one Al. The precipitation reaction for basaluminite can be written:

\[\text{Al}_4(\text{OH})_{10}\text{SO}_4 \text{ basaluminite} + 4x\text{H}^+ \rightarrow 4\text{Al(OH)}_{2.5-x} + 4x\text{H}_2\text{O} + \text{SO}_4^{2-}\]  \[41\]

which like the equation for alunite is not first order with respect to Al. Dividing the equation by 4 yields:

\[(1/4)\text{Al}_4(\text{OH})_{10}\text{SO}_4 \text{ basaluminite} + x\text{H}^+ \rightarrow \text{Al(OH)}_{2.5-x} + x\text{H}_2\text{O} + (1/4)\text{SO}_4^{2-}\]  \[42\]

which has the equilibrium concentration constant:

\[Q_{sly} = \frac{[\text{Al(OH)}_{2.5-x}^+][\text{SO}_4^{2-}]}{[\text{H}^+]^x} \]  \[43\]

which is first order with respect to Al.
Titration Analysis and the Determination of Aluminum Hydrolysis

Before titration analyses are used to determine the hydrolysis products of Al, it is believed to be first advantageous to determine the degree to which the Al hydrolysis products would affect the titration patterns. To do this a computer program, ALPHA, was written which can calculate titration patterns for any group of pK values. Values for the pK values for Al hydrolysis products were chosen which represented the full range of values observed in the literature (Table 1).

The calculated titration patterns (Figures 1-5) show that titration patterns are sensitive to the Al hydrolysis products except possibly the first pK (Figure 1). In addition the calculated patterns show that titrations are sensitive to precipitation reactions (Figure 5). Titration patterns are shown to be most sensitive to the second (Figure 2) and third (Figure 3) hydrolysis products which is advantageous as these are the least well established.
Table 1. Sources for mononuclear hydrolysis constants of Al and the methods used for their determination. The high and low pK for each reaction is shown in bold and bold italics, respectively.

<table>
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<tr>
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<td>Dilution</td>
</tr>
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<td>Kubota, 1956</td>
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<td>Dilution and Potentiometry</td>
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<tr>
<td>Frink and Pech, 1963</td>
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</tr>
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</tr>
<tr>
<td>Nischide and Tsuchiya, 1965</td>
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<td>Conductivity</td>
</tr>
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<td>Iem and Roberson, 1967</td>
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</tr>
<tr>
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</tr>
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† Not significant in solution.
‡ Also proposed a scheme with no Al(OH)₂⁺.
Figure 1. Calculated titration curves showing the effects of changes in the first pK on the shape of a titration curve. The pK$_{11}$ was varied between 5.03 and 5.60 while the other pKs were set constant at pK$_{12}$ = 9.39, pK$_{13}$ = 15.09 and pK$_{14}$ = 23.06 with no precipitation or polymerization reactions assumed.
Figure 2. Calculated titration curves showing the effects of changes in the second pK on the shape of a titration curve. The pK$_{12}$ was varied between 9.39 and 10.40 while the other pKs were set constant at pK$_{11} = 5.03$, pK$_{13} = 15.09$ and pK$_{14} = 23.06$ with no precipitation or polymerization reactions assumed.
Figure 3. Calculated titration curves showing the effects of changes in the third pK on the shape of a titration curve. The pK$_{13}$ was varied between 15.09 and 16.20 while the other pKs were set constant at pK$_{11} = 5.03$, pK$_{12} = 9.39$ and pK$_{14} = 23.06$ with no precipitation or polymerization reactions assumed.
Figure 4. Calculated titration curves showing the effects of polynuclear complex formation. The $Al_{13}O_4(OH)_{24}$ pK was set at 100.40 while the other pKs were set constant at $pK_{11} = 5.03$, $pK_{12} = 9.39$, $pK_{13} = 15.09$ and $pK_{14} = 23.06$ with no precipitation reactions assumed.
Figure 5. Calculated titration curves for precipitation of amorphous Al(OH)$_3$ (b), gibbsite (c) and no precipitation (a). The pK$_{20}$ was set at 32.34 for amorphous Al(OH)$_3$ and 34.00 for gibbsite while the other pKs were set constant at pK$_{11} = 5.03$, pK$_{12} = 9.39$, pK$_{13} = 15.09$ and pK$_{14} = 23.06$ with no polymerization reactions assumed.
Aluminum Hydrolysis Constants

Many methods have been used to measure the hydrolysis constants of Al. The most commonly used methods for the determination of Al hydrolysis constants are the dilution method and potentiometry. Other methods which have been used to study Al hydrolysis include conductivity, solubility, equilibrium centrifugation, colorimetric complexes and various combinations of these and other supplementary methods. Before providing the results of these studies, the methods used to make the determinations are examined for better appreciation of the assumptions involved in each of the methods and the reliability of the results. The importance of the model chosen for data interpretation cannot be over emphasized since the model, rather than differences in experimental results, is responsible for the large discrepancies observed between Al speciation studies. Due to the importance of the dilution method in the study of Al hydrolysis, it will be considered separately in the discussion of methods.
Methods Used To Determine Hydrolysis Constants

The dilution method

The most commonly used method for the determination of Al hydrolysis constants is the dilution method. The dilution method has been used by Schofield and Taylor (1954), Aveston (1956), Kubota (1956), Frink and Peech (1963), and Volokhov et al. (1971) to examine the first hydrolysis reaction and by Schofield and Taylor (1954) and Frink and Peech (1963) to study the possibility of the second hydrolysis reaction. In this type of experiment, the pH of an Al solution is measured as a function of Al concentration. This very simple experimental design makes the method very popular for determining hydrolysis constants. The main problems with the use of the dilution method for the determination of Al hydrolysis products is the slowness of the approach of Al to equilibrium, limitations as to the constants which may be studied by the method and the need to know all the reactions involved in the experiment. The slowness of the approach of Al solutions to equilibrium can be overcome by determining the pH as a function of time to monitor the equilibrium of the solution, as was done by Frink and Peech (1962). The inability to determine all the hydrolysis constants by the dilution method undermines the general applicability of the method but not the results of studies for which it can be used. On the other hand, the need to know the identity of reactions which are affected by dilution casts serious doubts on the interpretations of dilution studies. Differences in the model used to interpret dilution studies can cause one researcher to obtain an entirely different set of solution species from a nearly identical set of data. A general model for the interpretation of dilution data is:

\[
[H^+] = \sum xy[Al_{x}(OH)_{xy}].
\]  

[44]

The differences between which species are allowed on the right side of the equation account for the differences between various studies. One example of interpretational differences would be that Aveston (1956) found only \(Al_{[\text OH]}^{3+}\) and \(Al_{[\text OH]}^{5+}\) polynuclear Al hydrolysis products, Kubota
(1956) found AlOH$^{2+}$ and Al$_2$(OH)$_3^{+}$, Frink and Peech (1963) found AlOH$^{2+}$ and possibly Al(OH)$_2^+$, while Schofield and Taylor (1954) and Volokhov et al. (1971) found only AlOH$^{2+}$ in nearly identical experiments.

**Potentiometry**

Potentiometry experiments differ from dilution experiments in that the pH is varied independently of Al concentration. This important difference allows for better detection and identification of multiple hydrolysis species in solution. The method shares the shortcoming of the dilution method (and for that matter all other methods) of being limited by the model being used to interpret the data but the more complex data allows for more complete reaction models. Results of these studies are not as easily comparable as in dilution studies because pH is independent of Al concentration. Still, the model used in the data interpretation can make large differences in the results obtained. Mesmer and Baes (1971) found only the Al$_2$(OH)$_3^{+}$, Al$_3$(OH)$_4^{+}$ and Al$_{13}$(OH)$_{20}^{+}$ species in their study. Hayden and Rubin (1976) found that their data was best fitted by the presence of AlOH$^{2+}$ and Al$_4$(OH)$_{26}^{+}$ using a comprehensive mononuclear-polynuclear hydrolysis model.

**Solubility methods**

Solubility is the third most commonly used method for the determination of hydrolysis constants. The main advantage to solubility studies is that as long as the species is significant in solution at some pH, its hydrolysis constant can be determined by the method. The main shortcomings of the method are the slow approach of the Al solutions to equilibrium especially from oversaturated states, the presence of many possible chemically identical precipitating species which differ only in solubility, the possibility of colloidal and subcolloidal suspensions which are difficult to describe thermodynamically and the low analytical accuracy at the low concentrations found in equilibrium with the solids (Hem and Roberson, 1967). Another problem in the solubility
method, which is only now receiving attention, is the effects of the edge charge of the actively growing or dissolving solid on the solution speciation near the surface. Raupach (1963d) was the first to hypothesize that surface reactions shift the speciation of Al in his solubility studies. May et al. (1979) found that they had to suggest that an undetected solid phase controlled the Al speciation in their solutions in order to interpret their data. Since the time of these studies, work by Zelazny and his coworkers (Hodges and Zelazny, 1983a,b; Jardine et al., 1985a,b) have demonstrated that solid surfaces have large effects on Al speciation promoting increased polymerization of Al with an increased $n$ for that Al adsorbed relative to that in solution. Leckie and James (1976) proposed a detailed model for the solid-solution interface which predicts a different surface speciation from that which would be at equilibrium in solution. These studies question the reliability of solubility studies as a method for the determination of Al hydrolysis constants.

**Equilibrium centrifugation**

A method which has been used for the identification and determination of polynuclear complexes present in Al solutions is equilibrium centrifugation. The equilibrium centrifugation method is based on the fact that each component in solution distributes itself in a centrifugal field such that, at equilibrium, the free energy associated with the concentration gradient is balanced by centrifugal effects (Baes and Mesmer, 1976). Problems arise if the method is used when multiple species are present. Uncertainties in the results arise due to difficulties in obtaining concentration gradients from refractive index measurements in polydispersed systems, assumptions of constant activity coefficients and charge per Al for all species and effects of the pH and concentration gradient distribution in rapidly reacting systems. As a result, equilibrium centrifugation is most commonly used in conjunction with other methods, such as in combination with the dilution method in the study of Aveston (1965).
Other methods

Two other methods which have been used to determine Al hydrolysis products have been colorimetry and conductivity. Nazarenko and Nevskaya (1969) used colorimetric reactions of Al with arsenazo I and pyrocatechol violet to determine the first, second and third hydrolysis constants. The calculated hydrolysis constants from their study are in the same range with those determined by other methods. This is somewhat surprising considering their assumptions of no polynuclear complexes and no shift in equilibrium due to the colorimetric complexes. Nischide and Tsuchiya (1965) used conductivity to determine the first hydrolysis constant for Al as a side study in their study of sulfate complexation of Al. Their use of conductivity allowed them to determine the first hydrolysis constant and to set limits on the presence of Al hydroxy sulfate complexes in solution.

Measured Values for Mononuclear Aluminum Hydrolysis Reactions

The first hydrolysis constant for Al have been the subject of many studies. At first glance, a tabulation of the values determined for the first pK of Al are very constant (Table 1). The tabulation is, however, misleading because four out of the eleven studies used the dilution method and three of the other studies used solubility. In all the dilution studies, it was basically assumed that

\[ H^+ = AlOH^{2+}. \]  \[45\]

The importance of this assumption cannot be understated and will be investigated in detail in the discussion section. In some of the studies, the presence of \( Al_2(OH)_4^{4+} \) was allowed (Kubota, 1956), in others the presence of \( Al(OH)_3^+ \) was allowed (Schofield and Taylor, 1954; Frink and Pech, 1963), but in those studies, the second species was only present to help in the fit at high (for \( Al_2(OH)_4^{4+} \)) or low Al concentrations (for \( Al(OH)_3^+ \)) depending on the concentrations used in the
study. The results of the solubility studies are also questionable because of surface effects noted in the literature, due to the fact equilibrium may not have been established and because only total Al concentration was measured and the possibility of polynuclear complexes was not investigated.

As questionable as the values for the first hydrolysis constant may be, at least the values are somewhat consistent. The same cannot be said for the values determined for the second hydrolysis constant (Table 1). Even when the same methods were applied to its determination, the values were variable. Two dilution studies found the second hydrolysis product to be of little significance with Schofield and Taylor (1954) not detecting the species and Frink and Pech (1963) hedging whether to give the species a pK of 11.02 or to say it was not present and ascribing the deviation of their results to the precipitation of gibbsite. Three solubility studies give values of 8.64 (Gayer et al., 1958), 9.78 (Raupach, 1963b), and 10.13 (May et al., 1979). Nazarenko and Nevskaya (1971) obtained a value of 10.32 by use of two colorimetric methods to determine the first three mononuclear pK values. Hayden and Rubin (1976) using potentiometry joined the researchers using the dilution method in questioning the presence of the second hydrolysis product. In other words, the second pK may be assumed to be any value from 8.64 to somewhere above 12.00 depending on the source.

The third pK also has a wide variety of values assigned depending on the source (Table 1). Dalal (1975) gave the lowest value for the third hydrolysis constant, 13.02, as determined by hydrolysis. Nazarenko and Nevskaya (1969) and May et al. (1979) obtained similar pK values of 16.19 and 16.76 as a result of colorimetric and solubility methods, respectively. In a comprehensive potentiometric study, Hayden and Rubin (1976) concluded that their data was best fitted by the presence of AlOH^{2+} and Al_{4}(OH)_{10}^{4+} and that Al(OH)_{6}^{3+} was not significant in their solutions.

Values for the fourth hydrolysis constant have been obtained only through solubility studies. The range in values is between 22.16 and 23.57 for the fourth pK. May et al. (1979) questioned their results and those of the others who had previously determined the fourth pK by concluding that a different mineral controls Al solubility above pH 6.7. Their recognition of a problem with solubility results is in accordance with the work of Zelazny and his coworkers (Hodges and Zelazny, 

Literature Review
1983a,b; Jardine et al., 1985a,b) who demonstrated increased degrees of hydrolysis near surfaces, and the surface hydrolysis model of Leckie and James (1976).

Measured Constants for Polynuclear Aluminum Hydrolysis Reactions

Polynuclear hydrolysis constants for Al have been measured using computer analysis of potentiometric data. The exception to this statement would be Aveston (1956), who combined ultracentrifugation with computer analysis of his dilution data. In some cases (Kubota, 1956 and Hayden and Rubin, 1976), the polynuclear complexes have been refined allowing for both mononuclear and polynuclear complexes, while in others (Mesmer and Baes, 1971), only polynuclear complexes were contained in the hydrolysis model. The most completely modeled system was that of Hayden and Rubin (1976) who allowed for the presence of AlOH$_2^+$, Al(OH)$_2^+$, Al(OH)$_3^+$ and any grouping of polynuclear complexes in their computer analysis of potentiometric data obtained for $\Pi$ between 0 and 1.6 in aged solutions which were $10^{-3}$, $5.0 \times 10^{-4}$ and $10^{-4}$M with respect to Al. They found better computer fits when the Al(OH)$_2^+$ and Al(OH)$_3^+$ species were not included in the computer model. The results could not conclusively identify the polynuclear complex present in his solution but the authors preferred the Al$_6$(OH)$_{20}^{5-}$ over the Al$_4$(OH)$_{13}^{3-}$ and Al$_6$(OH)$_{17}^{4+}$ polynuclear complexes in solution with only the AlOH mononuclear species. They concluded that any other combination of complexes did not result in a curve fit even remotely close to those obtained with these three combinations of one mononuclear and one polynuclear complex.

Examination of the tabulated values for the polynuclear hydrolysis complexes (Table 2) shows that only certain species appear to show up in the curve fits of potentiometric data. In most studies, the authors concluded that the best fit to the data is to use at least one small polynuclear complex or AlOH$_2^+$ and at least one relatively large polynuclear complex. Kubota obtained his best fit to his dilution and limited potentiometric data using AlOH$_2^+$ and Al$_2$(OH)$_4^{2+}$ but his calculated value for the pK of 4.27 for the Al$_2$(OH)$_4^{2+}$ species is very much removed from the pK between 7.07 and 7.55 obtained by the other three studies. The intermediate (Al of 6, 7, or 8) and large
Table 2. Sources for polynuclear hydrolysis constants of Al. The high and low pK for each reaction is shown in bold and bold italics, respectively.

\[ x\text{Al}^{3+} + y\text{H}_2\text{O} \rightarrow \text{Al}_x\text{OH}_{y}^{3x-y} + y\text{H}^+ \]

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† Quoted from Nair and Prenzel, 1978.
(Al 13) sized species are all used to represent a species with \( n = 2.5 \) in the data set. This \( n \) value is approached as the ring structures start to form with only bridging hydroxyls assumed to occur in polynuclear complexes. The correct combination of polynuclear complexes for use in models of Al hydrolysis is highly controversial with some authors quoting hydrolysis constants and others (Hem and Roberson, 1967, for instance) believe that polynuclear complexes are not equilibrium species with their presence and identity being more the result of method of preparation than equilibrium processes.

**Interactions of Sulfate With Aluminum Hydrolysis**

The effects of the sulfate anion on Al solution chemistry is one of the least understood areas in the environmental chemistry of Al. It has been hypothesized that mineral acids from acid deposition mobilize Al which had previously been unavailable for solution reactions due to ion exchange and precipitation processes (Driscoll, 1984). Whether the interactions between Al and acid deposition is a direct expression of increased levels of acidity and/or anions, or the result of an indirect process involving mobilization of organic carbon is highly controversial.

Equally controversial is the effects of sulfate in the solution chemistry of Al. Behr and Wendt (1962), Nanda and Aditya (1962), Nishide and Tsuchiya (1965), Izatt et al. (1969), and Lo et al. (1982) found strong interactions between sulfate and Al\(^{3+} \) and calculated thermodynamic constants describing the proposed reactions (Table 3). Hayden and Rubin (1976) and Lo et al. (1982) found large changes on the critical coagulation concentration of Al accompanying the presence of sulfate. These results suggest that the pH range at which Al undergoes hydrolysis would be higher in sulfate solutions than in non-sulfate containing solutions. This assumption may not be the case.

Volokhov et al. (1971) obtained the same \( pK \) values for the first hydrolysis constant in a dilution study with sulfate as with perchlorate, chloride, bromide and nitrate without assuming any
Table 3. Sources for Al sulfate complexation products. The high and low pK for each reaction is shown in bold and bold italics, respectively.

\[ x\text{Al}^{3+} + z\text{SO}_4^{2-} \rightarrow \text{Al}_x(\text{SO}_4)_2^{3x-2z} \]

<table>
<thead>
<tr>
<th>x</th>
<th>z</th>
<th>Source</th>
<th>pK</th>
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<tbody>
<tr>
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<td>1</td>
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<td>3.21</td>
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<tr>
<td></td>
<td></td>
<td>Nanda and Aditya, 1962</td>
<td>2.04</td>
</tr>
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<td>Izatt et al., 1969</td>
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<td></td>
<td></td>
<td>Nishide and Tsuchiya, 1965</td>
<td>3.73</td>
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<tr>
<td>2</td>
<td>2</td>
<td>Behr and Wendt, 1962</td>
<td>5.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Izatt et al., 1969</td>
<td>4.90</td>
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Al$^{3+}$ complexes. Nishide and Tsuchiya (1965) reported a pK of 4.90 for the first hydrolysis product in sulfate solutions using conductivity. This value is very close to that obtained by other studies in non-sulfate solutions. Raupach (1963b,d) obtained the first and second Al hydrolysis constants using the solubility of gibbsite which were the same in sulfate solutions as in chloride solutions. These results point to either no interactions between Al and sulfate or a higher degree of interactions than there are thermodynamic values for at this time.

For these reasons, Hayden and Rubin (1976) suggested the presence of Al hydroxy sulfate polymers. Nishide and Tsuchiya (1965) in their conductivity study of Al-sulfate interactions proposed a limit for the reaction:

$$\text{AlOH}_2^+ + \text{SO}_4^{2-} \rightarrow \text{AlOHSO}_4^0$$ \[46\]

as not higher than that of:

$$\text{Al}^{3+} + \text{SO}_4^{2-} \rightarrow \text{AlSO}_4^+.$$ \[47\]

However, Lo et al. (1982) found that the inclusion of the AlHSO$_4^+$ and AlOHSO$_4^+$ complexes did not improve the regression results in their study of Al-sulfate interactions. In other words, the interactions are between Al and sulfate have not been unequivocally determined.

**Kinetics of Solution Aluminum Reactions**

Hem and Roberson (1967) considered any study of Al chemistry in dilute solutions to be seriously hindered by kinetic factors. They considered all workers to be in general agreement that the reactions of Al and OH between pH 4 and 7 are slow, and that the products of the reactions may be influenced by concentration of reagents, kinds of anions present, and the manner in which
the solutions are prepared. These problems caused Hem and Roberson (1967) to conclude that the assumption of chemical equilibrium to be invalid for solutions which have aged only a few days. In addition, they considered it to be erroneous to apply pH data, total Al and bound hydroxyl values alone to characterize Al hydroxy complexes below pH 7.5. To determine the validity of this statement, it is important to examine the kinetics of the various types of Al solution reactions. The three general kinetic divisions of Al solution reactions can be considered to be mononuclear hydrolysis-complexation reactions, polymerization and precipitation.

**Mononuclear Hydrolysis Reactions**

Mononuclear hydrolysis reactions have been considered to react quickly to changes in pH since the earliest studies of Al hydrolysis (Hem and Roberson, 1967). Holmes et al. (1968) determined the kinetics of mononuclear Al hydrolysis using dissociation field effect relaxation times. They found that reactions were practically instantaneous with a rate constant $K_{-1}$ equal to $4.4 \times 10^6 \text{M}^{-1}\text{s}^{-1}$. This result was considered consistent with other diffusion controlled reactions and caused the authors to conclude that Al hydrolysis involved only proton gains or losses with no $\text{OH}_2^-$ - OH exchange. Other researchers studies (Turner and Ross, 1970; Smith and Hem, 1972) found that longer periods of time were required for the mononuclear concentration to reach steady state values but the delay was considered the result of polymerization or precipitation reactions with the mononuclear fraction responding instantaneously to changes in pH.

