

DATE ISSUED JAN 23 1980

ORNL-5623

79 12 13

# ornl

OAK  
RIDGE  
NATIONAL  
LABORATORY

UNION  
CARBIDE

## The Solubility of Gibbsite ( $\alpha$ -Al(OH)<sub>3</sub>) in 1 Molal NaCl as a Function of pH and Temperature

B. F. Hitch  
R. E. Mesmer  
C. F. Baes, Jr.  
F. H. Sweeton

OPERATED BY  
UNION CARBIDE CORPORATION  
FOR THE UNITED STATES  
DEPARTMENT OF ENERGY

Printed in the United States of America. Available from  
National Technical Information Service  
U.S. Department of Commerce  
5285 Port Royal Road, Springfield, Virginia 22161  
NTIS price codes—Printed Copy: A03; Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States nor any agency thereof, nor any of their employees, makes any warranty, expressed or implied, or assumes any legal liability or responsibility for any third party's use or the results of such use of any information, apparatus, product or process disclosed in this report, or represents that its use by such third party would not infringe privately owned rights.

ORNL-5623  
Dist. Category UC-4

Contract No. W-7405-eng-26

CHEMISTRY DIVISION

THE SOLUBILITY OF GIBBSITE ( $\alpha$  -  $\text{Al}(\text{OH})_3$ ) in 1 MOLAL NaCl  
AS A FUNCTION OF pH AND TEMPERATURE

B. F. Hitch, R. E. Mesmer<sup>6\*</sup>, C. F. Baes, Jr.<sup>01</sup>, and F. H. Sweeton<sup>04</sup>

Date Published - January 1980

OAK RIDGE NATIONAL LABORATORY  
Oak Ridge, Tennessee 37830  
operated by  
UNION CARBIDE CORPORATION  
for the  
DEPARTMENT OF ENERGY



## CONTENTS

	<u>Page</u>
Abstract . . . . .	1
1. INTRODUCTION . . . . .	1
1.1 General . . . . .	1
1.2 Aluminum(III) Hydrolysis. . . . .	3
1.3 Column Method . . . . .	6
1.4 Crystal Size Effect . . . . .	10
2. EXPERIMENTAL . . . . .	12
2.1 Analytical Methods for Aluminum . . . . .	12
2.1.1 Greater Than $10^{-6}$ m Al(III) . . . . .	12
2.1.2 Less Than $10^{-6}$ m Al(III) . . . . .	13
2.2 Sizing Gibbsite Crystals . . . . .	15
2.2.1 Elutriation . . . . .	15
2.2.2 Mechanical Seiving . . . . .	15
2.3 pH Measurements . . . . .	16
2.4 Columns and Apparatus . . . . .	16
3. RESULTS AND OBSERVATIONS . . . . .	18
3.1 High pH . . . . .	18
3.2 Low pH . . . . .	22
3.3 Neutral pH . . . . .	24
3.4 Comparison with Other Results . . . . .	27
REFERENCES . . . . .	30



THE SOLUBILITY OF GIBBSITE ( $\alpha$  -  $\text{Al}(\text{OH})_3$ ) in 1 MOLAL NaCl  
AS A FUNCTION OF pH AND TEMPERATURE

B. F. Hitch, R. E. Mesmer, C. F. Baes, Jr., and F. H. Sweeton

ABSTRACT

This report summarizes the status of our project on hydroxide solubilities at the time of departure of one of the staff (BFH) from the laboratory. Herein are discussed the advantages and disadvantages of the column approach to study the pH dependence of the solubility of well crystallized hydroxides, and preliminary results on gibbsite ( $\text{Al}(\text{OH})_3$ ) are presented. Good results have been obtained in the basic region, and the temperature dependence of the equilibrium quotient for the reaction  $\text{Al}(\text{OH})_3(\text{c}) + \text{OH}^- \rightleftharpoons \text{Al}(\text{OH})_4^-$  in 1m NaCl is given by

$$\log Q_{s14}^b = 3.3766 - 1326.4/T$$

with an agreement faster of 0.035 (unit weights). These measurements were made over the temperature range 35-90°C at the base concentrations of 0.01 m and 0.1 m NaOH.