**Polymerization Kinetics**

Polymerization reactions continue over a longer period of time than mononuclear hydrolysis reactions. The initial rate of formation of polynuclear complexes is fast (Stol et al., 1976), but the polynuclear species formed in the initial stages is likely to be intricately branched, with many rings
and OH in OH positions and vice versa (Hem and Roberson, 1967). These initially formed species then rearrange from the quickly formed unstable structures into more stable forms (Hem and Roberson, 1967). The initial formation of the unstable polynuclear species appears finished within the first day of the reaction but the second stage of structural rearrangement and growth of larger, more stable polynuclear forms takes up to 40 days (Smith and Hem, 1972). Aged polynuclear species are considered highly resistant to acid attack (Brosset et al., 1954; Hem and Roberson, 1967; Stol et al., 1976) with decomposition considered to be second order (Stol et al., 1976). This resistance to acid attack caused Hem and Roberson (1967) to conclude that polymers are so slow to change at the temperatures found in the weathering environment that their presence must be considered in any evaluation of the chemical behavior of dilute Al solutions in natural systems. The rate controlling step in the formation of polynuclear complexes is considered to be the formation of the double hydroxyl bridges between adjacent Al in the complex. The presence of the hydroxyls in double bridging positions results in a much slower equilibration of polynuclear Al complexes to changes in pH (Hem and Roberson, 1967; Smith and Hem, 1972; Stol et al., 1976). Hem and Roberson's (1967) rate experiments showed that a somewhat greater amount of acid had to be added to obtain a desired dissolution pH than could be accounted for by the free OH. They ascribed this difference to a rapidly reacting bound OH fraction which is generally small in aged solutions and solutions with $n$ greater than 2.0. They considered the slow reacting fraction to be polymerized in a form with $n$ approximately 3.0 and the fast reacting fraction to be present as the equivalent of AlOH$^+$. Stol et al. (1976) found in stop-go-reverse titration experiments that the acid breakdown of fresh Al polynuclear complexes is second order. The slow step in the second order process is considered to be the loosening of the double bridging OH complex with a fast following step involving OH$_2$ uptake.
Precipitation Kinetics

Precipitation of dilute Al solutions is a two step process. The initial step is the precipitation of a noncrystalline solid. This step is considered to be first order with respect to the amount of polynuclear Al. The kinetics of this reaction is much slower than polymerization at $\bar{n}$ less than about 2.5 but becomes much faster than polymerization reactions at higher pH ($\bar{\nu}$). At the lower $\bar{n}$ values, precipitation becomes so slow that the effects of precipitation may be ignored (Brosset et al., 1954; Stol et al., 1976). Only in experiments where base is added dropwise (allowing for high levels of supersaturation), such as in the experiments described in Turner and Ross (1970), has precipitation been noted at such low values for $\bar{n}$. In general, it has been found that it takes longer for the level of precipitation to become detectable as $\bar{n}$ decreases (Hem and Roberson, 1967). Smith and Hem (1972) found that the formation of microcrystalline Al(OH)$_3$ is paralleled by the disappearance of polynuclear Al species with the levels of mononuclear Al remaining nearly constant. From a nonequilibrium thermodynamic examination of their rate data, they concluded that the reaction of polynuclear species to form Al(OH)$_3$ was first order with respect to polynuclear Al concentration over much of the aging times they studied. They found that the mononuclear Al concentration was independent of method of solution preparation but the fractionation of Al between polynuclear species and the precipitant was affected by rate of base addition. They concluded that the more slowly base is added, the further from equilibrium the solution starts.

Summary of Aluminum Kinetics

In summary, it is concluded that mononuclear hydrolysis can be considered instantaneous. Polymerization has a fast formation step and a slower step in which the initially formed polynuclear species rearrange into more stable forms. Precipitation, in solutions formed by base injection, is so slow as to be nondetectable in solutions with $\bar{n}$ below 2.5. At pH values above about 2.80,
polymerization rate far outstrips precipitation rate and precipitation can be ignored. In solutions formed by dropwise base addition, precipitation occurs even at low values for $\bar{n}$ because local disequilibrium where the base addition to the solution allows for the formation of seeds for crystal growth.

**Titration Studies of Aluminum Hydrolysis**

If the modeling of titration curves of dilute Al solutions is to be used to determine the mononuclear hydrolysis products for Al, it is important to review the results of past workers who have described the reactions of Al during titrations. Very few workers have used titration patterns in the study of Al chemistry (Turner, 1968; Shah Singh, 1969; Stol et al., 1976). Good observations of the results of the initial stages of aging studies such as those of Hem and Roberson (1967) and Smith and Hem (1972) are available, however, and can be applied to the description of reactions occurring during titration of Al solutions especially as many of these solutions were prepared for aging by use of titration addition of base (Hem and Roberson, 1967, for instance).

Hem and Roberson (1967) concluded that it is erroneous to apply methods using pH data with total Al and bound OH data to characterize Al-hydroxyl complexes at pH less than 7.5. They concluded that the polynuclear complexes formed in the initial stages of equilibration of Al solutions to changes in pH have unstable defect structures which given sufficient time rearrange their structures into more stable polynuclear structures containing the double bridging hydroxyl bonds between Al cations. Smith and Hem (1972), in a followup study, found that the mononuclear Al concentration in solutions which have aged over 24 hours were independent of the rate of base addition but the fractionation of the remainder of the Al between the polynuclear and microcrystalline fractions was highly influenced. They concluded that the more slowly base is added to solution, the further the solution starts from equilibrium at time zero. Slow addition of base gives less
opportunity for local excess of base and the formation of noncrystalline Al(OH)$_3$ and results in the formation of more mononuclear and polynuclear complexes. Rapid addition of base promotes the formation of solid Al(OH)$_3$ which can reorganize directly into gibbsite.

Turner (1968) published a theoretical treatment of the behavior of Al during potentiometric titrations. In his treatment, he examined the effects of the precipitation of noncrystalline Al(OH)$_3$ (or gibbsite) and the formation of polynuclear species on the titration patterns of $10^{-2}$, $10^{-3}$ and $10^{-4}$ M Al solutions. Like the theoretical development in the earlier section, precipitation was found to yield flat titration plateaus relative to mononuclear curves, and the presence of polynuclear complexes was found to result in a second Al plateau at high $\bar{E}$. Unlike the treatment earlier in this work, the effects of changing pK values for the various reactions were not examined. No attempt was found in the rest of this series of papers (in which this work was the first), of any attempt to apply the results of this paper to the direct determination of pK values from titration patterns, although the results of real titration patterns were compared to the results. Turner (1968) concluded from this study that precipitation was very slow relative to titration speed in his experiments. In addition, he determined that the slow formation of polynuclear complexes was a more likely explanation for the pH drift observed by Frink and Peech (1963) than precipitation.

A co-worker of Turner's, Shah Singh (1969) used a similar approach to examine the neutralization of dilute Al sulfate solutions with a base. In his study, the AlOH$^{2+}$, AlSO$_4^-$ solution species and a solid Al hydroxy sulfate, Al(OH)$_{3-x}$(SO$_4$)$_x$ with $n = 2.5$ were used as solution species in simulated titration patterns which were compared to $10^{-2}$, $10^{-3}$ and $10^{-4}$ M Al$_3$(SO$_4$)$_2$ solutions. The results of the theoretical patterns compared relatively well with the observed patterns until about 80% neutralization.

In an exhaustive study, Stol et al. (1976) used continuous acid and base titrations, relaxation techniques (stop-go and go-stop-reverse titrations) and dilution tests to determine the Al reactions occurring in titration curves. They observed two types of titration curves depending on Al concentration. At Al concentrations higher than $5 \times 10^{-5}$ M, they found two plateaus with 3 inflections in the Al region of the titration curves. The first plateau, occurring at $\bar{n}$ less than about 2.5, was found to have a lower midpoint pH as Al concentration and ionic strength went up. The $\bar{n}$ of the
Inflection between the two plateaus was also found to increase as Al concentration and ionic strength increased. Visible precipitation was observed to occur on the second plateau of the titration curve. Like the first plateau, the midpoint pH of the plateau was observed to decrease as the ionic strength increased. They determined from stop-go titrations that very little pH drift occurred on the first Al plateau. The drift of pH was found to be much faster on the second plateau but the total pH change was small. They came to the conclusion from a combination of continuous acid and base titrations that base is slowly but continuously saturating solutions with respect to some form of solid Al(OH)₃ while acid titrations involve the dissolution of the solids. They determined that the degradation of newly formed polymers is second order from their go-stop-reverse experiments. They summarized their experimental results by concluding that titrations give kinetic results rather than equilibrium results if the reaction rate is slower than the rate of base addition.

The summary of these results is that precipitation can be ignored as an important constituent of Al solutions at $\bar{n}$ less than 2.5 if solutions are titrated using slow base injection techniques. The effects of polynuclear complexes cannot be ignored at lower $\bar{n}$ values with the formation of poorly ordered polynuclear complexes likely.

**Interpretation of Titration Pattern Characteristics**

Baes and Mesmer (1976) went into detail in the interpretation of experimental results of hydrolysis measurements. They used the gross features of a solution hydroxyl to metal ratio ($\bar{n}$) versus pH plot to identify the principle types of species present and to give their approximate composition. A titration pattern is basically a plot of this type.

For $\bar{n}$ to be found independent of the concentration of the cation undergoing hydrolysis is considered conclusive proof that only monomeric species are present. They found that
mononuclear complexes are dominant only at low $\bar{n}$ and cation concentrations. In such systems, separate curves of $\bar{n}$ versus pH for different cation concentrations should converge only at lower values for $\bar{n}$ and concentration.

If $\bar{n}$ is found to depend on concentration as well as pH, this is considered conclusive proof of the presence of polynuclear species. If the $\bar{n}$ versus pH curves show no tendency to converge to a single curve at lower concentrations and $\bar{n}$ values then polynuclear species are dominant. If the curves can be overlain by plotting $\bar{n}$ versus $\log(\text{conc.}/[H^+])$ with $t$ determined by inspection, then only one polynuclear species is present or there are multiple species present which share a single value for $t$. In this expression $t = y/(x-1)$.

If two or more polynuclear species are present, the $\bar{n}$ versus pH curves for various Al concentrations may not be superimposable. If, during hydrolysis, polynuclear species are formed initially followed by less polynuclear species of a higher n value, then the loss of polynuclear dominance is shown by a crossover of the $\bar{n}$ versus pH curves.
Materials and Methods

Solutions were mixed just prior to the titration with water freshly produced by a reverse osmosis water system to reduce effects due to CO₂ on the titration patterns of the dilute Al solutions. Solutions were mixed at ionic strengths of 1M, 0.1M, and 0.001M with respect to KCl, at 0.5, 0.05, and 0.005M ionic strength with respect to K₂SO₄ and at Al concentrations of 10⁻³, 10⁻⁴, and 10⁻⁵ M with sufficient free acid to allow for the detection of the H⁺ inflection in the Al³⁺ titration patterns. Only those solutions were mixed in which the ionic strength was high enough as to not be affected by the changes in Al speciation during the titration. All titrations were performed at 25 °C under a N₂ atmosphere.

A Radiometer autotitration system with a PHM64 research pH meter, ABU13 autoburette and a REC servograph were used to perform the titrations. This system injects base into the rapidly stirred solution. By doing so, increments of less than drop size are possible thereby lessening effects due to droplet size and the regions of of increased pH due to poor mixing of the droplets. In this system there are two controls on the rate of base addition. The first control on base addition sets a maximum rate at which the pH can rise in the solution being titrated. For all solutions in this study, this limit was set at 0.5 pH units per minute. This control is present to prevent pH from rising faster than can be followed due to pH electrode response and to prevent mixing problems. The second base addition rate control sets an absolute limit on the maximum rate of base addition.
This control is present to prevent very rapid rates of base addition during periods in which the solution is highly buffered. Due to the many possible reaction schemes which could occur in the titrated solution, titrations for selected solutions were carried out at several rates to determine whether titration speed affected the results. The speeds used were 0.03125, 0.0625, and 0.25 ml per minute maximum titration speed and 0.5 pH units per minute maximum rate of pH change.

The concentration of Al and the activity coefficient for the hydronium ion were calculated from the titration pattern (Figure 6). This method of pattern interpretation is consistent with theory and past usage (Stol et al., 1976). The base was standardized with potassium hydrogen phthalate (KHP).

Points were taken from the continuous titration patterns for computer refinement of the hydrolysis products at least every 0.10 ml with the pH extrapolated between the 0.05 pH divisions of the titration paper by measurement using a binocular microscope with a measuring lense. The concentration constants representing best fit of the observed to calculated titration patterns were determined to the closest 0.01 pQ using TIFIT, a FORTRAN computer program written expressly for this purpose by the author. In addition to refining the titration patterns as monomeric reactions, a separate version of TIFIT, TIF, which includes a 2.5 OH/Al species simulating a polymer, was used to refine the patterns.

All patterns were first refined using TIFIT, which assumes only species with n equal to 1, 2, 3, and 4. The data was rerefined to see if the precipitation of a solid results in a better fit. After this refinement, the possibility of a species with n = 2.5 was added using TIF and the data rerefrined with and without precipitation assumed.

Two more sets of titrations were performed to determine the effects of experimental parameters on the resulting titration pattern. In these titrations, a 10⁻³M Al solution was titrated at 0.03125, 0.0625, 0.125, 0.25, 0.50 and 1.00 ml per minute base addition rate. In addition, another set of titrations were conducted at 0.0625 ml per minute, with the maximum rate of pH change equal to the response time of the electrode, and at 0.4, 1.0, 2.0, 4.0 and 10.0 minutes per pH unit change. These titration patterns were not refined to give pQ values.
Figure 6. Inflection point method for determining total Al and activity coefficient for hydronium from potentiometric titration curves

\[ \chi_H = \frac{10^{-PH_i}}{[H']} \]
Another set of titrations were performed in which the effects of doping a 10⁻³ M Al solution with 50 mg of < 2 μm Al(OH)₃ (synthetic gibbsite RCHC-29 from Reynolds Aluminum) were examined. If the second plateau of a titration pattern were the result of the sudden precipitation of gibbsite as proposed by Stol et al. (1976), then the addition of gibbsite to the solution should have removed this inflection. To test this hypothesis, Al solutions were titrated before the addition of the gibbsite, immediately after the addition, and after aging periods of one hour and one day.
Results

The titrations for the Al solutions in the KCl system in general show a lessening in slope of the end of the first Al plateau with decreasing Al concentration (Figure 7). The second Al plateau is visible for the $10^{-3}$ molar Al solutions, is less visible but present for the $10^{-4}$ molar Al solutions and is not detectable for the $10^{-5}$ molar Al solutions. This finding is in agreement with the results of Stol et al. (1976).

The titrations for the Al solutions in the $\text{K}_2\text{SO}_4$ system show less extreme effects on titration slope with changes in Al concentration (Figure 8). The second Al plateau is not visible for the solutions which is in agreement with the results of Stol et al. (1976).

Interpretation of Hydrolysis-pH Relationships

The $\overline{n}$ - pH plots of the titration patterns (Figures 9-14) show conclusively that polynuclear species dominate the solution chemistry of Al during all except the very end of the $10^{-5}$ KCl titrations. This change in speciation at low Al concentrations in the KCl system is indicated by the large deviation in the $\overline{n}$ - pH relationship between the $10^{-5}$ M curves and the remaining curves.
Figure 7. Observed potentiometric titration curves for Al in KCl solutions. The Al concentration was varied between $10^{-3}$ and $10^{-5}$ M and the ionic strength was controlled by 1.0, 0.1 or 0.01 M KCl.
Figure 8. Observed potentiometric titration curves for Al in K₂SO₄ solutions. The Al concentration was varied between 10⁻³ and 10⁻⁵ M and the ionic strength was controlled by 0.16666, 0.016666 or 0.0016666M K₂SO₄ (ionic strength of 0.5, 0.05 or 0.05M, respectively).
Figure 9. A plot of the observed $\bar{n}$ - pH relationship for Al in 1M KCl solutions. The Al concentration was either $10^{-3}$, $10^{-4}$ or $10^{-5}$ M. The symbols are shown to delineate the curves and do not represent points used to generate the curves. Curves were plotted at 0.1pH unit intervals.
Figure 10. A plot of the $\bar{n}$ - pH relationship for Al in 0.1M KCl solutions as observed from titration data. The Al concentration was either $10^{-3}$, $10^{-4}$ or $10^{-5}$ M. The symbols are shown to delineate the curves and do not represent points used to generate the curves. Curves were plotted at 0.1pH unit intervals.
Figure 11. A plot of the $\bar{n}$ - pH relationship for Al in 0.01M KCl solutions as observed from titration data. The Al concentration was either $10^{-4}$ or $10^{-5}$ M. The symbols are shown to delineate the curves and do not represent points used to generate the curves. Curves were plotted at 0.1pH unit intervals.
Figure 12. A plot of the observed $\bar{n}$ bar - pH relationship for Al in 0.5 M IS K$_2$SO$_4$ solutions. The Al concentration was either $10^{-3}$, $10^{-4}$ or $10^{-5}$ M. The symbols are shown to delineate the curves and do not represent points used to generate the curves. Curves were plotted at 0.1pH unit intervals.
Figure 13. A plot of the observed $\bar{n}$-pH relationship for Al in 0.05 M K$_2$SO$_4$ solutions. The Al concentration was either $10^{-3}$, $10^{-4}$ or $10^{-5}$ M. The symbols are shown to delineate the curves and do not represent points used to generate the curves. Curves were plotted at 0.1pH unit intervals.
Figure 14. A plot of the observed $\bar{n}$ - pH relationship for Al in 0.005 M $\text{K}_2\text{SO}_4$ solutions. The Al concentration was either $10^{-4}$ or $10^{-5}$ M. The symbols are shown to delineate the curves and do not represent points used to generate the curves. Curves were plotted at 0.1pH unit intervals.
That the curves for a given ionic strength are not parallel in the polynuclear region is indicative of the presence of two or more polynuclear species. The deviation between curves even at low $\bar{n}$ indicate a polynuclear dominance of the Al solutions even at very low values for $\bar{n}$ ($< 0.10$).

**Hydrolysis in KCl Solutions**

The first refinement of the hydrolysis constants of Al was made with the assumption of only species with $n = 1, 2, 3,$ and $4$. Results of these refinements (Table 4) gave an $pQ_{12}^{\text{obs}}$ of $11.02 \pm 0.27$ if the anomalous value of $13.00$ is ignored and $11.27 \pm 0.74$ if all results are taken into account. These results are almost identical to the results of Frink and Peech (1963) but about one $pK$ unit lower than those of Nazarenko and Nevskaya (1969) whose results are more commonly cited (Table 1). The average value of $15.77 \pm 1.34$ obtained for the $pQ_{13}^{\text{obs}}$ is also in the range of values obtained by a search of the literature. The values obtained are, however, obviously dependent on the concentration of Al with the $pQ_{13}^{\text{obs}}$ values obtained by refinement rising one to two $pQ$ units as Al concentration goes down an order in magnitude.

The inclusion of the $n = 2.5$ species results in a much better fit of the calculated pattern to the observed pattern with the main difference being the decreased importance of the second hydrolysis product with $n = 2.5$ species replacing the second hydrolysis species in importance. The effects of inclusion of the new species was not as important to the third hydrolysis species as for the second hydrolysis species.

The refinements show best fit $pQ$ values which decrease with Al concentration except for the $pQ_{12}$ which increases with increasing Al (Table 5). An important consideration is to determine whether the observed concentration constants are affected by ionic strength. If the Al hydroxy complexes are not affected by ionic strength, this can be considered conclusive proof that solute Al complexes are not present. No trend for changes in ionic strength effects are observable from
Table 4. Calculated concentration constants for Al hydrolysis in KCl solutions assuming no $n=2.5$ species. The Al concentration was either $10^{-3}$, $10^{-4}$, or $10^{-5}$ M in 1M, 0.1M or 0.01M KCl except for the $10^{-3}$ M Al solution which was only prepared in the 1M and 0.1M KCl solutions.

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<tr>
<td>0.01 Molar</td>
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Results
Table 5. Calculated concentration constants along with standard deviations for Al hydrolysis in KCl solutions. The Al concentration was either $10^{-3}$, $10^{-4}$, or $10^{-5}$ M in 1M, 0.1M or 0.01M KCl except for the $10^{-3}$ M Al solution which was only prepared in the 1M and 0.1M KCl solutions.

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<th>Ionic Strength</th>
<th>Aluminum Concentration (Molar)</th>
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<td></td>
<td>$10^{-3}$</td>
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<td>$pQ_{12 , \text{obs}}$</td>
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<td>$pQ_{1.5 , \text{obs}}$</td>
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† Not a significant species in solution (less than 1% of total).
the data (Table 5). This lack of significance for ionic strength is shown statistically by the > 0.90 F-statistics observed.

Furthermore, the F-statistics for the significance of Al concentration on the observed pQ values (Table 6) is highly significant for the raw data with the level of significance becoming less with increasing polymer sizes for the calculated polynuclear pQ values. This is consistent with predicted theory except the significance of Al concentration should fall to a minimum at the true size of the polynuclear complex. This is not observed and can be considered the result of experimental error or due to the presence of multiple polynuclear species with the same n value - an explanation consistent with the metastable character of the polynuclear complexes.

Baes and Mesmer (1976) considered the minimum, in a plot of standard deviations of the calculated $pQ_{nx}$ values divided by of the number of cations in the polynuclear species, $x$, versus the number of cations in the species, $x$, to determine the the size of the polynuclear species. As the calculated values (Table 7) are determined using a more complex model, the identical statistic cannot be used on the data. If the residual sum of squares of the calculated data are divided by polymer size and plotted versus complex size to result in a statistic analogous to Baes and Mesmer (1976), unusual results are obtained (Figure 15). Rather than obtaining a consistent polymer size, no or multiple polynuclear complex sizes are obtained with the best choice for polymer size being dependent on whether and how the data was sorted. For instance, the plots of the statistic versus polymer size for the $n=2.00$ species shows an apparent polymer size of 3 for the unsorted data, 1 molar ionic strength solutions and for $10^{-4}$ molar Al solutions. The 0.01 molar solutions yields a polymer size of 1, while the 0.1 molar solution gives a polymer size of 6 and the $10^{-3}$ and $10^{-4}$ Al concentrations yield polymer sizes of 2. If this data were truly a measure of polynuclear species size then the pQ data for these solutions would not be significantly correlated to Al concentration. The data does not support this conclusion as the best result obtained by the Baes and Mesmer (1976) method often occurs at polymer sizes which result in calculated pQ values which are significantly related to Al concentration (Table 6).

The apparent decrease in pQ would be predicted by equation 19 for cases where polynuclear species dominate solution. That a decreasing $pQ_{12}$ is not observed is an indicator of nonequilibrium
Table 6. Significance level (F) for Al concentration on polynuclear complex pQ values in KCl solutions. The calculations are only valid for the $pQ_{x,2.5x}$ with even numbers of Al in the complex.

<table>
<thead>
<tr>
<th>Polymer Size</th>
<th>$pQ_{x,2x}$</th>
<th>$pQ_{x,2.5x}$</th>
<th>$pQ_{x,3x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>.0021</td>
<td></td>
<td>.0045</td>
</tr>
<tr>
<td>2</td>
<td>.0132</td>
<td>.0133</td>
<td>.0302</td>
</tr>
<tr>
<td>3</td>
<td>.0516</td>
<td></td>
<td>.0834</td>
</tr>
<tr>
<td>4</td>
<td>.1017</td>
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<td>.1366</td>
</tr>
<tr>
<td>5</td>
<td>.1412</td>
<td></td>
<td>.1791</td>
</tr>
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<td>6</td>
<td>.1668</td>
<td>.3974</td>
<td>.2111</td>
</tr>
<tr>
<td>7</td>
<td>.1823</td>
<td></td>
<td>.2353</td>
</tr>
<tr>
<td>8</td>
<td>.1913</td>
<td>.4075</td>
<td>.2358</td>
</tr>
<tr>
<td>9</td>
<td>.1966</td>
<td></td>
<td>.2682</td>
</tr>
<tr>
<td>10</td>
<td>.1997</td>
<td>.4071</td>
<td>.2798</td>
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<tr>
<td>11</td>
<td>.2013</td>
<td></td>
<td>.2891</td>
</tr>
<tr>
<td>12</td>
<td>.2021</td>
<td>.4052</td>
<td>.2968</td>
</tr>
<tr>
<td>13</td>
<td>.2024</td>
<td></td>
<td>.3032</td>
</tr>
<tr>
<td>14</td>
<td>.2023</td>
<td>.4032</td>
<td>.3087</td>
</tr>
<tr>
<td>15</td>
<td>.2021</td>
<td></td>
<td>.3134</td>
</tr>
</tbody>
</table>
Table 7. Calculated Al polynuclear complex pQ values along with standard deviations in KCl solutions. The calculations are only valid for the $pQ_{x,2.5x}$ with even numbers of Al in the complex.