The principal difficulty with the column approach is the strong buffering capacity of the column itself for equilibrations in the near neutral pH region. We found that the capacity could be accounted for in terms of monolayer adsorption (or reaction) of  $\text{H}^+$  ions. Although insufficient evidence for equilibrium was obtained, data in the pH range 3-4 gives the value of  $-7.20 \pm 0.15$  at 60°C for the  $\log Q_{s10}$  for the reaction  $\text{Al}(\text{OH})_3(\text{c}) + 3\text{H}^+ \rightleftharpoons \text{Al}^{3+} + \text{H}_2\text{O}$ .

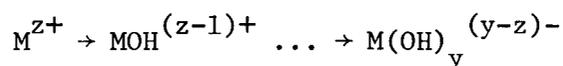
Results of the solubility measurements in the near neutral region are only preliminary due to difficulties with the analytical method and the very low levels attained,  $4 \times 10^{-8}$  m -  $7 \times 10^{-7}$  m, are sometimes impossibly low to be consistent with the amounts of  $\text{Al}(\text{OH})_4^-$  expected. Modifications of the approach and analytical methods are being made to better establish the important mononuclear equilibria in the near neutral region and to extend the measurements to high temperatures.

---

## 1. INTRODUCTION

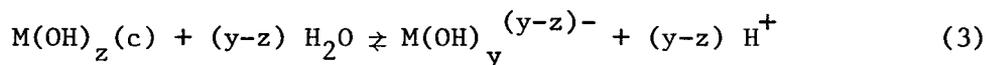
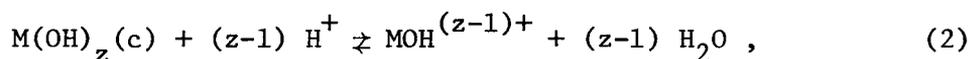
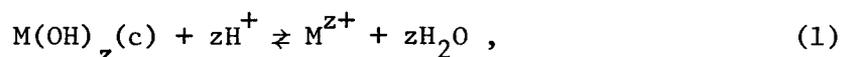
### 1.1 General

Most metal cations form a series of mononuclear hydrolysis products



(where  $y$  usually does not exceed 4), each of which can be an important species over the appropriate range of pH, provided the concentration of the metal is low enough that polynuclear species  $M_x(OH)_y^{(xz-y)+}$  are not formed in appreciable amounts. Such mononuclear species therefore determine the chemistry of the metal valence - for example, its stability with respect to oxidation or reduction, the tendency to form other soluble complexes, and the solubility of the hydroxide  $M(OH)_z$  - whenever the metal occurs at low concentration in aqueous systems. Such systems that are becoming increasingly important include the pressurized aqueous systems at elevated temperatures in LWRs, geothermal brines, natural waters, and the aqueous solutions in living systems.

The stability and other thermodynamic properties of the mononuclear hydrolysis products are often poorly known because polynuclear hydrolysis products interfere at the (higher) metal concentrations accessible to study by the usual methods. The most promising means to investigate mononuclear hydrolysis products is the measurement of the low concentration of the metal in solutions at equilibrium with the stable hydroxide or oxide phase. From such data, taken as a function of pH, the equilibrium constants for the reactions



can be determined, and by appropriate combination of these, the stability constants of the separate hydrolysis products can be derived. In such measurements it is essential that (1) equilibrium between the solid and aqueous phase is attained, (2) the solid phase is crystalline material of sufficiently large crystal size that surface energy effects are negligible, and (3) the ionic strength is controlled to minimize activity coefficient variation. Most previous efforts to employ this method have been compromised by failure to meet one (usually the second) or more of these requirements.

The results for a given  $M^{z+}$ -OH system, coupled with the known thermodynamic properties of the solid phase (e.g.,  $M(OH)_z$ ), will yield the thermodynamic properties of all the mononuclear hydrolysis products of the cation that are stable.

The purpose of this study was to study the mononuclear hydrolysis steps for aluminum(III) as a function of pH, temperature, and medium for the several aluminum hydroxide and oxide phases using the column method. The objective was met to a limited extent when the project was interrupted by the departure of one of us (BFH) from the Laboratory. This report is written to summarize the status of the project at that time and to preserve the information.

## 1.2 Aluminum(III) Hydrolysis

Aluminum hydrolysis behavior is important in understanding (1) corrosion behavior of aluminum and aluminum bearing alloys, (2) the complex chemistry of aluminosilicates and other natural materials, and (3) industrial and commercial applications such as gels in water treatment.

The principal emphasis in this program is the hydrolysis behavior of  $Al^{3+}$  ion in dilute solution. The solubility method is relatively insensitive to the precise identity of polynuclear species but sometimes reflects their contribution in the regions of high solubility. It is, however, most useful in evaluating the mononuclear equilibria. The hydrolysis behavior of  $Al^{3+}$  has been reviewed recently and the following general conclusions can be made [Baes and Mesmer (1976)].

The stable hydrolysis products are indicated on the distribution plots and the solubility plot in Figs. 1 and 2. Of the four mononuclear species  $Al(OH)_n^{(3-n)+}$ , the well established ones are  $Al(OH)^{2+}$  and  $Al(OH)_4^-$ . A large species, probably  $Al_{13}O_{14}(OH)_{24}^{7+}$ , is predominant in the pH region 3.5 to 4.5 at 25°C in supersaturated solutions. Also, small polynuclear species such as dinuclear and trinuclear ones exist over narrow composition limits in the acidic region. Gibbsite,  $\alpha-Al(OH)_3$ , is the stable crystalline hydroxide at low temperatures.