<table>
<thead>
<tr>
<th>Polymer Size</th>
<th>$pQ_{1,2x}$</th>
<th>$pQ_{x,2.5x}$</th>
<th>$pQ_{x,3x}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>12.55 ± 1.59</td>
<td>23.80 ± 0.65</td>
<td>15.85 ± 1.38</td>
</tr>
<tr>
<td>2</td>
<td>19.36 ± 1.64</td>
<td>42.54 ± 1.16</td>
<td>28.47 ± 1.74</td>
</tr>
<tr>
<td>3</td>
<td>25.88 ± 1.88</td>
<td>42.54 ± 1.16</td>
<td>40.81 ± 2.23</td>
</tr>
<tr>
<td>4</td>
<td>32.27 ± 2.25</td>
<td>65.19 ± 3.39</td>
<td>53.04 ± 2.79</td>
</tr>
<tr>
<td>5</td>
<td>38.61 ± 2.69</td>
<td>60.99 ± 2.20</td>
<td>77.31 ± 4.00</td>
</tr>
<tr>
<td>6</td>
<td>44.90 ± 3.17</td>
<td>89.40 ± 4.62</td>
<td>77.31 ± 4.00</td>
</tr>
<tr>
<td>7</td>
<td>51.17 ± 3.69</td>
<td>79.33 ± 3.30</td>
<td>101.47 ± 5.25</td>
</tr>
<tr>
<td>8</td>
<td>57.42 ± 4.22</td>
<td>97.60 ± 4.42</td>
<td>113.52 ± 5.89</td>
</tr>
<tr>
<td>9</td>
<td>63.65 ± 4.76</td>
<td>97.60 ± 4.42</td>
<td>125.56 ± 6.53</td>
</tr>
<tr>
<td>10</td>
<td>69.86 ± 5.30</td>
<td>115.83 ± 5.54</td>
<td>137.59 ± 7.17</td>
</tr>
<tr>
<td>11</td>
<td>76.07 ± 5.86</td>
<td>115.83 ± 5.54</td>
<td>149.61 ± 7.81</td>
</tr>
<tr>
<td>12</td>
<td>82.27 ± 6.42</td>
<td>115.83 ± 5.54</td>
<td>161.62 ± 8.46</td>
</tr>
<tr>
<td>13</td>
<td>88.46 ± 6.98</td>
<td>134.03 ± 6.67</td>
<td>173.63 ± 9.11</td>
</tr>
<tr>
<td>14</td>
<td>94.65 ± 7.54</td>
<td>134.03 ± 6.67</td>
<td>185.64 ± 9.75</td>
</tr>
<tr>
<td>15</td>
<td>100.83 ± 8.11</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure 15. A plot of scaled standard deviations of the calculated $n=2$ polynuclear species in KCl sorted by IS and total Al. The scaled standard deviation was determined by dividing the standard deviation by the number of Al ions in the polynuclear complex. The Al concentration was varied between $10^{-3}$ and $10^{-5}$ M and the ionic strength was controlled by 1.0, 0.1 or 0.01M KCl.
in the polynuclear fraction of the solutions. If the loss of importance of the \( n = 2.00 \) species was due to a smaller number of Al ions than for the other polynuclear complexes, one would predict a lesser concentration with a decreasing \( pQ \). The observed \( pQ \) would be decreasing at a lower rate with increasing Al concentration than the other concentration constants. Two explanations can be invoked to explain the increasing \( pQ \) values, kinetics of polymerization and that the \( n = 2.00 \) species is an unstable intermediate in the formation of larger species. If reaction kinetics is assumed to be related to the degree of reaction supersaturation, then the kinetics of polymerization of a small polymer would be less affected by Al concentration than that of a larger polymer. This would result in an increase in importance of the smaller species in solutions of lower Al concentrations. Conversely, if this same small polymer was an intermediate in the formation of a larger polymer, then it would be less likely to be observed at higher Al concentrations. For these reasons, it is concluded that the polynuclear \( n = 2.00 \) species has a small number of Al ions. This species, although of no importance at intermediate and high Al concentrations, may be of importance in Al solutions at environmental levels. A true \( pQ \) cannot be given because of inadequate data, although a \( pQ \) of approximately 11.00 could be used to calculate apparent \( Al(OH)_2 \) concentrations at low Al levels. Recall from equation 17 that, in the absence of polynuclear species, the \( pQ \) value observed would be the mononuclear species constant. As no species with \( n = 2.00 \) was observed at high Al concentrations, then it can be concluded that the mononuclear species is not significant and if present at all has a \( pQ_{12} \) of much greater than 14.00.

The \( n = 2.50 \) species can only be present as a polynuclear species with an even number of Al. The observed \( pQ \) values are consistent with what would be predicted for a relatively stable, quickly formed polynuclear species. If only one polynuclear species of \( n = 2.50 \) was to be present, equation 19 would predict a linear slope for a plot of \( -\log \left( \frac{[AP^+]_n}{[H^+]_{n-y}} \right) \) versus \( pQ_{obs,x,y} \) with a slope of \( 1-x \) and an intercept of \( \log x + pQ_{x,y} \). This is not observed suggesting the presence of multiple polymers of \( n = 2.50 \).

That the \( n = 3.00 \) species is probably present as both mononuclear and polynuclear species, has been suggested earlier. The \( \overline{n} - p\text{H} \) plots suggest that the \( n = 3.00 \) species at \( 10^{-5} \) Al solutions may be mostly mononuclear. The \( pQ_{13} \) values obtained for \( 10^{-5} \) molar solutions are somewhat
higher than obtained by May et al. (1979) using gibbsite solubility data. The close agreement of
the data for the 10^{-5} M solutions suggests that the mononuclear species with n = 3.00 has a pQ_{13}
in the range of 17.4 - 17.8. Again, measures of polymer size is hampered by inconsistent results
due to the presence of multiple polymeric species.

**Hydrolysis in sulfate solutions**

Like the Al in KCl solutions, analysis of the titration curves using the Baes and Mesmer
(1976) method shows the titration characteristics of Al in K_2SO_4 solutions to be dominated by
polynuclear hydroxy complexes (Figures 12-14). Refinement of the data indicated precipitation of
basaluminate in all cases, therefore one has to approach these results with caution as the effects of
precipitation were not included in the Baes and Mesmer (1976) model. The findings of
basaluminate as a precipitant is at odds with the findings of DeHek et al. (1978) who found gibbsite
as a precipitant in their titration studies of dilute Al solutions but is in agreement with Nordstrom
(1982) who predicted basaluminate would precipitate rather than less soluble forms because of faster
precipitation kinetics. The log Q_{st} calculated for the precipitant (Table 8) are reasonably constant
(average pQ = -4.10) over a concentration range in which the precipitant is present. The
precipitant is not a dominant Al source in solution and the disagreement with the results of DeHek
et al. (1978) may be due to the instability of the precipitants in the wash solutions.

Better fits were generally obtained for the titration patterns in the sulfate system as compared
to the chloride system (Table 9). The lower calculated pQ values obtained from analysis of the
titration data is immediately apparent from a comparison of the K_2SO_4 solution results (Table 10)
with that obtained from KCl solutions (Table 5). Statistical analysis of the pQ_{st,obs} - ionic strength
data indicates that ionic strength is only important in the raw pQ_{13,obs} (or mononuclear only) data
with Al concentration effects (Table 11) similar to those obtained with KCl (Table 6). Also like
the KCl system, determination of polymer size using the methods of Baes and Mesmer (1976)
Table 8. Observed concentration constants for the solubility of basaluminite in sulfate solutions during potentiometric titrations. The Al concentration was either $10^{-3}$, $10^{-4}$, or $10^{-5}$ M in 0.16666, 0.016666 or 0.0016666 M $K_2SO_4$ except for the $10^{-3}$ M Al solution which was only prepared in the 0.16666 and 0.016666 M $K_2SO_4$ solutions.

\[
Al(OH)_{2.5}(SO_4)_{0.5\text{ppt}} + 2.5H^+ \rightarrow Al^{3+} + 2.5H_2O + 0.5SO_4^{2-}
\]

<table>
<thead>
<tr>
<th>Ionic Strength</th>
<th>Aluminum Concentration (Molar)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$10^{-3}$</td>
</tr>
<tr>
<td>0.5 Molar</td>
<td>-4.61 ± 0.01</td>
</tr>
<tr>
<td>0.05 Molar</td>
<td>-3.61 ± 0.02</td>
</tr>
<tr>
<td>0.005 Molar</td>
<td>-4.53 ± 0.02</td>
</tr>
</tbody>
</table>
Table 9. Residual sum of squares (and $r^2$) for fits of observed data to theoretical titration patterns. The Al concentration was either $10^{-3}$, $10^{-4}$, or $10^{-5}$ M in 0.16666, 0.016666 or 0.0016666 M $K_2SO_4$ for the sulfate system and 1.0, 0.10 or 0.01 M KCl for the chloride system except for the $10^{-3}$ M Al solution which was only prepared in the 0.16666 and 0.016666 M $K_2SO_4$ or in 1.0 or 0.1 M KCl solutions.

<table>
<thead>
<tr>
<th>Ionic Strength</th>
<th>$10^{-3}$</th>
<th>$10^{-4}$</th>
<th>$10^{-5}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>KCl system</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.0 Molar</td>
<td>0.05966(.9841)</td>
<td>0.06027(.9953)</td>
<td>0.01844(.9962)</td>
</tr>
<tr>
<td>0.1 Molar</td>
<td>0.03989(.9940)</td>
<td>0.01134(.9959)</td>
<td>0.02887(.9972)</td>
</tr>
<tr>
<td>0.01 Molar</td>
<td>0.05873(.9960)</td>
<td>0.00167(.9994)</td>
<td></td>
</tr>
<tr>
<td>K$_2$SO$_4$ system †</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.5 Molar</td>
<td>0.004509(.9987)</td>
<td>0.06114(.9953)</td>
<td>0.04878(.9962)</td>
</tr>
<tr>
<td>0.05 Molar</td>
<td>0.006105(.9989)</td>
<td>0.00783(.9972)</td>
<td>0.00754(.9921)</td>
</tr>
<tr>
<td>0.005 Molar</td>
<td>0.01491(.9988)</td>
<td>0.01099(.9980)</td>
<td></td>
</tr>
</tbody>
</table>

† Basaluminite is assumed to precipitate in all cases.
Table 10. Calculated concentration constants for Al hydrolysis in K₂SO₄ solutions. The Al concentration was either 10⁻³, 10⁻⁴, or 10⁻⁵ M in 0.16666, 0.016666 or 0.0016666 M K₂SO₄ except for the 10⁻³ M Al solution which was only prepared in the 0.16666 and 0.016666 M K₂SO₄ solutions.

<table>
<thead>
<tr>
<th>Ionic Strength</th>
<th>Aluminum Concentration (Molar)</th>
<th>10⁻³</th>
<th>10⁻⁴</th>
<th>10⁻⁵</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 Molar</td>
<td>pQ₁₂obs</td>
<td>11.60†</td>
<td>7.68 ± 0.13</td>
<td>6.30 ± 0.07</td>
</tr>
<tr>
<td>0.05 Molar</td>
<td>pQ₁₂obs</td>
<td>11.00†</td>
<td>8.63 ± 0.14</td>
<td>9.14 ± 0.18</td>
</tr>
<tr>
<td>0.005 Molar</td>
<td>pQ₁₂obs</td>
<td>10.21 ± 0.10</td>
<td>9.78 ± 0.03</td>
<td></td>
</tr>
<tr>
<td>0.5 Molar</td>
<td>pQ₁₃obs</td>
<td>11.60 ± 0.02</td>
<td>12.65 ± 0.03</td>
<td>11.88 ± 0.11</td>
</tr>
<tr>
<td>0.05 Molar</td>
<td>pQ₁₃obs</td>
<td>11.72 ± 0.05</td>
<td>13.22 ± 0.04</td>
<td>14.55 ± 0.20</td>
</tr>
<tr>
<td>0.005 Molar</td>
<td>pQ₁₃obs</td>
<td>15.18 ± 0.03</td>
<td>16.17 ± 0.06</td>
<td></td>
</tr>
</tbody>
</table>

† Not a significant species in solution (less than 1% of total).
yielded inconsistent results (Figure 16). These results strongly suggest that there is not significant polynuclear Al hydroxy sulfate complexation in the K₂SO₄ system. A possible explanation for the decreased pQ values could be that sulfate acts as a catalyst, promoting polymerization. One manner in which this catalysis could occur would be if there are significant mononuclear Al hydroxy sulfate complexes present which by decreasing the charge of the Al hydroxy complexes decreases ionic repulsion. The presence of these mononuclear complexes could easily be obscured from view by the increased polymerization rate.

One aspect of the sulfate system which needs examination is the effects of the strong SO₄²⁻ complexes of trivalent Al on the $\bar{n}$ - pH curves used by Baes and Mesmer (1976). To determine these effects, plots were calculated with constant pQ values but with different levels of solution sulfate (Figure 17). These plots indicate that the trivalent Al sulfate complexes provide large initial deviations between the curves calculated for the case with and without sulfate. As hydrolysis strips the solution of trivalent Al, the deviation between titration curves lessens until an $\bar{n}$ of above 2.00 where they become coincident.

Plots of the observed data show an entirely different relationship (Figures 18 and 19). Instead of becoming more coincident at higher $\bar{n}$ values, the observed titration curves show less coincidence at higher values. One would predict this type of behavior only if there were significant mononuclear or polynuclear Al hydroxy sulfate complexation. As there is only a weak statistical correlation between ionic strength and the calculated pQ values (Table 11), one may interpret these plots as suggesting mononuclear Al hydroxy sulfate complexes. These complexes would not be as significant a speciation component as the nonsulfate containing polynuclear Al hydroxy complexes and would cause an increase in statistical significance of ionic strength. In addition, by increasing the effective Al concentration and decreasing the charge of the mononuclear species, the mononuclear Al hydroxy sulfate complexes would act as the growth nuclei and promote polymerization.
Table 11. Significance level (F) for ionic strength and Al concentration on polynuclear complex pQ values in K₂SO₄ solutions.

<table>
<thead>
<tr>
<th>Polymer Size</th>
<th>Ionic Strength</th>
<th>Al Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>pQₓ₁,₂ₓ</td>
<td>pQₓ₁,₃ₓ</td>
</tr>
<tr>
<td>1</td>
<td>.6836</td>
<td>.0285</td>
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<tr>
<td>2</td>
<td>.7381</td>
<td>.7628</td>
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<tr>
<td>3</td>
<td>.8590</td>
<td>.9846</td>
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<td>.8989</td>
<td>.9091</td>
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<td>5</td>
<td>.9050</td>
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<tr>
<td>15</td>
<td>.8845</td>
<td>.6736</td>
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</tbody>
</table>
Figure 16. A plot of scaled standard deviations of the calculated $n=2$ polynuclear species sorted by IS and total Al (sulfate). The Al concentration was varied between $10^{-3}$ and $10^{-5}$ M and the ionic strength was controlled by $0.16666$, $0.016666$ or $0.0016666$ M $K_2SO_4$ (negative log ionic strength of 0, 1 or 2, respectively). The scaled standard deviation was determined by dividing the standard deviation by the number of Al ions in the polynuclear complex.
Figure 17. Theoretical effects of sulfate on titration curves assuming only the trivalent Al complexes of Behr and Wendt (1962). For the calculation, the pKs for the Al hydrolysis reactions were assumed to be $pK_{11} = 5.00$, $pK_{12} = 9.39$, $pK_{13} = 15.09$ and $pK_{14} = 23.06$ and the constants for the reactions leading to $\text{Al(SO}_4\text{)}^+$ and $\text{Al(SO}_4\text{)}_2^-$ were assumed to have pKs of 3.20 and 5.11 respectively, in agreement with Behr and Wendt (1962), with no precipitation or polymerization reactions assumed. The curves were calculated assuming no sulfate was present and that sulfate was present at concentrations of 0.001666, 0.01666 and 0.1666M with Al assumed to be at concentrations such that complexation does not affect sulfate concentration. The symbols are shown to delineate the curves and do not represent points used to generate the curves. Curves were plotted at 0.1pH unit intervals.
Figure 18. Observed effects of the presence of sulfate on the titration of 0.0001 M Al solutions. The sulfate concentration was 0.16666 or 0.016666M and the Al concentration was $10^{-4}$ M. The symbols are shown to delineate the curves and do not represent points used to generate the curves. Curves were plotted at 0.1pH unit intervals.
Figure 19. Observed effects of the presence of sulfate on the titration of 0.00001 M Al solutions. The sulfate concentration was 0.16666 or 0.016666 M and the Al concentration was $10^{-5}$ M. The symbols are shown to delineate the curves and do not represent points used to generate the curves. Curves were plotted at 0.1pH unit intervals.
Calculated Aluminum Speciation

One of the byproducts of the refinement process used in this experiment is the calculated speciation of the solutions as a function of pH, ionic strength and sulfate concentration. From these results, the effects of these parameters can be examined.

Aluminum Speciation in Chloride Solutions

The chloride system showed some interesting trends in calculated speciation as a function of ionic strength and Al concentration (Figure 20). As Al concentration and ionic strength decreased, the polynuclear fraction tends to decrease in concentration and $\bar{n}$. The fraction of the polynuclear species with $n = 3$ reaches a maximum importance at the highest ionic strength and Al concentration. The effects of ionic strength are not as marked for this fraction as that of Al concentration. As Al concentration decreases, the $n = 3$ fraction decreases from nearly one hundred percent of the solution at $10^{-3}$ M Al concentration to only a few percent for $10^{-5}$ M Al concentration. The $n = 2.5$ species is most important in the $10^{-4}$ M Al and 1 M ionic strength solution and is less important in the other solutions. Ionic strength appears to strongly affect this species in combination with Al concentration but there is a trend for the species to be present in all low Al concentration ($10^{-5}$ M) solutions with decreasing importance at higher Al concentrations. In addition, a polynuclear species with $n = 2$ appears in only the low concentration ($10^{-5}$ M Al solutions). As a result of the appearance of the $n = 2$ polynuclear species at $10^{-5}$ M Al and the increased importance of the $n = 2.5$ species combined with the decreased importance of the $n = 3$ species, the $\bar{n}$ for the polynuclear species decreases as Al concentration decreases in chloride solutions.

Results
Figure 20. Aluminum speciation in chloride solutions as a function of Al concentration and ionic strength. The Al concentration was varied between $10^{-3}$ and $10^{-5}$ M and the ionic strength was controlled by 1.0, 0.1 or 0.1M KCl. In the speciation diagrams, most curves are marked with a number representing the n value for the species which is either mononuclear (M) or polynuclear (P). Total concentration of Al$^{3+}$ and total polynuclear concentration (poly) are plotted.

Results
Aluminum Speciation in Sulfate Solutions

The sulfate anion has a significant effect on Al speciation calculated from titration results. The most obvious effect of the presence of sulfate is the appearance of a precipitant during the titration (Figure 21). This precipitant was found by the titration refinement to be best modeled by a solid with a formula equivalent to basaluminite. Another difference between the calculated Al speciation for the chloride and sulfate solutions was the lack of a species with $n = 2.5$ in the sulfate solutions. This result is somewhat surprising considering that the precipitant which best fitted titration results had an $n$ equal to that value. Another difference between the sulfate solutions and the chloride solutions was the increased importance of the $n = 2$ species in the sulfate solutions. The $n = 2$ species in sulfate solutions is still highly dependent on Al concentration as in the chloride system but rather than being present only in the $10^{-5}$ molar Al solutions, is found both in those solutions as well as those with $10^{-4}$ molar Al. This is somewhat surprising as the sulfate would be expected to be a better shielder of the charge of the polynuclear species and therefore one would predict a lesser importance of this species in the sulfate solutions. A possible explanation for this phenomena is the presence of a mononuclear Al hydroxy sulfate species with $n = 2$. The $n = 3$ species has an importance in sulfate solutions equal to its importance in chloride solutions when the Al concentration is $10^{-3}$ and $10^{-4}$ molar and increased importance at $10^{-5}$ molar Al. This difference in importance is obviously the result of the presence of the sulfate as the calculated $pQ_{13}$ is much lower than in the chloride system (Tables 5 and 10). Whether this difference is due to a mononuclear Al hydroxy sulfate complex or to increased polymerization due to ion shielding is not clear due to the lack of significance of sulfate on the calculated $pQ$ values (Table 11).
Figure 21. Aluminum speciation in sulfate solutions as a function of Al concentration and ionic strength. The Al concentration was varied between $10^{-3}$ and $10^{-5}$ M and the ionic strength was controlled by 0.16666, 0.016666 or 0.016666M K$_2$SO$_4$ (ionic strength of 0.5, 0.05 or 0.05M, respectively). In the speciation curves, the hydrolyzed species are denoted by their n value, the concentration of basaluminite assumed to precipitate is denoted by an "s", and the other species are as written.

Results
Supplementary Experiments

In addition to the titrations used to refine the pQ values, other titrations were performed to help in the interpretation of the titration parameters and to insure that the model used for the refinement of the titration patterns matched the reactions actually occurring in solution. In these experiments, the effects of titration speed parameters and doping the solutions with gibbsite were determined.

Effects of Titration Speed on Titration Characteristics

According to Smith and Hem (1972), slowing the rate of base addition should result in the formation of more polynuclear complexes, slowing the precipitation kinetics of Al(OH)$_3$ prep. Later workers, Stol et al. (1976), ascribed the formation of any precipitant at low II values to be the result of the dropwise addition of base and found using light scattering that precipitation was not significant until on the second Al plateau. With this in mind, a set of titrations were performed with a $10^{-3}$ molar solution in which the rate of base addition and the maximum rate of pH rise were varied. The maximum rate of pH change was not found to affect the titration pattern with all other factors remaining constant. Apparently, it is the rate of base addition in the highly buffered region of the titration curve which affects titration pattern characteristics and not the rate of base addition during the parts of the titration curve in which the pH is rising rapidly. This makes sense as the highly buffered portion of the titration curve is that part in which the Al reactions are most rapid.

The effects of titration speed were much more marked (Figure 22). The titration patterns at 0.03125 and 0.0625 ml per minute maximum titration speed had a much higher slope than those run at faster speeds. The titrations performed at 0.125, 0.25 and 0.50 ml per minute maximum titration speed formed a second grouping with the 0.125 and 0.25 ml per minute being almost identical with the 1.0 ml per minute speed being slightly higher. The titration performed at 0.50
ml per minute has a much lower slope than the other titrations. This pattern is believed to represent the effects of insufficient mixing speed as acid solutions were not found to be mixed fast enough to show an equilibrium titration pattern.

If we compare the characteristics of these titration patterns to the titration patterns which were refined (Figure 7), we find that the slower base addition titration patterns closely resemble those obtained at high Al concentrations (which they should as the parameters and Al concentration was identical to these solutions) while the titrations performed at higher speeds more closely resemble the results of slow titrations of solutions with lower Al concentrations. The titration patterns for solutions with lower Al concentrations were found to have a lower proportion of lower n value polynuclear material than those patterns for higher concentration Al solutions. By drawing an analogy, it can be concluded that by speeding up a titration, one causes the increase in importance of the mononuclear and lower n value polynuclear complexes at the expense of the higher n value polynuclear complexes. From these results, it is concluded that the use of titration patterns for the determination of pQ values for polynuclear complexes is erroneous as the kinetics of polymerization is of the same order of magnitude as the rate of base addition.