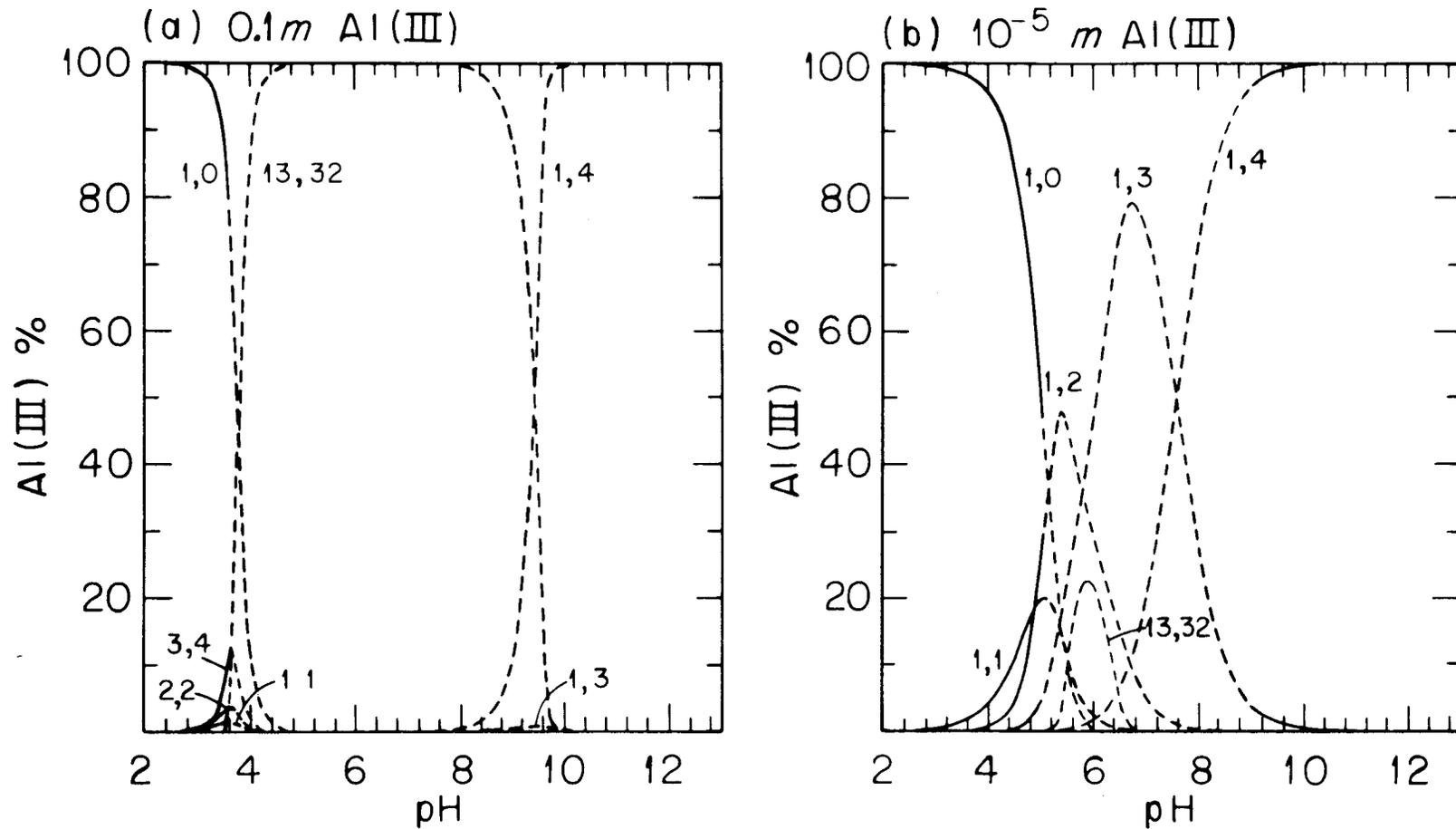


Fig. 1. The Distribution of Hydrolysis Products  $\text{Al}_x(\text{OH})_y^{(z-x-y)+}$  designated as (x,y) at  $I = 1 \text{ m}$  and  $25^\circ\text{C}$  in (a)  $0.1 \text{ m Al(III)}$  and (b)  $10^{-5} \text{ m Al(III)}$  from the data in Table I. Dashed lines indicate regions of supersaturation.

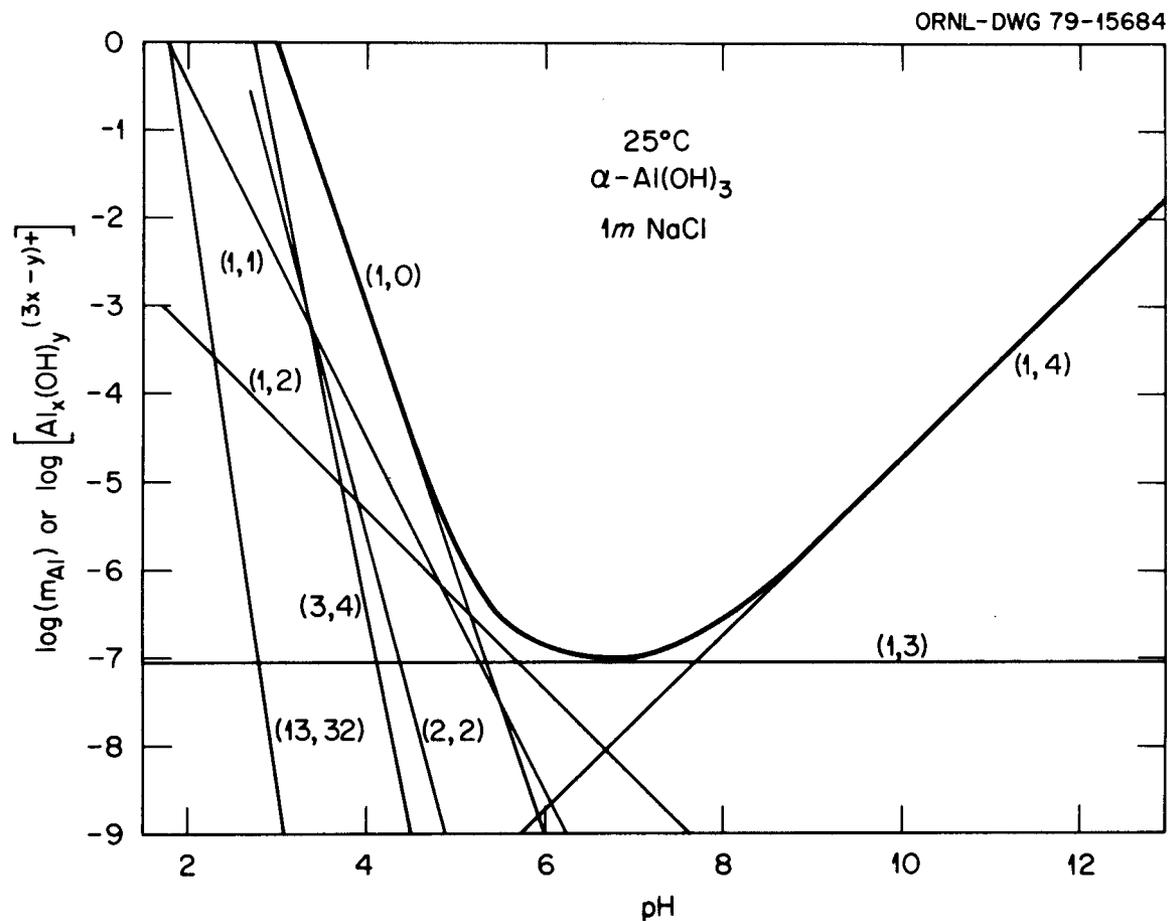
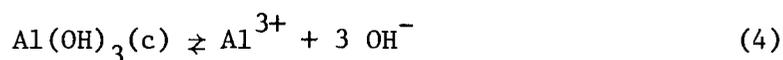