Effects of the Presence of Gibbsite on Titration Patterns

Stol et al. (1976) concluded from the results of combining titration experiments with light scattering that the second Al plateau observed in titration patterns of solutions with Al concentrations greater than $5 \times 10^{-5}$ M was the result of the precipitation of a noncrystalline Al(OH)$_3$ppt. If this were true, the addition of gibbsite to these solutions prior to the beginning of the titration should result in a lower first Al plateau and the absence of the second Al plateau. To test this hypothesis, 50 mg of <2 μm were added to $10^{-3}$ solutions just prior, one hour before and one day before a titration was performed. The results show that although gibbsite has large effects on the concentration of Al remaining in solution and the titratable H$^+$ (Table 14), it does not otherwise change the characteristics of the titration patterns leaving the main Al plateau and the
Figure 22. The effects of titration speed on observed titration patterns. The solution used for the titration experiment was 1M with respect to KCl and $10^{-3}$ M in Al. The numbers on the figure are the titration speeds in ml per minute.
second Al plateau unchanged (patterns identical to that for $10^{-3}$ Al at 1 molar ionic strength except for concentration). The presence of the second Al plateau in the solutions containing gibbsite casts doubt upon the interpretation of Stol et al. (1976). Also disturbing is the fact that the titratable H$^+$ does not appear to be related to the pH in these solutions. It may be that this is due to suspension effects caused by the presence of the gibbsite (approximately 10 million particles per ml). The change in apparent activity for H$^+$ as a result of the presence of solid gibbsite in the stirred solutions casts doubt upon the method used by Stol et al. (1976) and here for the determining the activity coefficient of H$^+$ in solutions containing solids.
Table 12. Effects of time on pH, titratable Al and Al adsorbed from a 0.001 molar Al solution with added gibbsite. The adsorbed and residual Al values represent that Al which was adsorbed and not adsorbed after the time indicated.

<table>
<thead>
<tr>
<th>Time</th>
<th>pH</th>
<th>H⁺</th>
<th>Adsorbed</th>
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<tr>
<td>0 added</td>
<td>4.03</td>
<td>5.71 × 10⁻⁵</td>
<td>0.00</td>
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<tr>
<td>0.0 min.</td>
<td>4.14</td>
<td>3.81 × 10⁻⁵</td>
<td>1.46 × 10⁻⁴</td>
<td>7.93 × 10⁻⁴</td>
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<tr>
<td>1 hr.</td>
<td>4.23</td>
<td>0.00</td>
<td>1.46 × 10⁻⁴</td>
<td>7.93 × 10⁻⁴</td>
</tr>
<tr>
<td>1 day</td>
<td>4.11</td>
<td>5.71 × 10⁻⁵</td>
<td>2.92 × 10⁻⁴</td>
<td>6.47 × 10⁻⁴</td>
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</tbody>
</table>
Discussion

Reliability of the Fitted Data

Chance of error in this type of analysis for the fitted results cannot be overlooked. Baes and Mesmer (1976) gave four circumstances which could conceivably result in erroneous results. These circumstances were: poor initial values for one or more formation quotients; inclusion of unneeded species; covariance; and false minimums.

The use of poor initial values would probably not be a significant source of error in the results of this study. The initial values were chosen to surround the established pK values. If the fitted values are far removed from the established values, it is because the refinement reached these values by following the minimum through successive refinements.

The inclusion of unneeded species is demonstrated to not be a problem by examination of the data itself. The n = 2.00 species for most of the KCl system and the n = 2.50 species in the K₂SO₄ were shown to be of negligible importance through the refinement of the data.

Covariance of the data would not have been a problem in the refinement of the titration data, but could definitely have been a problem in the refinement for polymer size and pK especially for the K₂SO₄ system. It is highly possible that ionic strength and Al concentration may both have
significant effects on the fitted pK values such that the statistical correlation of the fitted data to either ionic strength or Al concentration alone may be insignificant while in truth the parameters were highly correlated with the correlation hidden by an interaction with another parameter. An example of such a situation would be if the size of the polymer was correlated to Al concentration. Such a correlation would render the determination of polymer size and pK impossible. Overcoming covariance would require much more data than is available from this study.

Overcoming the effects of false minimums is more difficult than might be expected on first observation. Basically, a false minimum is a fortuitous set of data parameters which result in a residual sum of squares which is lower than the data around it but higher than the true best data fit. To illustrate the effects on the type of refinement, let us consider a two dimensional plane represented by the equation

\[ z = |25 - xy| \]  \[ \text{[48]} \]

where \( z \) can be thought of as the residual in a refinement (Figure 23). There will be only one value in the region where \( x \) and \( y \) are less than nine where this residual is equal to zero, that is where \( x \) and \( y \) equal five. This would be the best answer. On the other hand we cannot assume that there will be a perfect answer and so may stop with a less perfect answer such as a residual equal to one. This result occurs at (3,8), (4,6), (6,4), and (8,3). We would arrive upon the correct answer if we happen upon the (4,6) and (6,4) points as they are adjacent on a diagonal to the correct answer. Such is not the case for the (3,8) and (8,3) minima since these points are entirely surrounded by points with higher residuals and therefore would be easily mistaken for a true minima. These two points would be examples of false minima. The number of false minima increases greatly with more unknowns as in the refinement of hydrolysis data. This problem occurs in all refinements of hydrolysis data, not just the present work. At least the possibility of all mononuclear hydrolysis products with or without precipitants was included, thus errors would occur only in the data refinement. All titration patterns were also refined multiple times with many starting points in an effort to reduce the possibility of false minima.
|xy - 25| = z

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Figure 23. Residuals (z) calculated from the relation |xy - 25| = z as an example of false minima.
Another possible source of error, which may be somewhat unique to the method of data refinement would be the possibility of finding a less than correct answer due to choosing the size of increments for the pK values. It was noted during data refinement that the best result determined when refinement to the tenths in pK units was not similar to that found when the data was further refined to the hundredths of a pK unit. It may be that this difference may continue further and an answer to the thousandths of a pK unit would be equally removed. The only way in which it may be possible to get around this problem and that of the false minimas would be to use a different manner of refinement. Statistical methods would be equally prone to the finding of false minima but a matrix solving method may result in a more correct answer.

Another potential source of errors in the data refinement would arise from systematic errors in the measurement of pH. With titration data, there would be no effect on the \( \bar{\nu}_{\text{obs}} \) but there would be an effect on the \( \bar{\nu}_{\text{calc}} \). The effects due to this source of error were removed as much as possible by use of measured rather than calculated hydronium activity coefficients. In addition, the pH electrodes used in this study were so stable as to show only very small pH deviations (< 0.01 pH) between days according to the buffers used in standardization. This leads to the conclusion that any pH measurement errors were negligible. On the other hand, the results of the experiment determining the effects of addition of gibbsite show that the method used to determine the activity coefficient for \( H^+ \), \( \gamma_{H^+} \), may not be correct when solutions contain solids.

One of the assumptions used in the data refinement is that the concentration constants for the polynuclear species may be simulated by the use of an equivalent n value mononuclear species. This can also be a considerable source of error. For instance, assume for the comparison that the only hydrolysis species forming in an Al solution are the mononuclear AlOH species or its polynuclear n value equivalent, \( Al_n(OH)_2 \) with pQ values of 5.00 and 10.30, respectively. Both these species would represent half of all the Al at pH 5.00 but their proportion of the Al species would not be equivalent at other pH values (Figure 24). This difference may cause an error in the polynuclear pQ determined and might result in an error in the determination of the other pQ values in solution.

Discussion
Figure 24. Difference between the calculated speciation when the $n = 1$ species is mononuclear and polynuclear. For purposes of calculation, the only hydrolyzing species are $\text{AlO}^2+$ and $\text{Al}_2(\text{OH})_2^+$ which are assumed to have pK values (5.0 and 10.3, respectively) such that both would lead to 50% complexation at a pH of 5.00.
The potential errors involved with the data analysis in this study are, however, less than those in many studies of Al hydrolysis. The model used in this study was more complex than in many studies in that it allowed for the presence or absence of many possible species. Many of the early studies of hydrolysis had very simple models which had large potentials for error. The most common assumption in these early studies was the presence of only one or two species. If we recall equation 44 from the literature review on the dilution method:

\[
[H^+] = \Sigma_{xy} [Al_{x}(OH)_{xy}]
\]

it is immediately obvious that the species present in solution must be known to interpret the results. Often, however, solution speciation was assumed to consist of only one or at most two species. This can lead to large errors. For instance if this equation is solved using the presently assumed pK values, one finds that the results of Schofield and Taylor (1954) cannot be obtained because the effects of the accepted second and third pK values are so large that even if the highest values for the second and third pKs are chosen, the first pK must be increased to much higher values before pH values are calculated which are in the range of those obtained from experiments. As the presently accepted values were determined in a similar manner, their accuracy must not be overestimated.

Some Hypotheses on Aluminum Solution Chemistry

The results of these experiments have shown that polymerization is occurring during titrations at a rate comparable to the rate of base addition during the titration. The effects of speed on the solution speciation during a titration is shown to be comparable to the effects of lowering Al concentration. The effects of base addition rate changes point to the rate of collisions between Al particles as being the rate controlling factor in the formation of polynuclear Al hydroxy-complexes. The second and third mononuclear hydrolyzed species have been shown to
have pK values which are much lower than commonly assumed with the second mononuclear hydrolysis species being unimportant if present at all. The lowest probable pK for the the third mononuclear hydrolysis reaction is at least one pK unit higher than any value recorded in the literature. When these results are combined with the results presented in the literature certain conclusions may be drawn about the nature of hydrolysis in dilute Al solutions.

**Mononuclear Aluminum Hydrolysis**

The accepted view of hydrolysis involves an Al$^{3+}$ cation which is surrounded by 6H$_2$O with each of three waters losing a proton as the pH rises. The bond strength to each of the initial H$_2$O groups is one half with a partial one half charge present on each water. When each of the three waters loses a proton and becomes a hydroxyl, the bondlength on that water losing the proton decreases due to the increase in bond strength from one half to one with the bondlength of the waters decreasing due to the loss charge coming from the Al which was shifted to the hydroxyl. This loss of charge makes the partial charge on the waters go from 0.5 to 0.4 with the first hydrolysis reaction, to 0.25 with the second hydrolysis reaction and to zero with the third hydrolysis reaction.

This reaction scheme assumes that each water and hydroxyl coordinated to the Al tends to a partial charge of zero whenever possible. This may not be the case as a certain amount of bondstrength must be allocated to the waters or they would not be coordinated to the Al and would be transient on the surface. Rather, there would be some bondlength (bondstrength) which would be a maximum at which the Al – H$_2$O bond is stable. There are various ways to estimate the maximum bondlength in this situation. Donnay and Allmann (1970) gave a maximum bondlength for Al bonds which could be considered a bond as 0.226 nm. This corresponds to a bondstrength of 0.24 according to the bondstrength equations of Brown and Shannon (1973). The radius ratio could also be applied by the determination of the maximum and minimum bondlengths which would allow for octahedral coordination. Assuming a 0.13 nm constant size for the oxygen, a bondlength range of 0.187 to 0.230 nm is obtained for the range of bondlengths consistent with
octahedral geometry. The upper bondlength limit is very close to the Donnay and Allmann (1970) result and corresponds to a bondstrength of 0.22 bondstrength units. The lower bondlength limit corresponds to a bondstrength of 0.54 units. It must be considered, however, that these limits are general and assume equal bondlengths for all bonds and that a shorter (or longer) bondlength may be stable in an octahedral geometry if the bond on the other side of the cation has a bondlength which is longer (or shorter) to keep the average between the two bondlengths within this range. The distance at which a bondstrength of zero units can be determined from data such as that contained in Gibbs and Boisen (1986). From their data, a zero bondstrength bond would be about 0.33 nm long. This is much larger than that which is allowed by octahedral coordination. Therefore, to keep the octahedral character of the mononuclear hydroxy complexes some type of bond rearrangement would be required to keep the structure stable.

In order to determine the bondlength of an octahedral Al – H₂O bond, G. V. Gibbs (personal communication, 1987) used a molecular orbital computer program, Gaussian 82, to determine the structure of the Al(OH)₃(H₂O)₃. He assumed an octahedral Al with a 3-21G* bonding basis with six d-type polarization functions on the Al. It was expected that most of the valence of the Al would be used to neutralize the hydroxyl groups simultaneously neutralizing the bound waters as this would have resulted in a neutral structure. Instead, a shorter bondlength of 0.198 nm was found for the Al – H₂O which corresponds to a partial charge on the water of 0.43. The Al-OH bondlength was found to be 0.180 nm leaving a partial charge of -0.35 on the hydroxyls (note: the equations used to calculate the bondstrengths do not necessarily add up to the ideal valence). This geometry is well within that required for octahedral coordination. If we consider the 0.230 nm bondlength to be the maximum bondlength of an octahedral Al complex, then the first Al mononuclear complex is structurally stable and the second mononuclear species is on the stability borderline with bondlengths barely within that allowed while keeping an octahedral geometry. That the charge transfer required for minimum average partial charge on the six oxygens may not be possible due to structural considerations would result in an increase in the free energy of the complexes making their presence less likely. This conclusion is in agreement with the results of this study and those of the earlier researchers, such as Hayden and Rubin (1976), who concluded that
the second and third solution hydrolysis species do not exist. The structural considerations also explain the tetrahedral geometry of the Al(OH)₄ mononuclear species as the tetrahedral geometry removes the requirement for two Al – H₂O bonds with longer bondlengths than octahedral geometry allows leaving a structure with bondlengths well within those required for tetrahedral geometry. If the second and third mononuclear hydrolysis species do exist, the charge rearrangements possible for the first hydrolysis species are not possible for structural reasons and so their pK values would reflect this instability by being larger than would be calculated by the interpolation between the stable first and fourth species as was done by Baes and Mesmer (1976).

Polynuclear Aluminum Hydrolysis

The bondlength requirements for the formation of polynuclear complexes are not as important as those for the mononuclear complexes. In the polynuclear complexes, the geometry of Al cations without charge saturation is constrained by structural considerations inherited from the internal portions of the structure. This results from the fact that polynuclear species are not equilibrium species but are instead the unstable growth nuclei for precipitants which are in a state of supersaturation. For that reason, it is convenient to consider the structure of polynuclear species to be finite structures related to much more infinite crystalline solids (Hem and Roberson, 1967). As precipitants have solubilities which are related to their size due to the excess surface free energy, the concepts of solubility or complexation constants would not be applicable to the description of their solution chemistry (Hem and Roberson, 1967; Baes and Mesmer, 1976). At the same time, however, careful study of the crystalline structures which are supersaturated with respect to solution should give clues as to the structure of the polynuclear complexes.

The most likely solids which may be used to model the structures of Al polynuclear complexes are the various Al(OH)₃ and AlOOH polymorphs and possibly some Al hydroxy salts. Each would result in their own polynuclear complexes if supersaturated and therefore, the possibility
exists for several types of polynuclear structures to be coexisting in solution at any given pH and Al concentration.

A hint as to the polynuclear structures which may be present in dilute Al solutions may be found in the identity of the precipitants which have been found to occur in Al solutions. Most Al hydrolysis studies have recorded the precipitation of gibbsite (or some other Al(OH)$_3$ polymorph) during the course of their hydrolysis studies (Frink and Peech, 1963; Turner and Ross, 1970; Smith and Hem, 1972; Hayden and Rubin, 1976; and Stol et al., 1976) if aged at low values for $\bar{n}$ and boehmite for high $\bar{n}$ in systems with Cl as the anion. Results for systems high in sulfate or phosphate show the precipitation of some Al salt which may or may not be hydrolyzed (Brosset, 1954; Hem and Roberson, 1967; Hayden and Rubin, 1976; Lo et al., 1982).

The observed precipitation of gibbsite predicts polynuclear structures which are in agreement with the linear single chain and ring structures commonly proposed as representative of polynuclear complexes (Figure 25). The ringlike structure for the complexes is highly conducive to fast growth as three planar growth directions are found in the structure (Figure 26). These polynuclear structures, although often proposed, do not agree with the most often proposed polynuclear complex formulae obtained from hydrolysis data. Most proposed Al polynuclear complexes are chosen with as low a number of Al atoms as possible for curve fitting reasons and an $n$ value of 2.50. The linear chain cannot be proposed as a structure base as the maximum $n$ value for a linear single chain species is 2.00. The gibbsite-like ring structures can potentially reach an $n$ of 3.00 without requiring one coordinated hydroxyls but requires 24 Al cations to reach an $n$ of 2.50 (Figure 27).

One possible method of obtaining $n$ values for polynuclear complexes consistent with the results of hydrolysis studies which has been overlooked is the possibility of polynuclear structures with a linear double chain consistent with the structures of the AlOOH polymorphs (Figure 25). These chains are joined together such that all oxygens with three coordination in the structure of diasporic and in a manner which leaves half of the oxygens two coordinated and half with three coordination in the structure of boehmite (Figure 28). These chains differ from the linear single chain and the ring based structures by the presence of three coordinated oxygens in rows in the central plane of the chain and rows of two and one coordinated oxygens along the chain edges.
Figure 25. Possible polynuclear complex structures. The linear single chain and ring polynuclear models are derived from the structure of Al(OH)$_3$ while the linear double chain polynuclear model is derived from the structure of the AlOOH polymorphs. Only the tops of the octahedra are shown in this representation.
Figure 26. Growth chain directions in gibbsite-like polynuclear complex structures. The three growth directions are highlighted. In this representation, the Al cations are at the line segment intersections while the double OH bonds are the line segments.
Figure 27. Growth of gibbsite-like polynuclear complex structures. The basic polynuclear ring structure is shown at selected n values to show the large amount of polymerization required to reach high n values. In this representation, the Al cations are at the line segment intersections while the double O\(\text{II}\) bonds are the line segments.
Figure 28. Diagrammatic structure of diasporé (top) and boehmite (bottom) looking along the chains. Shown are the octahedra, shaded for ease in viewing.
Figure 29. Growth of linear double chains and ring structures from linear single chain structures. The linear single chain and ring polynuclear models are derived from the structure of Al(OH)$_3$ while the linear double chain polynuclear model is derived from the structure of the AlOOH polymorphs. Only the tops of the octahedra are shown in this representation.
rather than the two coordinated rows along the central plane with one coordinated edge sites. To obtain a neutral internal structure, the excess charge of the three coordinated sites can be used to neutralize the one coordinated sites. This results in a general formula for the polynuclear structure of \((\text{Al(OH)}_2)_n(\text{Al(OH)}_2)_3^+\). This structure reaches high \(n\) values with a much lower number of Al cations in agreement with the literature polynuclear hydrolysis constants. An \(n\) value of 2.50 requires only 4 Al rather than the 24 required for the same \(n\) value with a ring structure. As the energy requirement for the formation of the three coordinated oxygens would be higher than that required for the formation of two coordinated oxygens, one can predict a higher pH for the onset of this polymerization scheme than would be required for the formation of linear single chain and ring type polynuclear structures. This is in agreement with the observed presence of AlOOH precipitants only at high pH values. A complete dissolution of the preexisting linear single chain based structures may not be required for the formation of the linear double chain type structures. Instead, an Al may move into the linear single chain structure and form the double chain structure (Figure 29). This manner of growth allows for much faster growth in the initial stages of polymerization.

Precipitation

The results of the supplementary experiments showed that the observed second Al plateau observed in titrations of Al with concentrations above \(5 \times 10^{-5}\) M was not due to the onset of precipitation as stated by Stol et al. (1976). For that reason, other possibilities must be explored to explain the second plateau. One possibility which may explain the sudden change in kinetics of Al precipitation at pH values in the 6 to 7 range is a change of some of the one coordinated edge H\(_2\)O sites into hydroxyls. White and Zelazny (1987a,b) proposed changes in the edge sites for Al and Fe containing minerals in this pH range. In their model, the edge sites lose protons in response to pH changes. As a result of this process, the edge of the mineral changes from a net positive to a net negative charge. If such a process occurs for a mineral in a dilute Al solution, the rate of
precipitation would immediately increase. This is a result of a change in the charge on the surface which had previously been the same charge as the polynuclear species and therefore repelling growth nuclei would then be oppositely charged relative to the polynuclear species causing an increase in growth rate. In cases in which no precipitant had been present previously such as in the experiments of Stol et al. (1976), the sudden increase in the kinetics of precipitation would be interpreted as the onset of precipitation where in truth it is simply an increase in precipitation rate.

Some Ideas On Al$_{13}$O$_4$(OH)$_{24}$

A polynuclear structure which is often proposed in the literature (Mesmer and Baes, 1974; Baes and Mesmer, 1976 for instance) is the Al$_{13}$O$_4$(OH)$_{24}^+$ molecule. The structure for this molecule is derived from a synthetic sulfate mineral and contains both octahedral and tetrahedral Al. A structural problem arises in that three octahedral and one tetrahedral Al ions are bonded to a single oxygen. This causes an apparent charge of the oxygen of 2.50. This charge tends to point to an error with the structure. NMR data such as obtained by P. Bertsch et al. (1986) support the existence of a molecule with both tetrahedral and octahedral Al but does not prove the existence of that particular complex or even that only one complex is present. The only manner in which such structures can be balanced at the atomic level is to increase the bondlength of the octahedral Al bonds going to the four coordinated oxygen thereby obtaining local neutralization of the charge by decreasing the bondstrength from the octahedral Al to the oxygen. The one sixth charge removed from each bond would then be moved to a one coordinated site along the edge resulting in a two thirds bondstrength for the bonds. This higher bondstrength is greater than is obtained for the Al-OH bond in the Al(OH)$_3$(H$_2$O)$_3^+$ molecule modeled by Gibbs (personal communication, 1987). In addition, the mineral from which this molecule is derived is very uncommon and definitely would not be a possible precipitant from a chloride or perchlorate solution such as is used in most Al studies (including that of Bersch et al., 1976). For these reasons, the proposed structure of the Al$_{13}$O$_4$(OH)$_{24}$ mixed octahedral-tetrahedral polynuclear Al complex to be unlikely and the observed
band for tetrahedral Al in a complex is the result of the formation of an unstable complex whose structure contains both octahedral and tetrahedral Al and whose breakdown kinetics is slowed by the decrease in charge for the edge sites required by the charge rearrangement required due to the presence of the tetrahedral Al in the system.

Effects of Sulfate

In general, a better fit was obtained for the titrations of sulfate containing Al solutions (Table 9). In addition, lower pQ values were observed for this system. The better fit for the curves may be due to the much faster kinetics of precipitation for the sulfate mineral. Another possibility for the better fit may be that the sulfate solutions may have been better modeled by the mononuclear hydrolysis model used in the computations because of the presence of significant Al hydroxy sulfate complexation. Separation of mononuclear Al hydroxy sulfate complexation from polynuclear Al complexation cannot be determined from the results but the tendency for lower pQ values point to this conclusion. This is especially true as sulfate would bind tighter to the edges of the polynuclear complexes shielding their charge increasing the kinetics of polymerization. On the other hand, solution species with an n = 2.00 were found for higher Al concentrations in the sulfate system than in the chloride system. For that reason, I conclude that mononuclear Al hydroxy sulfate complexes are present in solution and agree with Nishide and Tsuchiya (1965) who set a preliminary limit for the presence of AlOHSO₄ / AlOH as not higher than Al³⁺/ AlSO₄ .
Summary and Conclusions

Mathematical analysis of titration data is shown to result in information unavailable from other sources. The results from such modeling can show the effects of concentration, kinetic and speed factors in a manner more mechanistic than from kinetic plots alone. In addition, the results can give constraints on the values usable for the lower limits on the second and third pK values and give the researcher a better feeling for what is taking place in solution.