Fig. 2. Solubility and Solution Composition for Gibbsite,  $\alpha\text{-Al(OH)}_3$ , at 25°C and  $I = 1\text{ m}$  from the data in Table I. The heavy curve is the total concentration of Al(III) and the straight lines represent the concentration of the species  $\text{Al}_x(\text{OH})_y(3x-y)^+$  designated as (x,y).

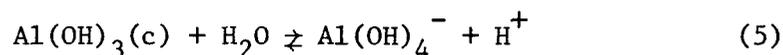
A summary of selected values for the hydrolysis reactions of aluminum(3+) taken from the literature along with estimates of their salt effects are given in Table I using the format employed by Baes and Mesmer (1976).

A reevaluation of data on the equilibrium of the gibbsite with the  $\text{Al}^{3+}$  ion in dilute solution suggests that the results of Kittrick (1966)\* and of Singh (1974) are probably most accurate for  $K_{s10}^b$  (see Eq. 4). This gives for 25°C



$$\log K_{s10}^b = -34.06 \pm 0.05.$$

Also, from the results of Kittrick



$$\log K_{s14} = -15.30 \pm .06.$$

### 1.3 Column Method

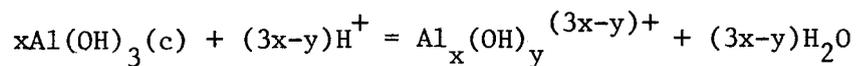
There are four principal considerations in equilibrium studies of this kind: the characterization of the solid phase, the pH measurements, the metal ion concentration determinations, and the criterion of establishment of equilibrium. The purity of the phase and the crystal size (to be discussed in the next section) must be controlled. Also, the precision of the pH measurements must be high since the dependence of the solubility on pH varies greatly (the slope of log solubility vs pH is  $y - xz$  or minus the charge on the species). One factor affecting the accuracy of such measurements is the low buffering in the solution

---

\*Small corrections were made for hydrolysis and temperature since these data pertained to  $24 \pm 1^\circ\text{C}$ . Other data in the table were taken from the review by Baes and Mesmer (1976).

Table I. SUMMARY OF  $\text{Al}^{3+}$  HYDROLYSIS BEHAVIOR AT 25°C

$$\log Q_{xy} = \log K_{xy} + aI^{1/2}/(1+I^{1/2}) + bm_X^*$$



Species or Phase	Log $K_{xy}$	a	b	Reference
$\text{Al}(\text{OH})^{2+}$	-4.97	-2.044	0.52	a
$\text{Al}(\text{OH})_2^+$	-9.3	-3.066	0.55	a
$\text{Al}(\text{OH})_3(\text{aq})$	-15.0	-3.066	0.45	a
$\text{Al}(\text{OH})_4^-$	-23.12	-2.044	0.36	a, b
$\text{Al}_2(\text{OH})_2^{4+}$	-7.7	0	(0)	a
$\text{Al}_3(\text{OH})_4^{5+}$	-13.94	1.022	(0)	a
$\text{Al}_{13}\text{O}_4(\text{OH})_{24}^{7+}$	-98.73	-18.40	3.55	a
$\alpha\text{-Al}(\text{OH})_3(\log Q_{s10})$	7.97 <sup>**</sup>	3.066	-0.45	a, b, c

<sup>a</sup>Baes and Mesmer (1976)

<sup>b</sup>Kittrick (1966)

<sup>c</sup>Singh (1974)

\*  $m_X$  represents the molality of the medium salt

\*\*  $\log K_{s10}$

in some regions of pH. Likewise, the metal ion concentrations are sometimes quite low and difficult to determine with precision. Finally measurements must be made from super- and undersaturation to establish that equilibrium is attained.

Two generally different approaches are available for carrying out such equilibrations - static (or batch) and flow-through packed-column experiments. In the more traditional batch method a dilute slurry is equilibrated and sampled (after filtering or settling) for analysis. Column equilibrations have been used extensively especially for rapidly equilibrating systems such as ion-exchange resins. One of the principal users of solubility measurements on hydroxides has been D. Dyrssen of Sweden (Dyrssen and Tyrrell, 1961; Dyrssen and Lumme, 1962).

There are several important advantages of the column approach which are listed below:

- (1) the high (maximum) solid-to-liquid ratio and therefore rapid equilibration,
- (2) elimination of attrition of the solid in the bed,
- (3) ease of filtering, sampling, and delivery of solution to auxiliary systems for pH or metal ion measurements.

The principal disadvantages are:

- (1) the effects of impurities or adsorption phenomena,
- (2) great analytical demands for efficient use of the columns,
- (3) greater difficulty of replication compared with batch methods.

The sizing of the column is a simple matter only when the kinetics of the dissolution and deposition processes are known in detail, although this is rarely, if ever, the case. Probably the best approach is to begin with a few kinetic experiments so that a refined apparatus can be designed to produce the desired samples in a practical time. If, for example, the reaction follows the simple rate expression (for slow reactions),

$$\frac{dC}{dt} = k \frac{A}{V} (C_e - C) \quad (6)$$

where A is the total area of the solid, V is the liquid volume in the packed column and  $C_e$  is the equilibrium concentration, the half-life is

$$t_{1/2} = \frac{0.693 V}{kA} \quad (7)$$

The residence time for the desired attainment of equilibrium is

$$t_n = \frac{V \ln(1-n)^{-1}}{kA} = -t_{1/2} \ln(1-n) \quad (8)$$

where n is the fraction of the equilibrium value desired or  $C/C_e$ . The residence time is also given by the liquid volume V divided by f, the flow rate. Therefore the area of solid needed is

$$A = \frac{f (\ln(1-n)^{-1})}{k} \quad (9)$$

When the desired values of f and n are chosen and the specific rate constant is known, the required area of the saturating phase can be calculated.

From the data in the literature it is evident that the equilibrium with gibbsite is reaction limited. Apps (1970) reported that a 2% slurry attained equilibrium in 24 hours in the pH range 8-12 at temperatures from 303°K to 363°K. Russell et al. (1955) reported times ranging from eleven days to one day for equilibrations at 313 to 373°K with no dependence given for the base concentration which ranged from 0.5 m to 8 m NaOH. (Also, the solid-liquid ratio was not specified.) The latter gibbsite can be presumed to have been large crystals since it was prepared by the Bayer process. The pictured apparatus suggests the use of a dilute slurry (ca. 20%). More quantitative measurements of the kinetics of the dissolution of gibbsite were reported by Packter and Dhillon (1973). An approximate value of k in Eq. 6 above derived from their data at 65°C is  $1.7 \times 10^{-4} \text{ cm hr}^{-1}$ . For a flow rate of 10 ml/hr and  $n = 0.99$ , Eq. 9 gives an area of  $2.7 \times 10^5 \text{ cm}^2$

(27 m<sup>2</sup>). For 10 μm cubic particles this corresponds to 112 g of saturating bed.