Titration curves are shown to be a feasible method for use in the refinement of the second and third hydrolysis products of Al. Problems arise from the large degree of polynuclear character of Al solutions even at Al concentrations as low as $10^{-5}$ molar. The $n$ value and size of the polynuclear complexes are affected by Al concentration. In $10^{-5}$ molar solutions, polynuclear Al complexes with $n = 2.00$ and $n = 2.50$ dominate solutions with the mononuclear Al(OH)$_3$ species. The lower limit for the concentration constant, $pQ_{13}$, is found to be 17.4-17.7 according to these results. This mononuclear species and the $n = 2.00$ species decreases in importance with increasing Al concentration being replaced by a polynuclear species with $n$ approaching 3.00. The increase in the calculated $pQ_{12\, \text{obs}}$ is indicative of a species which is either an unstable intermediate in the formation of other higher $n$ value polynuclear species or due to a smaller size is kinetically slower forming than the higher $n$ value species at higher Al concentrations. Assuming that the lowest concentration for the $n = 2.00$ species would correspond to a solution with only mononuclear spe-
cies, it must be concluded that the mononuclear Al(OH)\textsuperscript{2+} species either does not exist or has a pK at least as high as 14.00 and therefore is never a significant species in solution. Statistics of the KCl data showed there to be no significant effect due to ionic strength. For that reason, the KCl data was chosen to determine the pK values as any Cl complexes should have caused some significance for ionic strength in the analysis. Use of statistical analysis of the data along with the graphical method of Baes and Mesmer (1976) did not result in consistent data for polymer size determination. The most likely polymer size by the Baes and Mesmer (1976) method corresponded to a size in which Al concentration had statistically significant effects on the calculated pQ for the polynuclear complex. Theoretically, the most likely polymer size should have pQ values with the least statistical correlation to Al concentration. This difference is probably the result of a mixture of polynuclear complexes with many different polymer sizes but with only one n value.

The sulfate containing solutions were also dominated by polynuclear complexes and were affected by the precipitation of a solid with a chemical formula close to that of basaluminite. In general, the pQ values determined from refinement of Al titration data from K\textsubscript{2}SO\textsubscript{4} solutions are one to three pQ units lower than those obtained from equivalent KCl solutions. A low level of statistical significance for ionic strength points to a catalytic rather than complexometric explanation for the increased polymerization present in the system. A mechanism involving the presence of mononuclear Al hydroxy sulfate complexes is used to explain this observation. In this model, the increased hydrolyzed concentration and lower ionic charge resulting from these complexes would increase the rate of polymerization in these systems. A general equation

\[ x\text{Al(OH)}_y(\text{SO}_4)_{2y-z}^z \rightarrow \text{Al}_{x,(\text{OH})_{xy-y}^x} + x\text{SO}_4^2- \]  \hspace{1cm} [49]

is proposed to describe the reactions involved. Graphical techniques lend credence to the proposed mechanism by showing that the observed titration curves have a deviation from theoretical calculations assuming no mononuclear Al hydroxy sulfate complexation that would be consistent with the presence of mononuclear Al hydroxy sulfate complexes. These conclusions are also supported by the better residual sum of squares obtained for the titration refinements as the better fit suggests a higher percentage of the solution species have integer n values which is unlikely without the

{Summary and Conclusions}
presence of mononuclear hydroxy sulfate complex species. These complexes may explain the higher (but still low) significance of ionic strength when compared to the chloride system.

The sources of possible errors in the results were examined and found, with the possible exception of false minima in data refinement, to be of reasonable reliability. Errors due to experimental technique were found to be very small and probably not significant. The results show that it is possible to determine to a reasonable accuracy the monomeric hydrolysis products of Al using titration pattern analysis. The determination of polynuclear complexation may not be possible due to kinetic factors involved in the growth of the polynuclear complexes, a possible dependence of polymer size on Al concentration, and the likely coexistence of many polynuclear complexes of equivalent hydroxide to Al ratio (n).

The lower pQ values for mononuclear Al hydrolysis are explained by the structural instability of the mononuclear complexes. The bond strengths required for the bonds in the second and third hydrolysis complexes are often larger than is allowed for octahedral coordination. For that reason, the pQ values would be lower than calculated by extrapolation between the stable first and fourth hydrolysis constants.

A new polynuclear complexation mechanism for Al is proposed to account for the high concentration of high n value polynuclear species in the titration refinements. The proposed linear double chain structure is consistent with the structure of boehmite and diaspore. The chains in this structure differ from the linear single chain and ring based polynuclear structures by the presence of rows of three coordinated oxygens in the bond central chain and rows of two and one coordinated oxygens along the plane edges. A rearrangement of internal charge in this structure is proposed in which part of the charge is removed from the three coordinated oxygens to result in an uncharged hydroxyl with the charge shifted to the one coordinated site neutralizing the hydroxyl. This results in a general formula for the polynuclear structure of \((\text{Al(OH)}_3)_n(\text{Al(OH)}_2)_j)^+\). This structure results in a higher n value for a lower number of Al than does the other polynuclear complexation schemes and therefore explains the presence of high n value polymers in unaged Al solutions which would have required polymers of greater than a hundred Al cations.

Summary and Conclusions
The results of the supplementary experiments showed that the observed presence of a second Al plateau on titration patterns with Al concentrations greater than $5 \times 10^{-5}$ M could not be the result of the onset of precipitation as proposed by Stol et al. (1976). Instead, it is proposed that at a pH in the 6 to 7 range, a change of some of the one coordinated sites on the edge of the larger polynuclear and precipitant structures from water to hydroxyls results in a change in net edge charge from net positive to net negative which causes an increased rate of crystal growth due to the unlike charge between the edges and the smaller polynuclear and mononuclear complexes.

Sulfate likewise increases the rate of precipitation by combining with the polynuclear and mononuclear complexes to form Al hydroxy sulfate complexes. Evidence for the presence of mononuclear hydroxy complexes comes from the better fit for the titration patterns in sulfate systems which would not have been observed for increased polymerization alone. The limits for the complexation constants for the Al hydroxy sulfate complexes is set equal to that for nonhydrolyzed Al sulfate species.


References
Appendix A. FORTRAN PROGRAMS

In this appendix, the FORTRAN programs used in the interpretation of the data are presented.

The TIFIT Family of Programs

TIFIT

The first of this family of programs presented is the original TIFIT. This program is based on equation 13 which assumes hydrolysis species with n = 1, 2, 3, and 4 (no n = 2.5 species present). This basic form of TIFIT allows for the formation of the solids, Al(OH)$_3$$_{sol}$, jurbanite, alunite, and basaluminite.
### Input Data

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### Output

Output includes input parameters and residuals calculated by subtracting calculated from observed ML titrated. The calculated residuals sum of squares can be used to compare the goodness of fit for different data sets. The print option is used to reduce the size of the output file when large numbers of iterations are used. The precip status on the output of the calculated residuals is compared to the individual patterns if negative or all **** means that the precipitation reaction is not occurring while a positive quantity means that precipitation reactions are occurring.

### FORTRAN Programs

```fortran
REAL OHC, GAMMAH, ALT, PKS0, PK11, PK12, PK13, PK14, ZKSO, ZK11, $ZK12, ZK13, ZK14, INC, MLT, PPH, ML, PH, AH, AIH, H, IH, ST, IST, $SDEN, SNUM, SDNUM, RESID, RSDSQ, MLCALC, RSUM, PST, PRT $SDO4, K, ZKSO4, CKSO, RLOW INTEGER OPTION, NUMV, POPT CHARACTER*72 TITLE
C SETS UP PH, ML ARRAY
DIMENSION PH(100), ML(100)
READ (5,1000) TITLE
READ (5,2000) OHC, GAMMAH, ALT
```

Appendix A. FORTRAN PROGRAMS
READ (5,3000) PKSO, PK11, PK12, PK13, PK14
READ (5,4000) ZKSO, ZK11, ZK12, ZK13, ZK14
READ (5,5000) INC, OPTION, MLT, PPH, POPT, PRT
READ (5,8000) SQ4, K

C READS IN TITRATION CURVE FOR FURTHER USE
C
DO 25 I=1,100
25 READ (5,6000,ED=30) PH(I), ML(I)
30 NUMV= I-1
RLCM = 10.0

C WRITES FIRST PAGE OF OUTPUT
C
WRITE (6,1001) TITLE
WRITE (6,2001) OHC, GAMMAH, ALT
WRITE (6,2002) SQ4, K
WRITE (6,3001) PKSO, PK11, PK12, PK13, PK14
WRITE (6,4001) ZKSO, ZK11, ZK12, ZK13, ZK14
IF (OPTION.EQ.0) WRITE (6,5001)
IF (OPTION.EQ.1) WRITE (6,5002)
IF (OPTION.EQ.2) WRITE (6,5004)
IF (OPTION.EQ.3) WRITE (6,5005)
IF (OPTION.EQ.4) WRITE (6,5006)
IF (OPTION.GE.5) THEN
WRITE (6,9001) TIT01080
WRITE (6,9002) TIT01090
WRITE (6,9003) TIT01100
WRITE (6,9004) TIT01110
WRITE (6,9005) TIT01120
WRITE (6,9006) TIT01130
WRITE (6,9007) TIT01140
GO TO 10
ELSE
END IF
IF (POPT.EQ.1) WRITE (6,7001)
IF (POPT.EQ.2) WRITE (6,7001)
IF (POPT.GT.2) THEN
WRITE (6,9008) TIT01200
WRITE (6,9009) TIT01210
WRITE (6,9010) TIT01220
WRITE (6,9011) TIT01230
WRITE (6,9012) TIT01240
GO TO 10
ELSE
END IF
C CHANGES INITIAL PH TO INITIAL HYDROGEN ION CONCENTRATION
C
AIH= 10.**(-PPH)
IH= AIH/GAMMAH
C ENTERS INITIAL PK VALUES
C
AKSO= PKSO
AK11= PK11
AK12= PK12
AK13= PK13
AK14= PK14
100 CONTINUE
C CHANGES PK VALUES TO K VALUES AND STARTS THE CALCULATION OF
C THE ML CALC. FOR THE POINTS ON THE TITRATION CURVE
C
BKSO= 10.**(-AKSO)
BK11= 10.**(-AK11)
8K12 = 10.**(-AK12) TIT01490
BK13 = 10.**(-AK13) TIT01500
BK14 = 10.**(-AK14) TIT01510

C CALCULATES SOLUTION STATUS AT THE INITIAL PH ALWAYS ASSUMING TIT01520
C MONOMERIC HYDROLYSIS WITH NO PRECIPITATION. TIT01530

INUN = BK11/IH + 2.*BK12/(IH**2) + 3.*BK13/(IH**3) + 4.*BK14/(IH**4) TIT01540
IDEN = 1. + BK11/IH + BK12/(IH**2) + BK13/(IH**3) + BK14/(IH**4) + TIT01550
9 (10.**3.2)*SO4 + (10.**5.1)*SO4**2) TIT01560
IST = ALT*INUN/IDEN TIT01570

C WRITES THE READOUT FOR AN INDIVIDUAL TITRATION PATTERN TIT01580
C
IF (POPT.EQ.0) HRITE (6,1001) TITLE TIT01590
IF (POPT.EQ.0) HRITE (6,2001) OHC, GAMMAH, ALT TIT01600
IF (POPT.EQ.0) HRITE (6,2002) SO4, K TIT01610
IF (POPT.EQ.0) HRITE (6,2003) AKSO, AK11, AK12, AK13, AK14 TIT01620
IF (POPT.EQ.0) HRITE (6,3001) TIT01630
IF (POPT.EQ.0) HRITE (6,3002) TIT01640
IF (POPT.EQ.0) HRITE (6,3003) TIT01650
IF (POPT.EQ.0) HRITE (6,3004) TIT01660
ELSE TIT01670
ENDIF TIT01680

C ' TIT01690
C SETS RESIDUAL SUM OF SQUARES TO ZERO TIT01700

RSUN = 0.0 TIT01710

C CALCULATES THE NL CALC FOR EACH POINT ON A TITRATION PATTERN TIT01720
C
DO 50 I=1,NUNV TIT01730
AH = 10.**(-PH(I)) TIT01740
H = AH/GAMMAH TIT01750

C DETERNINES THE PRECIPITATION STATUS OF THE SOLUTION IF TIT01760
C THE OPTION REOUIRES THEN USES THE APPROPRIATE TIT01770
C EQUATIION TO DETERNINE THE SOLUTION STATUS TIT01780
C
IF (POPT.EQ.1) THEN TIT01790
PST = ALT - (1.+ (10.**3.2)*504 + (10.**5.1)*(SO4**2))*BKSO*(H**3)· TIT01800
9 BKSO*BK11*(H**2)· BKSO*BK12*H - BKSO*BK13 - BK14*BKSO/H TIT01810
IF (PST.GE.0.0) THEN TIT01820
ST = 3.*ALT· 3.*(1+ (10**3.2)*504 + (10**5.1)*(SO4**2))*BKSO* TIT01830
9 (H**3)- 2*BK50*BK11*(H**2)· BKSO*BK12*H+ BKSO*BK14/H TIT01840
ELSE TIT01850
RNUN = BK11/H+ 2.*BK12/(H**2)+ 3.*BK13/(H**3)+ 4.*BK14/(H**4) TIT01860
DENOM = 1. + BK11/H+ BK12/(H**2)+ BK13/(H**3)+ BK14/(H**4) TIT01870
ST = ALT*RNUN/DENOM TIT01880
ENDIF TIT01890
ELSE TIT01900

C DETERMINES THE PRECIPITATION STATUS OF THE SOLUTION IF TIT01910
C THE OPTION REQUIRES THEN USES THE APPROPRIATE TIT01920
C EQUATION TO DETERNINE THE SOLUTION STATUS TIT01930
C
IF (POPT.EQ.1) THEN TIT01940
PST = ALT - (1.+ (10.**3.2)*SO4+ (10.**5.1)*SO4**2)*BKSO*(H**3)- TIT01950
9 BKSO*BK11*(H**2)- BKSO*BK12*H - BKSO*BK13 - BK14*BKSO/H TIT01960
IF (PST.GE.0.0) THEN TIT01970
ST = 3.*ALT· 3.*(1+ (10**3.2)*SO4+ (10**5.1)*(SO4**2))*BKSO* TIT01980
9 (H**3)-BKSO*BK11*H- BKSO*BK12- BKSO*BK14/H TIT01990
ELSE TIT02000
RNUN = BK11/H+ 2.*BK12/(H**2)+ 3.*BK13/(H**3)+ 4.*BK14/(H**4) TIT02010
DENOM = 1. + BK11/H+ BK12/(H**2)+ BK13/(H**3)+ BK14/(H**4) TIT02020
ST = ALT*RNUN/DENOM TIT02030
ENDIF TIT02040
ELSE TIT02050

C APPENDIX A. FORTRAN PROGRAMS


```
RNUM= BK11/H + 2.*BK12/(H**2) + 3.*BK13/(H**3) + 4.*BK14/(H**4)

DENOM= (10.*H**5.2)*SOD4 + (10.*H**5.1)*SOD4**2

ST= ALT*RNUM/DENOM

END IF

ELSE

ENDIF

IF (OPTION.EQ.3) THEN

CKSO= BKSO/(SOD4**0.25)

PST= ALT- (1. + (H**2.5) + 10.**(1.*5.1)) + (S04**2) + CKSO

$ (H**2.5) + CKSO*BK11/(H**1.5) + CKSO*BK12/(H**0.5) -

$ CKSO*BK13/(H**1.5) - CKSO*BK14/(H**1.5)

IF (PST.GE.0.0) THEN

ST= 2.5*PST + CKSO*BK11/(H**1.5) + 2.*CKSO*BK12/(H**0.5) +

$ 3.*CKSO*BK13/(H**0.5) + 4.*CKSO*BK14/(H**1.5)

ELSE

RNUM= BK11/H + 2.*BK12/(H**2) + 3.*BK13/(H**3) + 4.*BK14/(H**4)

DENOM= (10.*H**5.2)*SOD4 + (10.*H**5.1)*SOD4**2

ST= ALT*RNUM/DENOM

ENDIF

ELSE

ENDIF

IF (OPTION.EQ.4) THEN

CKSO= BKSO/SOD4

PST= ALT- (1. + (H**3.2)*SOD4 + (H**5.1)*SOD4**2) + CKSO

$ CKSO*BK11 - CKSO*BK12/H - CKSO*BK13/(H**2)

$ CKSO*BK14/(H**3)

IF (PST.GE.0.0) THEN

ST= PST + CKSO*BK11 + 2.*CKSO*BK12/(H**1.5) + 3.*CKSO*BK13/(H**1.5)

$ 4.*CKSO*BK14/(H**1.5)

ELSE

RNUM= BK11/H + 2.*BK12/(H**2) + 3.*BK13/(H**3) + 4.*BK14/(H**4)

DENOM= (10.*H**5.2)*SOD4 + (10.*H**5.1)*SOD4**2

ST= ALT*RNUM/DENOM

ENDIF

ELSE

ENDIF

IF (OPTION.EQ.0) THEN

RNUM= BK11/H + 2.*BK12/(H**2) + 3.*BK13/(H**3) + 4.*BK14/(H**4)

DENOM= (10.*H**5.2)*SOD4 + (10.*H**5.1)*SOD4**2

ST= ALT*RNUM/DENOM

ELSE

ENDIF

C C CALCULATE STATUS IF PST IS LESS THAN 0.

C IF (ST.LE.0.0) THEN

RNUM= BK11/H + 2.*BK12/(H**2) + 3.*BK13/(H**3) + 4.*BK14/(H**4)

DENOM= (10.*H**5.2)*SOD4 + (10.*H**5.1)*SOD4**2

ST= ALT*RNUM/DENOM

ELSE

ENDIF

C C DETERMINES ML CALC AND RESIDUALS (ML - ML CALC)

C OHCON= ST- IST+ IH- H

MLCALC= OHCON*MLT/OHC

RESID= ML/I- MLCALC

RSDSQ= RESID**2

C C CALCULATES THE RESIDUAL SUM OF SQUARES

C RSUM= RSUM+ RSDSQ

C
```

Appendix A. FORTRAN PROGRAMS 112
WRITE OUTPUT DEPENDING ON THE OPTION REQUIRED

IF (POPT.EQ.0) THEN
WRITE (6,6002) PH(I), ML(I), MLCALC, RESID, RSQ, PST
ELSE
END IF
50 CONTINUE
IF (POPT.EQ.0) THEN
WRITE (6,6003) RSUM
ELSE
END IF
IF (POPT.EQ.1) THEN
IF (RSUM.LE.PRT) WRITE (6,7002) RSUM, AKSO, AK11, AK12, AK13,
          AK14
ELSE
END IF
IF (POPT.EQ.2) THEN
IF (RSUM.LE.RLON) THEN
WRITE (6,7002) RSUM, AKSO, AK11, AK12, AK13, AK14
RLON = RSUM
ELSE
END IF
ELSE
END IF
C
DOES THE ITERATION OF THE PK VALUES BETWEEN THE DESIRED LIMITS

AK14=AK14+INC
IF (AK14.LE.ZK14) THEN
GO TO 100
ELSE
AK14= PK14
AK13= PK13
AK12=PK12
AK11= AK11+ INC
IF (AK11.LE.ZK11) THEN
GO TO 100
ELSE
AK14= PK14
AK13= PK13
AK12=PK12
AK11= AK11+ INC
IF (AK11.LE.ZK11) THEN
GO TO 100
ELSE
AK14= PK14
AK13= PK13
AK12=PK12
AK11= PK11
IF (OPTION.NE.0) THEN
AKSO= AKSO+INC
IF (AKSO.LE.ZKSO) THEN
GO TO 100
ELSE
END IF
ELSE
END IF
END IF
END IF
10 STOP
1000 FORMAT (A72)
Following is an example input and output for use with TIFIT. Use of the example data set should result in the example output.

```
TITRATION DATA FOR 1E-03M AL, H IN 1.0M KCL
9.7802E—02 0.7433 9.2586E-04
-10.190 7.900 11.100 14.340 24.500
-10.190 7.900 11.100 14.340 24.500
0.01 000000 50.0 4.00 000000 19.0076
9.6x, 'PK14',/ )
7002 FORMAT (F7.2,5X,F7.2)
TIT03760
9008 FORMAT (' ', 'YOU HAVE CHOSEN AN INVALID PRINT OPTION')
TIT03780
9009 FORMAT (' ', 'THE VALID PRINT OPTIONS ARE')
TIT03790
9010 FORMAT (' ', '= 0 READOUT FOR INDIVIDUAL TITRATION PATTERNS')
TIT03800
9011 FORMAT (' ', '= 1 SHORT READOUT FOR MANY PATTERNS')
TIT03810
9012 FORMAT (' ', '= 2 ALTERNATE READOUT FOR MANY PATTERNS')
TIT03820
9999 FORMAT (' ', 'YOU HAVE CHOSEN AN INVALID PRINT OPTION')
TIT03830
9008 FORMAT (' ', 'YOU HAVE CHOSEN AN INVALID PRINT OPTION')
TIT03840
9009 FORMAT (' ', 'THE VALID PRINT OPTIONS ARE')
TIT03850
9010 FORMAT (' ', '= 0 READOUT FOR INDIVIDUAL TITRATION PATTERNS')
TIT03860
9011 FORMAT (' ', '= 1 SHORT READOUT FOR MANY PATTERNS')
TIT03870
9012 FORMAT (' ', '= 2 ALTERNATE READOUT FOR MANY PATTERNS')
TIT03880
9999 FORMAT (' ', 'YOU HAVE CHOSEN AN INVALID PRINT OPTION')
TIT03890
END
TIT03900
TIT03910
```

Appendix A. FORTRAN PROGRAMS 114
This is the output which should be obtained if TIFIT is run with the data set shown above.

<table>
<thead>
<tr>
<th>OML TITRATED</th>
<th>INITIAL PH</th>
<th>RESIDUAL SUM OF SQUARES</th>
</tr>
</thead>
<tbody>
<tr>
<td>50.0</td>
<td>4.00</td>
<td>0.6274E-01</td>
</tr>
</tbody>
</table>

**TIF**

The next program in the TIFIT series of programs is TIF which varies from TIFIT in that it includes a \(n = 2.5\) mononuclear species, which is used to simulate the presence of a polynuclear species.
species with \( n = 2.5 \). This program was used to refine the data after TIFIT to see the effect of the inclusion of an \( n = 2.5 \) species on the experimental results.

C TIF -- AN ALUMINUM HYDROLYSIS CONSTANT REFINEMENT PROGRAM
C CALCULATES THE GOODNESS OF FIT OF A TITRATION PATTERN OF ALUMINUM SOLUTIONS TO THOSE CALCULATED WITH COMBINATIONS OF PK VALUES BETWEEN TWO LIMITS FOR ANY OF THE FOUR PK VALUES. AN OPTION IS INCLUDED WHICH ALLOWS FOR THE INCLUSION OF A PRECIPITATING SOLID PHASE OF VARIABLE SOLUBILITY. ALSO INCLUDED IS THE EFFECTS OF AL-SO4 COMPLEXES ON HYDROLYSIS AND THE PRECIPITATION OF SELECTED AL-OH-SO4 SOLIDS. THE ALSO4 AND AL(SO4)2 COMPLEX LOG K VALUES ARE ASSUMED TO BE 3.20 AND 5.10 BUT ARE EASILY ADJUSTED WITHIN THE PROGRAM. THIS VERSION INCLUDES A 2.5 N VALUE SPECIES.

C WRITEN BY NORMAN WHITE
C AGRONOMY DEPARTMENT
C SMYTH HALL
C VIRGINIA TECH
C BLACKSBURG, VA 24060

C INPUT DATA
C LINE COLUMNS FORMAT
C 1 : 1-72 TITLE A72
C 2 : 1-10 BASE CONCENTRATION E10.4
C 15-21 ACTIVITY COEFFICIENT FOR H F6.4
C 26-35 TOTAL SOLUTION AL CONC. MOLAR E10.4
C 3 : 1-7 LOWER PK50 LIMIT F7.3
C 12-18 LOWER PK11 LIMIT F7.3
C 23-29 LOWER PK12 LIMIT F7.3
C 34-40 LOWER PK13 LIMIT F7.3
C 45-51 LOWER PK14 LIMIT F7.3
C 56-63 LOWER PK25 LIMIT F7.3
C 4 : 1-7 UPPER PK50 LIMIT F7.3
C 12-18 UPPER PK11 LIMIT F7.3
C 23-29 UPPER PK12 LIMIT F7.3
C 34-40 UPPER PK13 LIMIT F7.3
C 45-51 UPPER PK14 LIMIT F7.3
C 56-63 UPPER PK25 LIMIT F7.3
C 5 : 1-4 PK INCREMENTS USED F4.2
C 11 OPTION = 0 NO PRECIPITATION I1
C = 1 AL(OH)3 PRECIP.
C = 2 ALUNITE PRECIP.
C = 3 BASALUMINITE PRECIP.
C = 4 JURBANITE PRECIP.
C 16-20 TOTAL ML SOLUTION TITRATED F5.1
C 26-30 INITIAL PH F5.2
C 36 PRINT OPTION = 0 INDIVIDUAL I1
C = 1 MANY
C = 2 MANY ALTERNATE
C 46-50 UPPER LIMIT FOR PRINTED RSS F6.4
C 6 1-7 SULFATE CONCENTRATION F7.5
C 16-22 POTASSIUM CONCENTRATION F7.5
C 7+ 1-5 PH OF SOLUTION WHEN F5.2
C 11-16 ML OF BASE ADDED F5.2

Appendix A. FORTRAN PROGRAMS
OUTPUT INCLUDES INPUT PARAMETERS AND RESIDUALS CALCULATED BY SUBTRACTING CALCULATED FROM OBSERVED ML TITRATED. THE CALCULATED RESIDUAL SUM OF SQUARES CAN BE USED TO COMPARE THE GOODNESS OF FIT FOR DIFFERENT DATA SETS. THE PRINT OPTION IS USED TO REDUCE THE SIZE OF THE OUTPUT FILE WHEN LARGE NUMBERS OF ITERATIONS ARE USED. THE PRECIP STATUS ON THE OUTPUT OF THE INDIVIDUAL PATTERNS IF NEGATIVE OR ALL ***** MEANS THAT THE PRECIPITATION REACTION IS NOT TAKING PLACE WHILE A POSITIVE QUANTITY MEANS THAT PRECIPITATION REACTIONS ARE OCCURRING.

REAL OHC, GAMMAH, ALT, PKSO, PK11, PK12, PK13, PK14, ZKSO, ZK11, ZK12, ZK13, ZK14, INC, MLT, PPH, ML, PH, AH, AIH, H, IH, ST, IST, $ZK15, ZK16, AKSO, AK11, AK12, AK13, AK14, BKSO, BK11, BK12, BK13, BK14, INUM, $IDEN, RNUM, DENOM, OHCON, RESID, RSDSQ, MLCALC, RSUM, PST, PRT, $04, K, KSO4, CKSO, RLON, PKZ5, ZKZ5, AK25, BKZ5, INTEGER OPTION, NUMV, POPT, CHARACTER*72 TITLE

DIMENSION PH(100), ML(100)

READ (5,1000) TITLE
READ (5,2000) OHC, GAMMAH, ALT
READ (5,3000) PKSO, PK11, PK12, PK13, PK14, PK25
READ (5,4000) ZKSO, ZK11, ZK12, ZK13, ZK14, ZK25
READ (5,5000) INC, OPTION, MLT, PPH, POPT, PRT
READ (5,6000) S04, K

READS IN TITRATION CURVE FOR FURTHER USE

DO 25 I=1,100
READ (5,6000,END=30) PH(I), ML(I)
NUMV= I-1
RLON = 10.0

WRITES FIRST PAGE OF OUTPUT

WRITE (6,1001) TITLE
WRITE (6,2001) OHC, GAMMAH, ALT
WRITE (6,2002) S04, K
WRITE (6,3001)
WRITE (6,3002) PKSO, PK11, PK12, PK13, PK14, PK25
WRITE (6,4001) ZKSO, ZK11, ZK12, ZK13, ZK14, ZK25
IF (OPTION.EQ.0) WRITE (6,5001)
IF (OPTION.EQ.1) WRITE (6,5002)
IF (OPTION.EQ.2) WRITE (6,5004)
IF (OPTION.EQ.3) WRITE (6,5005)
IF (OPTION.EQ.4) WRITE (6,5006)
IF (OPTION.GE.5) THEN
WRITE (6,9001)
WRITE (6,9002)
WRITE (6,9003)
WRITE (6,9004)
WRITE (6,9005)
WRITE (6,9006)
WRITE (6,9007)
GO TO 10
ELSE
END IF
IF (POPT.EQ.1) WRITE (6,7001)
IF (POPT.EQ.2) WRITE (6,7001)
IF (POPT.GT.2) THEN
WRITE (6,9008)
WRITE (6,9009)
WRITE (6,9010)
WRITE (6,9011)
GO TO 10
ELSE
END IF

Appendix A. FORTRAN PROGRAMS
WRITE (6,9012)  
GO TO 10  
ELSE  
END IF  
C  
C CHANGES INITIAL pH TO INITIAL HYDROGEN ION CONCENTRATION  
C  
AIH= 10.*(-PPH)  
IH= AIH/GAMMAH  
C  
C ENTERS INITIAL PK VALUES  
C  
AKSO= PKSO  
AK11= PK11  
AK12= PK12  
AK13= PK13  
AK14= PK14  
AK25= PK25  
100 CONTINUE  
C  
C CHANGES PK VALUES TO K VALUES AND STARTS THE CALCULATION OF  
C THE ML CALC. FOR THE POINTS ON THE TITRATION CURVE  
C  
BKSO= 10.*(-AKSO)  
BK11= 10.*(-AK11)  
BK12= 10.*(-AK12)  
BK13= 10.*(-AK13)  
BK14= 10.*(-AK14)  
BK25= 10.*(-AK25)  
C  
C CALCULATES SOLUTION STATUS AT THE INITIAL pH ALWAYS ASSUMING  
C MONOMERIC HYDROLYSIS WITH NO PRECIPITATION.  
C  
INUM= BK11/IH+ 2.*BK12/(IH**2)+ 3.*BK13/(IH**3)+ 4.*BK14/(IH**4)  
IDEN= 1.+ BK11/IH+ BK12/(IH**2)+ BK13/(IH**3)+ BK14/(IH**4)+ BK25/(IH**2.5)+ (10.*3.2)*SO4+ (10.*5.1)*SO4**2  
IST= ALT*INUM/IDEN  
C  
C WRITES THE READOUT FOR AN INDIVIDUAL TITRATION PATTERN  
C  
IF (POPT.EQ.0) WRITE (6,1001) TITLE  
IF (POPT.EQ.0) WRITE (6,2001) OHC, GAMMAH, ALT  
IF (POPT.EQ.0) WRITE (6,2002) SO4, K  
IF (POPT.EQ.0) WRITE (6,3001) AKSO, AK11, AK12, AK13, AK14, AK25  
IF (POPT.EQ.0) THEN  
IF (OPTION.EQ.1) WRITE (6,5001) MLT, PPH  
WRITE (6,6001)  
ELSE  
END IF  
C  
C SETS RESIDUAL SUM OF SQUARES TO ZERO  
C  
RSUM = 0.0  
C  
C CALCULATES THE ML CALC FOR EACH POINT ON A TITRATION PATTERN  
C  
DO 50 I=1,NUMV  
AH= 10.*(-PH(I))  
H= AH/GAMMAH  

Appendix A. FORTRAN PROGRAMS

118
IF (OPTION.EQ.1) THEN
  PST = ALT - (1. + (10.**3.2)*SO4 + (10.**5.1)*(SO4**2))*BK50/(H**3) -
  KBSO*BK11*H - KBSO*BK12*H - KBSO*BK13*H - KBSO*BK14*H/
  + 2.5*KBSO*BK25/(H**0.5)
  ELSE
    RNUM = BK11*H + 2.5*BK12/(H**2.5) + 3.*BK13/(H**3) + 4.*BK14/(H**4)
    + 2.5*BK25/(H**2.5)
    DENOM = 1. + BK11*H + BK12/(H**2.5) + BK13/(H**3) + BK14/(H**4)
    + BK25/(H**2.5) + (10.**3.2)*SO4 + (10.**5.1)*(SO4**2)
    ST = ALT*RNUM/DENOM
  END IF
ELSE
  END IF
ENDIF
IF (OPTION.EQ.2) THEN
  KSO4 = (K*(1./3.))**(SO4**(2./3.))
  CKSO = BKSO/KSO4
  PST = ALT - (1. + (10.**3.2)*SO4 + (10.**5.1)*(SO4**2))*CKSO*
  KBSO*BK11*H - KBSO*BK12*H - KBSO*BK13*H - KBSO*BK14*H/
  - CKSO*BK25/(H**0.5)
  ELSE
    RNUM = BK11*H + 2.5*BK12/(H**2.5) + 3.*BK13/(H**3) + 4.*BK14/(H**4)
    + 2.5*BK25/(H**2.5)
    DENOM = 1. + BK11*H + BK12/(H**2.5) + BK13/(H**3) + BK14/(H**4)
    + BK25/(H**2.5) + (10.**3.2)*SO4 + (10.**5.1)*(SO4**2)
    ST = ALT*RNUM/DENOM
  END IF
ELSE
  END IF
ENDIF
IF (OPTION.EQ.3) THEN
  CKSO = BKSO/SO4
  PST = ALT - (1. + (10.**3.2)*SO4 + (10.**5.1)*(SO4**2))*CKSO*
  KBSO*BK11*H - KBSO*BK12*H - KBSO*BK13*H - KBSO*BK14*H/
  - CKSO*BK25/(H**0.5)
  ELSE
    RNUM = BK11*H + 2.5*BK12/(H**2.5) + 3.*BK13/(H**3) + 4.*BK14/(H**4)
    + 2.5*CKSO*BK25/(H**0.5)
    DENOM = 1. + BK11*H + BK12/(H**2.5) + BK13/(H**3) + BK14/(H**4)
    + BK25/(H**2.5) + (10.**3.2)*SO4 + (10.**5.1)*(SO4**2)
    ST = ALT*RNUM/DENOM
  END IF
ELSE
  END IF
ENDIF
IF (OPTION.EQ.4) THEN
  CKSO = BKSO/SO4
  PST = ALT - (1. + (10.**3.2)*SO4 + (10.**5.1)*(SO4**2))*CKSO*
  KBSO*BK11*H - KBSO*BK12*H - KBSO*BK13*H - KBSO*BK14*H/
  - CKSO*BK25/(H**0.5)
  ELSE
    RNUM = BK11*H + 2.5*BK12/(H**2.5) + 3.*BK13/(H**3) + 4.*BK14/(H**4)
    + 2.5*CKSO*BK25/(H**0.5)
    END IF
ELSE
  END IF
ENDIF
DENOM = 1. + BK11/H + BK12/(H**2) + BK13/(H**3) + BK14/(H**4) +
        BK25/(H**2.5) + (10.**3.2)*SO4 + (10.**5.1)*SO4**2
ST = ALT/RUNUM/DENOM
END IF
ELSE
END IF
IF (OPTION.EQ.0) THEN
RUNUM = BK11/H + 2.*BK12/(H**2) + 3.*BK13/(H**3) + 4.*BK14/(H**4) +
        2.5*BK25/(H**2.5)
DENOM = 1. + BK11/H + BK12/(H**2) + BK13/(H**3) + BK14/(H**4) +
        BK25/(H**2.5) + (10.**3.2)*SO4 + (10.**5.1)*SO4**2
ST = ALT/RUNUM/DENOM
ELSE
END IF
C
C CALCULATE STATUS IF PST IS LESS THAN 0.
C
IF (ST.LE.0.0) THEN
RN = 1. + BK1/H + 2.*BK12/(H**2) + 5.*BK15/(H**5) + 4.*BK14/(H**4) +
        2.5*BK25/(H**2.5)
DENOM = 1. + BK1/H + BK12/(H**2) + BK13/(H**3) + BK14/(H**4) +
        BK25/(H**2.5) + (10.**3.2)*SO4 + (10.**5.1)*SO4**2
ST = ALT/RN/DENOM
ELSE
END IF
C
C DETERMINES ML CALC AND RESIDUALS (ML - ML CALC)
C
OHCON = ST - IST + IH - H
MLCALC = OHCON*MLI/OHC
RESID = ML(I) - MLCALC
RSDSQ = RESID**2
C
C CALCULATES THE RESIDUAL SUM OF SQUARES
C
RSUM = RSUM + RSDSQ
C
C WRITES OUTPUT DEPENDING ON THE OPTION REQUIRED
C
IF (POPT.EQ.0) THEN
WRITE (6,6002) PH(I), ML(I), MLCALC, RESID, RSDSQ, PST
ELSE
END IF
50 CONTINUE
IF (POPT.EQ.0) THEN
WRITE (6,6005) RSUM
ELSE
END IF
IF (POPT.EQ.1) THEN
IF (RSUM.LE.PRT) WRITE (6,7002) RSUM, AK50, AK11, AK12, AK13,
        AK14, AK25
ELSE
END IF
IF (POPT.EQ.2) THEN
IF (RSUM.LE.RLOW) THEN
WRITE (6,7002) RSUM, AK50, AK11, AK12, AK13, AK14, AK25
RLOW = RSUM
ELSE
END IF
ELSE
END IF
C
C DOES THE ITERATION OF THE PK VALUES BETWEEN THE DESIRED LIMITS
C
AK14 = AK14 + INC
IF (AK14.LE.ZK14) THEN
GO TO 100
C
Appendix A. FORTRAN PROGRAMS 120
ELSE
AK14= PK14
AK13= AK13+ INC
IF (AK13.LE.ZK13) THEN
  GO TO 100
ELSE
AK14= PK14
AK13= PK13
AK12= PK12
AK11= AK11+ INC
IF (AK11.LE.ZK11) THEN
  GO TO 100
ELSE
AK14= PK14
AK13= PK13
AK12= PK12
AK11= PK11
AK25= PK25
IF (OPTION.NE.0) THEN
  AKSO= AKSO+INC
  IF (AKSO.LE.ZKSO) THEN
    GO TO 100
  ELSE
    END IF
  ELSE
    END IF
ENDIF
ENDIF
ENDIF
ENDIF
10 STOP
1000 FORMAT (A72)
1001 FORMAT (A15,A72)
2000 FORMAT (E10.4,5X,F6.4,E10.4)
2001 FORMAT (A7,'BASE CONC. =',E10.4,5X,'GAMMA H =', F6.4,9X,'TOTAL ALTIF03780'
*,E10.4)
2002 FORMAT (A7,'SULFATE CONCENTRATION = ',F7.5,8X,'POTASSIUM CONC. =',F7.5)
3000 FORMAT (6(F7.3,4X))
3001 FORMAT (A0,15X,'PKSO',7X,'PK11',7X,'PK12',7X,'PK13',7X,'PK14',
  7X,'PK25')
3002 FORMAT (A0,'LOWER LIMITS ',1X,6(F7.3,4X))
3003 FORMAT (A0,'VALUES USED',4X,6(F7.3,4X))
4000 FORMAT (6(F7.3,4X))
4001 FORMAT (A0,'UPPER LIMITS',5X,6(F7.3,4X))
5000 FORMAT (F4.2,15X,7F5.1,9X,7F5.1)
5001 FORMAT (A0,'NO PRECIPITATION ASSUMED')
5002 FORMAT (A0,'PRECIPITATION OF ALOH1 ASSUMED')
5003 FORMAT (A0,'ML TITRATED =',2X,F5.1,12X,'INITIAL PH =',F5.2)
5004 FORMAT (A0,'PRECIPITATION OF ALUNITE ASSUMED')
5005 FORMAT (A0,'PRECIPITATION OF BASALUMINITE ASSUMED')
5006 FORMAT (A0,'PRECIPITATION OF JURBANITE ASSUMED')

Appendix A. FORTRAN PROGRAMS 121
Following is an example input and output for use with TIF. Use of the example data set should result in the example output.

TIMTRATION DATA FOR 1E-03M AL, H IN 1.0M KCL

9.7802E-02  0.7433  9.2586E-03
0.01  000000  50.0  4.00  0000000  19.0076
0.00000  1.00000

This is the output which should be obtained if TIF is run with the data set shown above.

1TIMTRATION DATA FOR 1E-03M AL, H IN 1.0M KCL

OAUE CONC. = 0.9780E-01  GAMMA H = 0.7433  TOTAL AL0.9259E-03
OSULFATE CONCENTRATION = 0.00000  POTASSIUM CONC. = 1.00000

Appendix A. FORTRAN PROGRAMS
### The ALPHA Family of Programs

The ALPHA family of programs were written to help the user of the TIFIT family of programs determine what effects their choice of pK values has on the speciation of solution. The programs accomplish this objective by calculating the solution speciation at pH intervals between pH 3.00 and 8.20. Three versions of ALPHA were written to cover specialized situations.
The first version, ALPHA, was written to calculate the speciation assuming solution species
with \( n = 1, 2, 3, \) or \( 4 \) and allows for precipitation of the same solids as TIFIT.

```
ALPHA - A PROGRAM TO CALCULATE THE SOLUTION STATUS OF ALUMINUM
SOLUTIONS BETWEEN PH 3 AND 8.2 BY .10 PH INCREMENTS
INPUT IS DESIGNED TO BE USED WITH TIFIT RESULTS. OPTIONS INCLUDE NO PRECIPITATION REACTIONS, PRECIPITATION OF AN AL(OH)3 PHASE OR THREE SELECTED AL-OH-SO4 SOLIDS.
WRITTEN BY NORMAN WHITE
AGRONOMY DEPARTMENT
SMYTH HALL
VIRGINIA TECH
BLACKSBURG, VA 24060

INPUT DATA
LINE COLUMNS FORMAT
1: 1-72 TITLE A72
2: 1-6 ACTIVITY COEFFICIENT FOR H F6.4
11-20 TOTAL ALUMINUM CONCENTRATION E10.4
31-37 SULFATE CONCENTRATION F7.5
46-52 POTASSIUM CONCENTRATION F7.5
60 OPTION = 0 NO PRECIPITATION I1
= 1 AL(OH)3 PRECIPITATES
= 2 ALUNITE PRECIPITATES
= 3 BASALUMINITE PRECIPITATES
= 4 JURBANITE PRECIPITATES
3: 1-7 PKSO F7.3
12-18 PK11 F7.3
23-29 PK12 F7.3
34-40 PK13 F7.3
45-51 PK14 F7.3

OUTPUT INCLUDES A LIST OF THE FRACTION OF TOTAL ALUMINUM PRESENT

REAL GAMMAH, ALT, PKSO, PK11, PK12, PK13, PK14, INC, PH, AH, H, $\text{AKSO, AK11, AK12, AK13, AK14, SO4, K, KSO4, CKSO, OHAL, ALPHA0, PKSO}}$, ALPHAO, ALPHA1, ALPHA2, ALPHA3, ALPHA4, ALPHAS, ALSO11, ALSO12, PST ALPHAO

INTEGER OPTION CHARACTER=72 TITLE
READ (5,1000) TITLE
READ (5,2000) GAMMAH, ALT, SO4, K, OPTION
READ (5,3000) PKSO, PK11, PK12, PK13, PK14
WRITE (6,1001) TITLE
WRITE (6,2001) ALT, GAMMAH
WRITE (6,2002) SO4, K
IF (OPTION.EQ.0) WRITE (6,2003)
IF (OPTION.EQ.1) WRITE (6,2004)
IF (OPTION.EQ.2) WRITE (6,2005)
IF (OPTION.EQ.3) WRITE (6,2006)
```
IF (OPTION.EQ.4) WRITE (6,2007)
IF (OPTION.GE.5) THEN
  WRITE (6,2008)
  WRITE (6,2009)
  WRITE (6,2010)
  WRITE (6,2011)
  WRITE (6,2012)
  WRITE (6,2013)
  WRITE (6,2014)
  WRITE (6,2015)
  GO TO 10
ELSE
  END IF
  WRITE (6,3001)
  WRITE (6,3002)
  PKS0, PK11, PK12, PK13, PK14
  WRITE (6,4001)
  PH = 3.00
  AKS0 = 10.**(-PKS0)
  AK11 = 10.**(-PK11)
  AK12 = 10.**(-PK12)
  AK13 = 10.**(-PK13)
  AK14 = 10.**(-PK14)
  100 AH = 10.0**(-PH)
  H = AH/GAMMAH
C
C CALCULATES THE FRACTIONS OF ALUMINUM IN EACH FORM USING THE
C CORRECT EQUATION.
C
IF (OPTION.EQ.0) THEN
  PHSA = 1./(1. + (10.**3.2)*S04 + (10.**5.1)*(S04**2) + AK11/H
  +AK12/(H**2) + AK13/(H**3) + AK14/(H**4))
  ALPHAO = 1./(1. + (10.**3.2)*S04 + (10.**5.1)*(S04**2) + AK11/H
  +AK12/(H**2) + AK13/(H**3) + AK14/(H**4))
  ALPHA1 = ALPHAO*AK11/H
  ALPHA2 = ALPHAO*AK12/(H**2)
  ALPHA3 = ALPHAO*AK13/(H**3)
  ALPHA4 = ALPHAO*AK14/(H**4)
  ALSO11 = ALPHAO*(10.**3.2)*S04
  ALSO12 = ALPHAO*(10.**5.1)*(S04**2)
  ALPHA5 = 0.00
  OHAL = ALPHA1 + 2.*ALPHA2 + 3.*ALPHA3 + 4.*ALPHA4
ELSE
  END IF
  IF (OPTION.EQ.1) THEN
    PSTM = ALT- (1.+ (10.**3.2)*S04 + (10.**5.1)*(S04**2))*AKS0*(H**3)
    1000 AH = 10.0**(-PH)
    H = AH/GAMMAH
    PHSA = 1./(1. + (10.**3.2)*S04 + (10.**5.1)*(S04**2) + AK11/H
    +AK12/(H**2) + AK13/(H**3) + AK14/(H**4))
    ALPHAO = 1./(1. + (10.**3.2)*S04 + (10.**5.1)*(S04**2) + AK11/H
    +AK12/(H**2) + AK13/(H**3) + AK14/(H**4))
    ALPHA1 = ALPHAO*AK11/H
    ALPHA2 = ALPHAO*AK12/(H**2)
    ALPHA3 = ALPHAO*AK13/(H**3)
    ALPHA4 = ALPHAO*AK14/(H**4)
    ALSO11 = ALPHAO*(10.**3.2)*S04
    ALSO12 = ALPHAO*(10.**5.1)*(S04**2)
    OHAL = 0.00
ELSE
  END IF
END IF
ELSE
  END IF
ENDIF
IF (OPTION.EQ.2) THEN
   K504 = (K**(1./3.))*(504**(2./3.))
   CKS0 = AKSO/K504
   PST= ALT- (1.+ ((10.**3.2)*SO4)+ ((10.**5.1)*(SO4**2)))*CKS0

   IF (PST.GE.0.0) THEN
      ALPHA0 = CKSO*(H**2)/ALT
      ALPHA1 = CKSO*AK11/H
      ALPHA2 = CKSO*AK12/(H**2)
      ALPHA3 = CKSO*AK13/(H**3)
      ALPHA4 = CKSO*AK14/(H**4)
      ALPHAS = 0.00
      OHAL = ALPHA1+ 2.*ALPHA2+ 3.*ALPHA3+ 4.*ALPHA4
      OHAL = ALPHA1+ 2.*ALPHA2+ 3.*ALPHA3+ 4.*ALPHA4
   END IF
   ELSE
      ALPHA0 = 1./(1. + (10.**3.2)*SO4+ (10.**5.1)*(SO4**2)+ AK11/H
   END IF
   ELSE
ENDIF