For the cases where the processes are diffusion controlled very small bed volumes would suffice if the solubilities were low. This can be demonstrated by the following example: One wishes to equilibrate 100 ml of solution with a solid (within 1% of the saturation concentration) where the kinetics are diffusion limited. Assume the crystals are 100 μm in diameter.

The equilibration time can be estimated from the expression given by Kraus et al. (1962) for a static packed bed

$$t_n < \frac{r^2}{D} [-0.05 - 0.233 \log (1-n)] \quad (10)$$

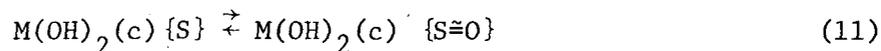
where  $r$  is the crystal radius ( $5 \times 10^{-3}$  cm),  $D$  is the diffusion coefficient ( $\sim 10^{-5}$  cm<sup>2</sup>/sec) and  $n$  is the fraction of the equilibrium value. The computed equilibration time for  $n$  equal to 0.99 is about one sec. If the void fraction in the column is 0.3, a column volume of 0.1 cm<sup>3</sup> is adequate to saturate 100 cm<sup>3</sup> of solution in one hour. Of course, the bed would dissolve if the solid is even slightly soluble. Alternatively, if the bed volume were 10 cm<sup>3</sup> a flow rate ( $f$ ) of 3 cm<sup>3</sup>/sec could be used since  $f = V/t_R$ , where  $t_R$  is the residence time and  $V$  is the volume of liquid in the column. These estimates show that sizing a column for diffusion controlled processes is no practical concern.

#### 1.4 Crystal Effect

The "ripening" of precipitates (or growth of crystals) was first recognized in 1813 by Wollaston and the effect of crystal size on the thermodynamic properties is now well known. The Kelvin equation for liquids was applied to solids by 1900. The Ostwald (1900)-Freundlich (1926) expression relates the solubility of solids to the radius of the solid. The situation for crystals is, however, not entirely analogous to liquids since there are no curved surfaces and there is anisotropy. It is the different activity associated with the different

faces of a crystal which leads to the characteristic crystal habits. In 1960 Enüstün and Turkevich expressed the effect of the average surface free energy,  $\bar{\gamma}$ , ( $\text{erg cm}^{-2}$ ) on the solubility for monodispersed crystals.

The change in free energy for the process



can be expressed according to the Enüstün and Turkevich treatment as

$$\Delta G = -\frac{2}{3} \bar{\gamma} S \quad (12)$$

where  $S$  is the surface area of one mole of  $\text{M(OH)}_2$ .

In terms of the equilibrium constant for the solubility reaction written in the hydrogen ion form,  $K_{s10}$ , [see reaction (1)] this becomes

$$-RT \ln [K_{s10}(S)/K_{s10}(0)] = -\frac{2}{3} \bar{\gamma} S \quad (13)$$

The molar surface area can also be related to a characteristic dimension of the crystals,  $d$  (a dimension such that  $\text{area} = kd^2$ ) or

$$S = M\alpha/\rho d \quad (14)$$

where  $M$ ,  $\rho$ , and  $\alpha$  are respectively the molecular weight, the density, and the geometrical factor ( $\alpha = kd^3/v$  where  $v$  is the volume of the crystal).

Usually finely divided crystals will grow only slowly under conditions of very low solubility (because of the small supersaturations which can be achieved). Therefore, it is necessary to find conditions of greatly enhanced solubility to attain significant growth rates. Likewise, metastable phases often do not readily convert to stable phases since the critical nuclei of the stable phase have enhanced solubilities over the macroscopic crystals of that phase.