IF (OPTION.EQ.3) THEN
   CK50 = AK50/504
   PST = ALT- (1.+ ((10.**3.2)*SO4)+ ((10.**5.1)*(SO4**2)))*CK50

   IF (PST.GE.0.0) THEN
      ALPHA0 = CK50*(H**2.5)/ALT
      ALPHA1 = CKSO*AK11/(H**1.5)
      ALPHA2 = CKSO*AK12/(H**2)
      ALPHA3 = CKSO*AK13/(H**3)
      ALPHA4 = CKSO*AK14/(H**4)
      OHAL = ALPHA1+ 2.*ALPHA2+ 3.*ALPHA3+ 4.*ALPHA4
      OHAL = ALPHA1+ 2.*ALPHA2+ 3.*ALPHA3+ 4.*ALPHA4
   END IF
   ELSE
ENDIF

IF (OPTION.EQ.4) THEN
   CK50 = AK50/SO4
   PST = ALT- (1.+ ((10.**5.2)*SO4)+ ((10.**5.1)*(SO4**2)))*CK50

   IF (PST.GE.0.0) THEN
      ALPHAS = 0.00
      OHAL = ALPHA1+ 2.*ALPHA2+ 3.*ALPHA3+ 4.*ALPHA4
      OHAL = ALPHA1+ 2.*ALPHA2+ 3.*ALPHA3+ 4.*ALPHA4
   END IF
   ELSE
ENDIF
ALPHA3 = CK50*AK13/((H**2)*ALT)
ALPHA4 = CK50*AK14/((H**3)*ALT)
ALPHAS = PST/ALT
ALSO11 = (10.**3.2)*SO4*ALPHA0
ALSO12 = (10.**5.1)*(SO4**2)*ALPHA0
OHAL = ALPHA1 + 2.*ALPHA2 + 3.*ALPHA3 + 4.*ALPHA4 + ALPHAS
ELSE
ALPHA0 = 1./(1. + (10.**3.2)*504 + (10.**5.1)*(SO4**2) + AK1/H + AK12/(H**2) + AK13/(H**3) + AK14/(H**4))
ALPHA1 = ALPHA0*AK11/H
ALPHA2 = ALPHA0*AK12/(H**2)
ALPHA3 = ALPHA0*AK13/(H**3)
ALPHA4 = ALPHA0*AK14/(H**4)
ALSO11 = ALPHA0*10.**3.2)*SO4
ALSO12 = ALPHA0*10.**5.1)*(SO4**2)
ALPHAS = 0.00
OHAL = ALPHA1 + 2*ALPHA2 + 3*ALPHA3 + 4*ALPHA4
ENDIF
ENDIF
WRITE (6,5001) PH, ALPHA0, ALPHA1, ALPHA2, ALPHAS, ALPHA4, ALPHA0, ALSO11, ALSO12, OHAL
IF (PH.LE.6.0) THEN
GO TO 100
ELSE
END IF
10 STOP
100 FORMAT (A72)
1001 FORMAT ('0',A72)
2000 FORMAT (F6.4,4X,E10.4,F7.5,8X,F7.5,7X,I1)
2001 FORMAT ('0','TOTAL ALUMINUM = ',E10.4,'GAMMA H = ',F6.4)
2002 FORMAT ('0','SULFATE CONC. = ',F7.5,'POTASSIUM = ',F7.5)
2003 FORMAT ('0','NO PRECIPITATION ASSUMED')
2004 FORMAT ('0','PRECIPITATION OF AL(OH)3 ASSUMED')
2005 FORMAT ('0','PRECIPITATION OF ALUNITE ASSUMED')
2006 FORMAT ('0','PRECIPITATION OF BASALUMINITE ASSUMED')
2007 FORMAT ('0','PRECIPITATION OF JURBANITE ASSUMED')
2008 FORMAT ('0','YOU HAVE CHOSEN AN INVALID OPTION')
2009 FORMAT ('0','THE VALID OPTIONS ARE')
2010 FORMAT ('0','NO PRECIPITATION ASSUMED')
2011 FORMAT ('0','PRECIPITATION OF AL(OH)3 ASSUMED')
2012 FORMAT ('0','PRECIPITATION OF ALUNITE ASSUMED')
2013 FORMAT ('0','PRECIPITATION OF BASALUMINITE ASSUMED')
2014 FORMAT ('0','PRECIPITATION OF JURBANITE ASSUMED')
2015 FORMAT ('0','PLEASE CHOOSE A VALID OPTION')
3000 FORMAT (5(F7.3,4X))
3001 FORMAT ('0','18X,'PKSO',7X,'PK11',7X,'PK12',7X,'PK13',7X,'PK14')
3002 FORMAT ('0','VALUES USED',4X,5(F7.3,4X))
4001 FORMAT ('0','PH ','6X,'ALPHA0',4X,'ALPHA1',4X,'ALPHA2',4X,'ALPHA3',4X,'ALPHA4',4X,'ALSO4',4X,'ALSO5',4X,'ALSO6',4X)
4002 FORMAT (5(F7.3,4X))
5000 FORMAT (18X,'OH/AL')
5001 FORMAT (5(F5.3,5X),5(F6.4,4X),F5.3)
ENDIF

Following is an example input and output for use with ALPHA. Use of the example data set should result in the example output.

TITRATION DATA FOR 1E-03M AL,H IN 1.00M KCL
0.7433 9.2586E-04 00.00000 1.00000 0000000
-10.190 7.900 11.100 16.340 24.500

Appendix A. FORTRAN PROGRAMS 127
This is the output which should be obtained if ALPHA is run with the data set shown above.
| 6.30 | 0.0001 | 0.0000 | 0.0012 | 0.9987 | 0.0001 | 0.0000 | 0.0000 | 0.0000 | 2.999 |
| 6.40 | 0.0000 | 0.0000 | 0.0009 | 0.9990 | 0.0001 | 0.0000 | 0.0000 | 0.0000 | 2.999 |
| 6.50 | 0.0000 | 0.0000 | 0.0007 | 0.9991 | 0.0002 | 0.0000 | 0.0000 | 0.0000 | 2.999 |
| 6.60 | 0.0000 | 0.0000 | 0.0006 | 0.9992 | 0.0002 | 0.0000 | 0.0000 | 0.0000 | 3.000 |
| 6.70 | 0.0000 | 0.0000 | 0.0005 | 0.9993 | 0.0003 | 0.0000 | 0.0000 | 0.0000 | 3.000 |
| 6.80 | 0.0000 | 0.0000 | 0.0004 | 0.9993 | 0.0003 | 0.0000 | 0.0000 | 0.0000 | 3.000 |
| 6.90 | 0.0000 | 0.0000 | 0.0003 | 0.9993 | 0.0004 | 0.0000 | 0.0000 | 0.0000 | 3.000 |
| 7.00 | 0.0000 | 0.0000 | 0.0002 | 0.9993 | 0.0005 | 0.0000 | 0.0000 | 0.0000 | 3.000 |
| 7.10 | 0.0000 | 0.0000 | 0.0002 | 0.9993 | 0.0006 | 0.0000 | 0.0000 | 0.0000 | 3.000 |
| 7.20 | 0.0000 | 0.0000 | 0.0001 | 0.9990 | 0.0006 | 0.0000 | 0.0000 | 0.0000 | 3.001 |
| 7.30 | 0.0000 | 0.0000 | 0.0001 | 0.9989 | 0.0008 | 0.0000 | 0.0000 | 0.0000 | 3.001 |
| 7.40 | 0.0000 | 0.0000 | 0.0001 | 0.9986 | 0.0008 | 0.0000 | 0.0000 | 0.0000 | 3.001 |
| 7.50 | 0.0000 | 0.0000 | 0.0001 | 0.9983 | 0.0008 | 0.0000 | 0.0000 | 0.0000 | 3.002 |
| 7.60 | 0.0000 | 0.0000 | 0.0001 | 0.9979 | 0.0008 | 0.0000 | 0.0000 | 0.0000 | 3.002 |
| 7.70 | 0.0000 | 0.0000 | 0.0000 | 0.9974 | 0.0009 | 0.0000 | 0.0000 | 0.0000 | 3.003 |
| 7.80 | 0.0000 | 0.0000 | 0.0000 | 0.9977 | 0.0009 | 0.0000 | 0.0000 | 0.0000 | 3.003 |
| 7.90 | 0.0000 | 0.0000 | 0.0000 | 0.9959 | 0.0009 | 0.0000 | 0.0000 | 0.0000 | 3.004 |
| 8.00 | 0.0000 | 0.0000 | 0.0000 | 0.9949 | 0.0009 | 0.0000 | 0.0000 | 0.0000 | 3.005 |
| 8.10 | 0.0000 | 0.0000 | 0.0000 | 0.9935 | 0.0009 | 0.0000 | 0.0000 | 0.0000 | 3.006 |
| 8.20 | 0.0000 | 0.0000 | 0.0000 | 0.9919 | 0.0009 | 0.0000 | 0.0000 | 0.0000 | 3.008 |
The second version of ALPHA, ALPH1, was written to use the results of TIF and therefore differs from ALPHA only in the presence of the $n=2.5$ species in the calculations.

ALPHA - A PROGRAM TO CALCULATE THE SOLUTION STATUS OF ALUMINUM SOLUTIONS BETWEEN PH 3 AND 8.2 BY .10 PH INCREMENTS

INPUT IS DESIGNED TO BE USED WITH TIFIT RESULTS. OPTIONS INCLUDE NO PRECIPITATION REACTIONS, PRECIPITATION OF AN Al(OH)3 PHASE OR THREE SELECTED AL-OH-SO4 SOLIDS. THIS VERSION INCLUDES A 2.5 N VALUE SPECIES.

WRITTEN BY NORMAN WHITE
AGRONOMY DEPARTMENT SMYTH HALL VIRGINIA TECH BLACKSBURG, VA 24060

INPUT DATA

LINE COLUMNS FORMAT
1: 1-72 TITLE A72
2: 1-6 ACTIVITY COEFFICIENT FOR H F6.4
11-20 TOTAL ALUMINUM CONCENTRATION E10.4
31-57 SULFATE CONCENTRATION F7.5
46-52 POTASSIUM CONCENTRATION F7.5
60 OPTION = 0 NO PRECIPITATION I1
= 1 Al(OH)3 PRECIPITATES
= 2 ALUNITE PRECIPITATES
= 3 BASALUMINITE PRECIPITATES
= 4 JURBANITE PRECIPITATES
3: 1-7 PKSO F7.3
12-18 PK11 F7.3
23-29 PK12 F7.3
34-40 PK13 F7.3
46-51 PK14 F7.3
56-63 PK25 F7.3


REAL GAMMAH, ALT, PKSO, PK11, PK12, PK13, PK14, PK25, INC, PH, $AH, H, AKSO, AK11, AK12, AK13, AK14, AK25, SO4, K, KSO4, CKSO,
$OHAL, ALPHAO, ALPHA1, ALPHA2, ALPHA3, ALPHA4, ALPHA5, ALPHA25, ALPHAS,
$ALSO11, ALSO12, PST
INTEGER OPTION CHARACTER*72 TITLE
READ (5,1000) TITLE
READ (5,2000) GAMMAH, ALT, SO4, K, OPTION
READ (5,3000) PKSO, PK11, PK12, PK13, PK14, PK25
WRITE (6,1001) ALT, GAMMAH
WRITE (6,1002) PKSO, PK11, PK12, PK13, PK14, PK25
WRITE (6,1003) INC, PH, $AH, H, AKSO, AK11, AK12, AK13, AK14, AK25, SO4, K, KSO4, CKSO,
$OHAL, ALPHAO, ALPHA1, ALPHA2, ALPHA3, ALPHA4, ALPHA5, ALPHA25, ALPHAS,
$ALSO11, ALSO12, PST
WRITE (6,1004) OPTION
WRITE (6,1005) TITLE
WRITE (6,1006) INC, PH, $AH, H, AKSO, AK11, AK12, AK13, AK14, AK25, SO4, K, KSO4, CKSO,
$OHAL, ALPHAO, ALPHA1, ALPHA2, ALPHA3, ALPHA4, ALPHA5, ALPHA25, ALPHAS,
$ALSO11, ALSO12, PST
WRITE (6,1007) OPTION
WRITE (6,1008) TITLE
WRITE (6,1009) INC, PH, $AH, H, AKSO, AK11, AK12, AK13, AK14, AK25, SO4, K, KSO4, CKSO,
$OHAL, ALPHAO, ALPHA1, ALPHA2, ALPHA3, ALPHA4, ALPHA5, ALPHA25, ALPHAS,
WRITE (6,2002) SO_4, K
IF (OPTION.EQ.0) WRITE (6,2003) ALP00530
IF (OPTION.EQ.1) WRITE (6,2004) ALP00540
IF (OPTION.EQ.2) WRITE (6,2005) ALP00550
IF (OPTION.EQ.3) WRITE (6,2006) ALP00570
IF (OPTION.EQ.4) WRITE (6,2007) ALP00580
IF (OPTION.GE.5) THEN ALP00590
WRITE (6,2008) ALP00600
WRITE (6,2009) ALP00610
WRITE (6,2010) ALP00620
WRITE (6,2011) ALP00630
WRITE (6,2012) ALP00640
WRITE (6,2013) ALP00650
WRITE (6,2014) ALP00660
WRITE (6,2015) ALP00670
GO TO 10
ELSE
END IF
WRITE (6,3001) ALP00680
WRITE (6,3002) PKS0, PK11, PK12, PK13, PK14, PK25 ALP00690
WRITE (6,5001) PH = 3.00 ALP00700
AKS0 = 10.**(-PKS0) ALP00710
AK11 = 10.**(-PK11) ALP00720
AK12 = 10.**(-PK12) ALP00730
AK13 = 10.**(-PK13) ALP00740
AK14 = 10.**(-PK14) ALP00750
AK25 = 10.**(-PK25) ALP00760
100
AH = 10.**(-PH) ALP00770
H = AH/GAMMAH ALP00780
C
C CALCULATES THE FRACTIONS OF ALUMINUM IN EACH FORM USING THE
C CORRECT EQUATION.
C
IF (OPTION.EQ.0) THEN ALP00790
ALPHA0 = 1./1. + (10.**3.2)*SO4 + (10.**5.1)*(SO4**2) + AK11/H ALP00800
ALPHA1 = ALPHA0*AK11/H ALP00810
ALPHA2 = ALPHA0*AK12/(H**2) ALP00820
ALPHA3 = ALPHA0*AK13/(H**3) ALP00830
ALPHA4 = ALPHA0*AK14/(H**4) ALP00840
ALPHA25 = ALPHA0*AK25/(H**2.5) ALP00850
ALPHA5 = 0.00 ALP00860
HALPHAS = 0.00 ALP00870
ELSE
END IF
IF (OPTION.EQ.1) THEN ALP00880
PST = - (1. + (10.**3.2)*SO4 + (10.**5.1)*(SO4**2))*/AKS0/(H**3) ALP00890
HALPHAS = 0.00 ALP00900
IF (PST.EQ.0.0) THEN ALP00910
ALPHA0 = AKS0/(H**3)/ALT ALP00920
ALPHA1 = AKS0/(H**2)/ALT ALP00930
ALPHA2 = AKS0/(H**2)/ALT ALP00940
ALPHA3 = AKS0/(H**2)/ALT ALP00950
ALPHA4 = AKS0/(H**2)/ALT ALP00960
ALPHA25 = AKS0/(H**2)/ALT ALP00970
ALPHA5 = 0.00 ALP00980
HALPHAS = 0.00 ALP00990
ELSE
END IF
Appendix A. FORTRAN PROGRAMS 132
ALPHA1 = ALPHA0*AK11/H
ALPHA2 = ALPHA0*AK12/(H**2)
ALPHA3 = ALPHA0*AK13/(H**3)
ALPHA4 = ALPHA0*AK14/(H**4)
ALPHA5 = ALPHA0*AK15/(H**5)
ALPH25 = ALPHA0*AK25/(H**2.5)
ALS011 = ALPHA0*(10.**3.2)*SO4
ALS012 = ALPHA0*(10.**5.1)*SO4
ALPHAS = 0.00
OHAL = ALPHA1 + 2.*ALPHA2 + 3.*ALPHA3 + 4.*ALPHA4 + 2.5*ALPH25
END IF
ELSE
END IF
IF (OPTION.EQ.2) THEN
KSO4 = (K*(1./3.))*(SO4**(2./3.))
CKS0 = AKS0/KSO4
PST = ALT - (1. + (10.**3.2)*SO4 + (10.**5.1)*(SO4**2))*CKS0*
$ (H**2) - CKS0*AK11*(H**1.5) - CKS0*AK12*(H**0.5) - CKS0*AK15/(H**0.5) - CKS0*AK25
IF (PST.GE.0.0) THEN
ALPHA0 = CKS0*(H**2)/ALT
ALPHA1 = CKS0*AK11/H
ALPHA2 = CKS0*AK12/(H**2)
ALPHA3 = CKS0*AK13/(H**3)
ALPHA4 = CKS0*AK14/(H**4)
ALPHA5 = CKS0*AK15/(H**5)
ALPH25 = CKS0*AK25/(H**2.5)
ALPHAS = 0.00
OHAL = ALPHA1 + 2.*ALPHA2 + 3.*ALPHA3 + 4.*ALPHA4 + 2.5*ALPH25
END IF
ELSE
ALPHA0 = 1./(1. + (10.**3.2)*SO4 + (10.**5.1)*(SO4**2) + AK11/H
AK12/(H**2) + AK13/(H**3) + AK14/(H**4) + AK25/(H**2.5))
ALPHA1 = ALPHAO*AK11/H
ALPHA2 = ALPHAO*AK12/(H**2)
ALPHA3 = ALPHAO*AK13/(H**3)
ALPHA4 = ALPHAO*AK14/(H**4)
ALPHA5 = ALPHAO*AK15/(H**5)
ALPH25 = ALPHAO*AK25/(H**2.5)
ALPHAS = 0.00
OHAL = ALPHA1 + 2.*ALPHA2 + 3.*ALPHA3 + 4.*ALPHA4 + 2.5*ALPH25
END IF
ELSE
END IF
IF (OPTION.EQ.3) THEN
CKS0 = AKS0/(SO4**0.25)
CKS0 = AKS0/(SO4**0.25)
PST = ALT - (1. + (10.**3.2)*SO4 + (10.**5.1)*(SO4**2))*CKS0*
$ (H**2) - CKS0*AK11*(H**1.5) - CKS0*AK12*(H**0.5) - CKS0*AK15/(H**0.5) - CKS0*AK25
IF (PST.GE.0.0) THEN
ALPHA0 = CKS0*(H**2.5)/ALT
ALPHA1 = CKS0*AK11*(H**1.5)/ALT
ALPHA2 = CKS0*AK12*(H**0.5)/ALT
ALPHA3 = CKS0*AK13/(H**1.5)*ALT)
ALPHA4 = CKS0*AK14/(H**0.5)*ALT)
ALPHA5 = CKS0*AK15/(H**0.5)*ALT)
ALPH25 = CKS0*AK25/ALT
ALPHAS = 0.00
OHAL = ALPHA1 + 2.*ALPHA2 + 3.*ALPHA3 + 4.*ALPHA4 + 2.5*ALPH25
END IF
ELSE
ALPHA0 = 1./(1. + (10.**3.2)*SO4 + (10.**5.1)*(SO4**2) + AK11/H
AK12/(H**2) + AK13/(H**3) + AK14/(H**4) + AK25/(H**2.5))
ALPHA1 = ALPHAO*AK11/H
ALPHA2 = ALPHAO*AK12/(H**2)
ALPHA3 = ALPHAO*AK13/(H**3)
ALPHA4 = ALPHAO*AK14/(H**4)
ALPHA5 = ALPHAO*AK15/(H**5)
ALPH25 = ALPHAO*AK25/(H**2.5)
ALPHAS = 0.00
OHAL = ALPHA1 + 2.*ALPHA2 + 3.*ALPHA3 + 4.*ALPHA4 + 2.5*ALPH25
END IF
ELSE
END IF
END IF

Appendix A. FORTRAN PROGRAMS
ALPHA3 = ALPHA0*AK13/(H**3) ALP01870
ALPHA4 = ALPHA0*AK14/(H**4) ALP01880
ALPH25 = ALPHA0*(10.**3.2)*SO4 ALP01900
ALSO11 = ALPHA0*(10.**3.2)*SO4 ALP01910
ALPHAS = 0.00 ALP01920
OHAL = ALPHA1 + 2.*ALPHA2 + 3.*ALPHA3 + 4.*ALPHA4 + 2.5*ALPH25 ALP01930
END IF ALP01940
ELSE ALP01950
END IF ALP01960
IF (OPTION.EQ.4) THEN ALP01970
CKS0 = AKSO/SO4 ALP01980
PST = ALT - (1.+ (10.**3.2)*504+ (10.**5.1)*(SO4**2))*CKS0* ALP01990
SH - CKS0*AK11 - CKS0*AK12/H - CKS0*AK13/(H**2) - CKS0*AK14/(H**3) ALP02000
ALPHAS = PST/ALT ALP02010
ALSO11 = (10.**3.2)*SO4*ALPHA0 ALP02100
ALSO12 = (10.**5.1)*(SO4**2)*ALPHA0 ALP02110
OHAL = ALPHA1 + 2.*ALPHA2 + 3.*ALPHA3 + 4.*ALPHA4 + ALPHAS ALP02120
END IF ALP02130
ELSE ALP02140
ALPHA0 = 1./(1.+ (10.**3.2)*504+ (10.**5.1)*(SO4**2)+ AK11/H ALP02150
ALPHA1 = ALPHA0*AK11/H ALP02170
ALPHA2 = ALPHA0*AK12/(H**2) ALP02180
ALPHA3 = ALPHA0*AK13/(H**3) ALP02190
ALPHA4 = ALPHA0*AK14/(H**4) ALP02200
ALPH25 = ALPHA0*(10.**3.2)*SO4 ALP02220
ALSO11 = (10.**3.2)*SO4*ALPHA0 ALP02110
ALSO12 = (10.**5.1)*(SO4**2)*ALPHA0 ALP02230
OHAL = ALPHA1 + 2.*ALPHA2 + 3.*ALPHA3 + 4.*ALPHA4 + ALPHAS ALP02250
END IF ALP02260
ELSE ALP02270
END IF ALP02280
WRITE (6,5001) PH, ALPHA0, ALPHA1, ALPHA2, ALPHA3, ALPHA4, ALP02290
END IF ALP02300
PH = PH + 0.10 ALP02310
IF (PH.LE.8.2) THEN ALP02320
GO TO 100 ALP02330
END IF ALP02340
1000 FORMAT (A72) ALP02350
1001 FORMAT (F6.4,F6.4,F6.4) ALP02360
1002 FORMAT (F7.5,F7.5,F7.5,F7.5) ALP02370
1003 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02380
1004 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02390
1005 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02400
1006 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02410
1007 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02420
1008 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02430
1009 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02440
1010 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02450
1011 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02460
1012 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02470
1013 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02480
1014 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02490
1015 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02500
1016 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02510
1017 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02520
1018 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02530
1019 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02540
1020 FORMAT (F7.5,F7.5,F7.5,F7.5,F7.5) ALP02550
Appendix A. FORTRAN PROGRAMS 134
Following is an example input and output for use with ALPH1. Use of the example data set should result in the example output.

TITRATION DATA FOR 1E-03M \text{AL}, \text{H} IN 1.00M KCL

\begin{verbatim}
0.7433 9.2586E-04 0.00000 1.00000 0.00000
\end{verbatim}

This is the output which should be obtained if ALPH1 is run with the data set shown above.
### Appendix A. FORTRAN Programs

**Titration Data for 1.0E-03 M Al₃⁺ in 1.00 M KCl**

- **Total Aluminum**: 0.9259E-03
- **Gamma H**: 0.7433
- **Sulfate Conc.**: 0.00000
- **Potassium**: 1.00E0

#### Table:

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<th>PK10</th>
<th>PK11</th>
<th>PK12</th>
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<td>0.0000</td>
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<tr>
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POLY

POLY, the last member of the ALPHA family of programs, was written with an entirely different purpose in mind than the other members of the ALPHA family. This program was written to calculate the polynuclear and mononuclear speciation for solutions which are not undergoing precipitation. To accomplish this objective, all \( n = 2 \) and \( n = 2.5 \) species are assumed to be polynuclear species. All \( n = 1 \) and \( 4 \) and that portion of the \( n = 3 \) which is contributed by a pK of 17.50 is assumed to be mononuclear.

C POLY - A VARIANT OFF OF ALPH1 WHICH TAKES OBSERVED PK VALUES AND POL00010
C CALCULATES THE SOLUTION MONOMER-POLYMER STATUS OF ALUMINUM POL00020
C SOLUTIONS BETWEEN PH 3 AND 8.2 BY .10 PH INCREMENTS POL00030
C INPUT IS DESIGNED TO BE USED WITH TIFIT RESULTS. OPTIONS INCLUDE POL00040
C NO PRECIPITATION REACTIONS ONLY WITH MONOMER AND POLYMERS POL00050
C ASSUMING ALL N=2 AND 2.5 SPECIES ARE POLYMER, AND A POL00060
C MIXTURE OF MONOMERIC AND POLYMERIC N=3 SPECIES WHERE THE POL00070
C PK13 = 17.5 (CAN BE CHANGED IN THE PROGRAM), POL00080
C WRITTEN BY NORMAN WHITE POL00090
C AGRONOMY DEPARTMENT POL0100
C SMYTH HALL POL0110
C VIRGINIA TECH POL0120
C BLACKSBURG, VA 24060 POL0130
C INPUT DATA POL0140
C LINE COLUMNS FORMAT POL0150
C 1: 1-72 TITLE A72 POL0160
C 2: 1-6 ACTIVITY COEFFICIENT FOR H F6.4 POL0170
C 11-20 TOTAL ALUMINUM CONCENTRATION E10.4 POL0180
C 31-37 SULFATE CONCENTRATION F7.5 POL0190
C 46-52 POTASSIUM CONCENTRATION F7.5 POL0200
C 3: 12-18 PK11 F7.3 POL0210
C 23-29 PK12 F7.3 POL0220
C 34-40 PK13 F7.3 POL0230
C 45-51 PK14 F7.3 POL0240
C 56-63 PK25 F7.3 POL0250
C OUTPUT INCLUDES A LIST OF THE FRACTIONS OF TOTAL ALUMINUM PRESENT POL0260
C AS MONOMERIC AND POLYMERIC SPECIES WITH THE OUTPUT POL0270
C INCLUDING THE N BAR VALUE FOR THE MONOMERIC AND POLYMERIC POL0280
C SPECIES AND THE MONOMERIC N=3 CONCENTRATION. COMBINED POL0290
C WITH THE ALPH1 OUTPUT, THIS OUTPUT GIVES THE WHOLE POL0300
C SPECIATION FOR NONPRECIPITATING SOLUTIONS. POL0310
C REAL GAIMAH, ALT, PKS0, PK11, PK12, PK13, PK14, PK25, INC, PH, POL0320
C $ AH, H, AKSO, AK11, AK12, AK13, AK14, AK25, SO4, K, KSO4, CKSO, POL0330
C $ CHAL, ALPHA0, ALPHA1, ALPHA2, ALPHA3, ALPHA4, ALPH25, ALPHAS, POL0340
C $ ALSO11, ALSO12, PST, MON, POLY, NMON, NPOLY, A3MON, A3POL, A3MS POL0350
C INTEGER OPTION POL0360
C
C "CALCULATES THE FRACTIONS OF ALUMINUM IN EACH FORM USING THE
   CORRECT EQUATION."
C
IF (OPTION.EQ.0) THEN
   ALPHAO = 1./((1. + (10.**3.2)**SO4 + (10.**5.1)**SO4**2) + AK11/H
   *AK12/(H**2) + AK13/(H**3) + AK14/(H**4) + AK25/(H**2.5))
   PH = 3.00
   AKSO = 10.**(-PKSO)
   AK11 = 10.**(-PK11)
   AK12 = 10.**(-PK12)
   AK13 = 10.**(-PK13)
   AK14 = 10.**(-PK14)
   AK25 = 10.**(-PK25)
   AKM3 = 10.**(-17.5)
   AH = 10.0**(-PH)
   H = AH/GAMMAH
   MON = ALPHA0 + ALPHA1 + A3MON + ALPHA4
   NMON = (ALPHA1 + 3.*A3MON + 4.*ALPHA4)/MON
   ELSE
   END IF
   WRITE (6,5001) PH, A3MON, ASPOL, MON, NMON, POLY, NPOLY,
   OHAL
   PH = PH + 0.10
   IF (PH.LE.8.2) THEN
   GO TO 100
   ELSE
   END IF
10 STOP

APPENDIX A. FORTRAN PROGRAMS
Following is an example input and output for use with POLY. Use of the example data set should result in the example output.

TITRATION DATA FOR 1E-03M AL•H IN 1.00M KCL
0.7433 9.2586E-04 0.00000 1.00000 0000000

This is the output which should be obtained if POLY is run with the data set shown above.

TITRATION DATA FOR 1E-03M AL•H IN 1.00M KCL
TOTAL ALUMINUM = 0.9259E-05 GAMMA H = 0.7433
SULFATE CONC. = 0.00000 POTASSIUM = 1.00000
NO PRECIPITATION ASSUMED

PK$0 PK11 PK12 PK13 PK14
PH AL3MON A3POL MONO NMON POLY NPOLY OHAL
3.00 0.0000 0.0000 1.0000 0.0000 0.0000 2.6275 0.0000
3.10 0.0000 0.0000 1.0000 0.0000 0.0000 2.6427 0.0000
3.20 0.0000 0.0000 1.0000 0.0000 0.0000 2.6581 0.0000
3.30 0.0000 0.0000 1.0000 0.0000 0.0000 2.6737 0.0001
3.40 0.0000 0.0000 0.9999 0.0000 0.0001 2.6894 0.0001
3.50 0.0000 0.0000 0.9999 0.0000 0.0001 2.7053 0.0001
3.60 0.0000 0.0000 0.9999 0.0000 0.0001 2.7211 0.0002
3.70 0.0000 0.0000 0.9999 0.0000 0.0001 2.7369 0.0002
3.80 0.0000 0.0000 0.9999 0.0000 0.0001 2.7525 0.0002
3.90 0.0000 0.0000 0.9999 0.0000 0.0001 2.7679 0.0002
4.00 0.0000 0.0000 0.9999 0.0000 0.0001 2.7831 0.0007
4.10 0.0000 0.0000 0.9999 0.0000 0.0001 2.7978 0.0149
4.20 0.0000 0.0000 0.9999 0.0000 0.0001 2.8121 0.0283
4.30 0.0000 0.0000 0.9999 0.0000 0.0001 2.8265 0.0528
4.40 0.0000 0.0000 0.9999 0.0000 0.0001 2.8409 0.1019
4.50 0.0000 0.0000 0.9999 0.0000 0.0001 2.8553 0.1905
4.60 0.0000 0.0000 0.9999 0.0000 0.0001 2.8698 0.3477
4.70 0.0000 0.0000 0.9999 0.0000 0.0001 2.8842 0.6067
4.80 0.0000 0.0000 0.9999 0.0000 0.0001 2.8986 0.9860
4.90 0.0000 0.0000 0.9999 0.0000 0.0001 2.9127 1.4548
5.00 0.0000 0.0000 0.9999 0.0000 0.0001 2.9268 1.9264
5.10 0.0000 0.0000 0.9999 0.0000 0.0001 2.9409 2.3124
5.20 0.0000 0.0000 0.9999 0.0000 0.0001 2.9549 2.5791
5.30 0.0000 0.0000 0.9999 0.0000 0.0001 2.9682 2.7433

Appendix A. FORTRAN PROGRAMS 140
TIF1 - The TIFIT-ALPHA Hybrid

In addition to the TIFIT and ALPHA family of programs, there exists TIF1, which uses TIFIT data minus the second pK line and calculates the solution speciation at the pH values observed in titration data.

Appendix A. FORTRAN PROGRAMS
INPUT DATA

LINE COLUMNS

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<tr>
<td>PH OF SOLUTION WHEN</td>
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<tr>
<td>ML OF BASE ADDED</td>
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REAL GAMMAH, ALT, PKS0, PK11, PK12, PK13, PK14, PK25, PH,
$ AH, H, AKS0, AK11, AK12, AK13, AK14, AK25, SO4, K, KSO4, CKS0,
$ MCA1, ALPHAO, ALPHA1, ALPHA2, ALPHA3, ALPHA4, ALPH25, ALPHAS,
$ ALSOI1, ALS012, PST, OH, INUM, IH, ST, IST, NOBS, INC, MLT,
$ PPH, ML

INTEGER OPTION, NUMV, POPT, PRT

CHARACTER*72 TITLE

SET UP PH, ML ARRAY

DIMENSION PH(100), ML(100)

READ (5,1000) TITLE

READ (5,2000) OHC, GAMMAH, ALT

READ (5,3003) MLT

READ (5,5000) INC, OPTION, MLT, PPH, POPT,PRT

READ (5,8000) S04, K

READ IN TITRATION CURVE FOR FURTHER USE

DO 25 I=1,100
25 READ (5,6000,END=30) PH(I), ML(I)

30 NUMV= I-1

WRITE (6,1001) TITLE

WRITE (6,2001) OHC, GAMMAH, ALT

WRITE (6,2002) SO4, K

WRITE (6,3003) MLT

WRITE (6,3006) PPH

IF (OPTION.EQ.0) WRITE (6,2003)

IF (OPTION.EQ.1) WRITE (6,2004)

IF (OPTION.EQ.2) WRITE (6,2005)

IF (OPTION.EQ.3) WRITE (6,2006)

IF (OPTION.EQ.4) WRITE (6,2007)

IF (OPTION.GE.5) THEN

WRITE (6,2008)

WRITE (6,2009)

WRITE (6,2010)
\text{WRITE} (6,2011) \\
\text{WRITE} (6,2012) \\
\text{WRITE} (6,2013) \\
\text{WRITE} (6,2014) \\
\text{WRITE} (6,2015) \\
\text{GO TO} 10 \\
\text{ELSE} \\
\text{END IF} \\
\text{WRITE} (6,3001) \\
\text{WRITE} (6,3002) \text{ PKSO, PK11, PK12, PK13, PK14, PK25} \\
\text{WRITE} (6,4001) \\
\text{C} \\
\text{CHANGE INITIAL PH TO INITIAL HYDROGEN ION CONCENTRATION} \\
\text{C} \\
\text{AIH} = 10.**(—PPH) \\
\text{IH} = \text{AIH}/\text{GAMMAH} \\
\text{AKSO} = 10.**(—PKSO) \\
\text{AK11} = 10.**(—PK11) \\
\text{AK12} = 10.**(—PK12) \\
\text{AK13} = 10.**(—PK13) \\
\text{AK14} = 10.**(—PK14) \\
\text{AK25} = 10.**(—PK25) \\
\text{C} \\
\text{CALCULATES SOLUTION STATUS AT THE INITIAL PH ALWAYS ASSUMING} \\
\text{MONOMERIC HYDROLYSIS WITH NO PRECIPITATION.} \\
\text{C} \\
\text{INUM} = \text{AK11}/\text{IH}\plus{}2.\times\text{AK12}/(\text{IH}\times2)\plus{}3.\times\text{AK13}/(\text{IH}\times3)\plus{}4.\times\text{AK14}/(\text{IH}\times4) \\
\text{IDEN} = 1.\plus{}\text{AK11}/\text{IH}\plus{}\text{AK12}/(\text{IH}\times2)\plus{}\text{AK13}/(\text{IH}\times3)\plus{}\text{AK14}/(\text{IH}\times4) \\
\text{IST} = \text{ALT}/\text{INUM}/\text{IDEN} \\
\text{ALPHA0} = 1./\text{IST} \\
\text{ALPHA1} = \text{ALPHA0}\times\text{AK11}/\text{IH} \\
\text{ALPHA2} = \text{ALPHA0}\times\text{AK12}/(\text{IH}\times2) \\
\text{ALPHA3} = \text{ALPHA0}\times\text{AK13}/(\text{IH}\times3) \\
\text{ALPHA4} = \text{ALPHA0}\times\text{AK14}/(\text{IH}\times4) \\
\text{ALPHA25} = \text{ALPHA0}\times\text{AK25}/(\text{IH}\times2.5) \\
\text{ALS011} = \text{ALPHA0}\times(10.\times3.2)\times\text{SO4} \\
\text{ALS012} = \text{ALPHA0}\times(10.\times5.1)\times(\text{SO4}\times2) \\
\text{ALPHAS} = 0.00 \\
\text{NCAL} = \text{ALPHA1}\plus{}2.\times\text{ALPHA2}\plus{}3.\times\text{ALPHA3}\plus{}4.\times\text{ALPHA4}\plus{}2.5\times\text{ALPHA25} \\
\text{C} \\
\text{WRITE} (6,3005) \text{AIT} \\
\text{DO} 50 \text{I}=1,\text{NUMV} \\
\text{BH} = 10.**(—PH(I)) \\
\text{H} = \text{BH}/\text{GAMMAH} \\
\text{C} \\
\text{CALCULATES THE FRACTIONS OF ALUMINUM IN EACH FORM USING THE} \\
\text{CORRECT EQUATION.} \\
\text{C} \\
\text{IF} (\text{OPTION.EQ.0}) \text{THEN} \\
\text{ALPHA0} = 1./\left(1.\plus{}(10.\times3.2)\times\text{SO4}\plus{}(10.\times5.1)\times(\text{SO4}\times2)\plus{}\text{AK11}/\text{H}\right) \\
\text{ALPHA1} = \text{ALPHA0}\times\text{AK11}/\text{H} \\
\text{ALPHA2} = \text{ALPHA0}\times\text{AK12}/(\text{H}\times2) \\
\text{ALPHA3} = \text{ALPHA0}\times\text{AK13}/(\text{H}\times3) \\
\text{ALPHA4} = \text{ALPHA0}\times\text{AK14}/(\text{H}\times4) \\
\text{ALPHA25} = \text{ALPHA0}\times\text{AK25}/(\text{H}\times2.5) \\
\text{ALS011} = \text{ALPHA0}\times(10.\times3.2)\times\text{SO4} \\
\text{ALS012} = \text{ALPHA0}\times(10.\times5.1)\times(\text{SO4}\times2) \\
\text{ALPHAS} = 0.00 \\
\text{NCAL} = \text{ALPHA1}\plus{}2.\times\text{ALPHA2}\plus{}3.\times\text{ALPHA3}\plus{}4.\times\text{ALPHA4}\plus{}2.5\times\text{ALPHA25} \\
\text{ELSE} \\
\text{END IF} \\
\text{IF} (\text{OPTION.EQ.1}) \text{THEN} \\
\text{PST} = \text{ALT}—\left(1.\plus{}(10.\times3.2)\times\text{SO4}\plus{}(10.\times5.1)\times(\text{SO4}\times2)\right)\times\text{AKSO}/(\text{H}\times3) \\
\text{ALPHA0} = 1./\left(1.\plus{}(10.\times3.2)\times\text{SO4}\plus{}(10.\times5.1)\times(\text{SO4}\times2)\right) \\
\text{ALPHA1} = \text{ALPHA0}\times\text{AK11}/\text{H} \\
\text{ALPHA2} = \text{ALPHA0}\times\text{AK12}/(\text{H}\times2) \\
\text{ALPHA3} = \text{ALPHA0}\times\text{AK13}/(\text{H}\times3) \\
\text{ALPHA4} = \text{ALPHA0}\times\text{AK14}/(\text{H}\times4) \\
\text{ALPHA25} = \text{ALPHA0}\times\text{AK25}/(\text{H}\times2.5) \\
\text{ALPHAS} = 0.00 \\
\text{NCAL} = \text{ALPHA1}\plus{}2.\times\text{ALPHA2}\plus{}3.\times\text{ALPHA3}\plus{}4.\times\text{ALPHA4}\plus{}2.5\times\text{ALPHA25} \\
\text{ELSE} \\
\text{END IF}
IF (PST.GE.0.0) THEN
    ALPHA0 = AKSO*(H**3)/ALT
    ALPHA1 = AKSO*AK11*(H**2)/ALT
    ALPHA2 = AKSO*AK12*H/ALT
    ALPHA3 = AKSO*AK13/ALT
    ALPHA4 = AKSO*AK14/(ALT*H)
    ALPHA25 = AKSO*AK25*(H**0.5)/ALT
    ALPHA5 = PST/ALT
    ALSO11 = (10.**3.2)*SO4/ALPHA0
    ALSO12 = (10.**5.1)*SO4/(ALPHA0+ALPHA25)
    NCAL = ALPHA1+ 2.*ALPHA2+ 3.*ALPHA3+ 4.*ALPHA4+ 3.*ALPHAS + 2.5*ALPHA25
ELSE
    ALPHA0 = (1./((1.+(10.**3.2)*SO4+ (10.**5.1)*SO4**2)+AK11/H)
    ALPHA1 = ALPHA0*AK11/H
    ALPHA2 = ALPHA0*AK12/(H**2)
    ALPHA3 = ALPHA0*AK13/(H**3)
    ALPHA4 = ALPHA0*AK14/(H**4)
    ALPHA25 = ALPHA0*AK25/(H**2.5)
    ALSO11 = ALPHA0*(10.**3.2)*SO4
    ALSO12 = ALPHA0*(10.**5.1)*SO4**2
    NCAL = ALPHA1+ 2.*ALPHA2+ 3.*ALPHA3+ 4.*ALPHA4+ 2.5*ALPHA25
END IF
ELSE
    NCAL = ALPHA1+ 2.*ALPHA2+ 3.*ALPHA3+ 4.*ALPHA4+ 2.5*ALPHA25
END IF
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ENDIF
ALPHA1 = CK50*AK11/(H**1.5)/ALT
ALPHA2 = CK50*AK12/(H**0.5)/ALT
ALPHA3 = CK50*AK13/(H**0.5)/ALT
ALPHA4 = CK50*AK14/(H**0.5)/ALT
ALPH25 = CK50*AK25/ALT
ALPHAS = PST/ALT
ALSO11 = (10.*3.2)*SO4*ALPHA0
ALSO12 = (10.*5.1)*SO4*ALPHA0
NCAL = ALPHA1+2.*ALPHA2+3.*ALPHA3+4.*ALPHA4+2.5*ALPHAS

ALPHA1 = CK50*AK11/H
ALPHA2 = CK50*AK12/(H**2)
ALPHA3 = CK50*AK13/(H**3)
ALPHA4 = CK50*AK14/(H**4)
ALPH25 = CK50*AK25/(H**2.5)
ALSO11 = ALPHA0/(10.*3.2)*SO4
ALSO12 = ALPHA0/(10.*5.1)*SO4
ALPHAS = 0.00
NCAL = ALPHA1+2.*ALPHA2+3.*ALPHA3+4.*ALPHA4+2.5*ALPHAS

END IF
ELSE
ALPHA0 = 1./(1.+(10.*3.2)*SO4+10.*5.1)*SO4*2+AK11/H
+AK12/(H**2)+AK13/(H**3)+AK14/(H**4)+AK25/(H**2.5))
ALPHA1 = ALPHA0*AK11/H
ALPHA2 = ALPHA0*AK12/(H**2)
ALPHA3 = ALPHA0*AK13/(H**3)
ALPHA4 = ALPHA0*AK14/(H**4)
ALPH25 = ALPHA0*AK25/(H**2.5)
ALPHAS = 0.00
NCAL = ALPHA1+2.*ALPHA2+3.*ALPHA3+4.*ALPHA4+2.5*ALPHAS

ENDIF
ENDIF
IF (OPTION.EQ.4) THEN
CKSO = AKSO/SO4
PST = ALT-1.+(10.*3.2)*SO4+10.*5.1)*SO4*2)*CKSO
+H-CK50AK11-CK50AK12/H-CK50AK13/(H**3)-CK50AK14/(H**4)-CK25/(H**2.5))
END IF

elseif
ALPHA0 = 1./(1.+(10.*3.2)*SO4+10.*5.1)*SO4*2+AK11/H
+AK12/(H**2)+AK13/(H**3)+AK14/(H**4)+AK25/(H**2.5))
ALPHA1 = ALPHA0*AK11/H
ALPHA2 = ALPHA0*AK12/(H**2)
ALPHA3 = ALPHA0*AK13/(H**3)
ALPHA4 = ALPHA0*AK14/(H**4)
ALPH25 = ALPHA0*AK25/(H**2.5)
ALPHAS = 0.00
NCAL = ALPHA1+2.*ALPHA2+3.*ALPHA3+4.*ALPHA4+2.5*ALPHAS

END IF
ELSE
NOS = (ML(I)*OHC/MLT-IH+H)/ALT+AIT
WRITE (6,5001) PHII,ML(I),ALPHA0,ALPHA1,ALPHA2,ALPHA3,
ALPHA4,ALPH25,ALPHAS,ALSO11,ALSO12,NCAL,NOS
50 CONTINUE
10 STOP
1000 FORMAT (A72)
1001 FORMAT (A72)
2000 FORMAT (E10.4,5X,E6.4,4X,E10.4)
2001 FORMAT (E0,'BASE CONC. =',E10.4,5X,'GAMMA H = ',E6.4,9X,'TOTAL ALTIF02810
+','E10.4)
Following is an example input and output for use with TIF1. Use of the example data set should result in the example output.

TITRATION DATA FOR 1E-03M Al;H IN 1.0M KCl
9.7802E-02 0.7433 9.2586E-04
0.01 000000 50.0 4.00 0000000 19.0076
0.00000 1.00000
 4.00 0.00
 4.43 0.08
 4.49 0.10
 4.67 0.18
 4.75 0.28
 4.76 0.38
 4.79 0.48
 4.82 0.58
 4.85 0.68
 4.89 0.78
 4.93 0.88
 4.98 0.98
 5.04 1.08
 5.14 1.18
 5.31 1.28
 5.90 1.38
 7.03 1.48

This is the output which should be obtained if TIF1 is run with the data set shown above.
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<th>pH</th>
<th>PK0</th>
<th>PK11</th>
<th>PK12</th>
<th>PK13</th>
<th>PK14</th>
<th>PK25</th>
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Appendix B. Data Sets

In this appendix, the data sets obtained from the titration patterns are presented. The data sets for the KCl solutions will be presented as TIF data, those from K₂SO₄ will be presented as TIFIT data sets as the n = 2.5 species was not found to be significant.
Data From the KCl Solution Titrations

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Appendix B. Data Sets
TITRATION DATA FOR 1E-04 M AL, H IN 1.0M KCL

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### TITRATION DATA FOR 0.001M AL₃⁺ IN 0.1M KCl

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<th>f</th>
<th>t (min)</th>
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- App. B: Data Sets 152
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TITRATION DATA FOR 1E-04M AL•H IN 0.01M KCL

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Appendix B. Data Sets
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