A number of previously studied systems summarized by Schindler (1967) indicate that most hydroxides have  $\bar{\gamma}$  values below  $1,000 \text{ erg cm}^{-2}$ . Assigning values for  $\bar{\gamma}$ ,  $M$ , and  $\rho$  ( $1,000 \text{ erg cm}^{-2}$ ,  $100 \text{ g mole}^{-1}$ , and  $3 \text{ g cm}^{-3}$ ), we calculate for spheres or cubes ( $\alpha=6$ )  $\log [K_{s10}(S)/K_{s10}(0)]$  is 0.023 where  $d$  is  $1 \text{ }\mu\text{m}$  or  $S$  is  $200 \text{ m}^2/\text{mole}$  (specific area is  $2 \text{ m}^2/\text{g}$ ), i.e., an increase in solubility of 5.4%. For very fine crystals ( $200 \text{ \AA}$ ) the solubility is increased by fourteen times. On the other hand, if the crystal size is greater than a few microns the effect on solubility becomes negligibly small.

## 2. EXPERIMENTAL

### 2.1 Analytical Methods for Aluminum

2.1.1 Greater Than  $10^{-6} \text{ m Al(III)}$ . There are numerous methods described in the literature which use aluminon to determine aluminum concentration spectrophotometrically. We chose one described by Hsu (1963) which worked well for all of our samples above  $10^{-6} \text{ m}$  (molal) aluminum. The developed lake appears to be stable over periods of several days. One difficulty with the aluminon method is the reagent itself; the aluminon absorbs in the same region (430-440 nm) as the aluminum complex. Several different batches of the reagent, which were obtained from Fischer Scientific Co., gave high blank values of 0.250 to 0.275 absorbance units. Frequent checks using aluminum standards showed that the high blanks were not a problem with samples containing greater than  $10^{-6} \text{ m}$  aluminum.

Our initial procedure was to develop the samples according to Hsu then to measure the absorbance of the sample against the absorbance of an aluminon blank at 530 nm with a Beckman DU spectrophotometer. Typically, several samples were prepared at one time along with three aluminum standards which bracketed the sample concentrations. The concentration of aluminum in the samples was determined from the calibration curves produced by the aluminum standards.

During the low pH runs we encountered interference from iron when the platinum liner in the column failed. Iron(III) causes serious

interference in the aluminon method since it absorbs at nearly the same wavelength as the aluminum complex. Iron(II) does not interfere, and several authors have described various reductants to eliminate the interference from iron(III). Ascorbic acid (Jayman and Swasubaramaniam, 1974) appears to be one of the few reductants which eliminates the interference of iron and does not bleach out the color of the aluminon reagent. All of our low and neutral pH samples were treated with ascorbic acid.

During the time when we first found iron interference in our samples we switched to a Carey 14 scanning spectrophotometer for sample analysis. This instrument was used in all subsequent analyses. Since many ions do interfere with the aluminon method, a scanning spectrophotometer is far superior to fixed wavelength machines. The recorded spectra allow one to see any change which might result from interfering ions (see Fig. 3).

2.1.2 Less Than  $10^{-6}$  m Al(III). The aluminon method of Hsu works well with samples which contain  $> 10^{-6}$  m aluminum. However, our samples in the neutral pH region contained much less than this so we attempted to concentrate them before applying the Hsu method. An ion-exchange column was used to concentrate the aluminum. The column consisted of a 2 ml pipette filled with 1 ml of Dowex 50W-X8 cation-exchange resin (from BiO-Rad Laboratories). A funnel was attached to the top end of the column and Teflon tubing with a pinch clamp was used to close off the lower end. After the resin was cleaned our usual procedure was to flush the column with 1 N HCl, then add the samples, which had been made 0.1 N in HCl. Flow rates of 8-15 ml an hour were typically used for a 200-250 ml sample. Deionized H<sub>2</sub>O was used to flush the column after the sample was passed. Aluminum was then eluted from the column as aluminate using 5 or 10 ml aliquots of 0.5 N NaOH. Usually at least 4-6 aliquots were used to ensure that all of the aluminum was taken off the resin. Deionized H<sub>2</sub>O again was used to flush the column before acid was added for the next cycle.

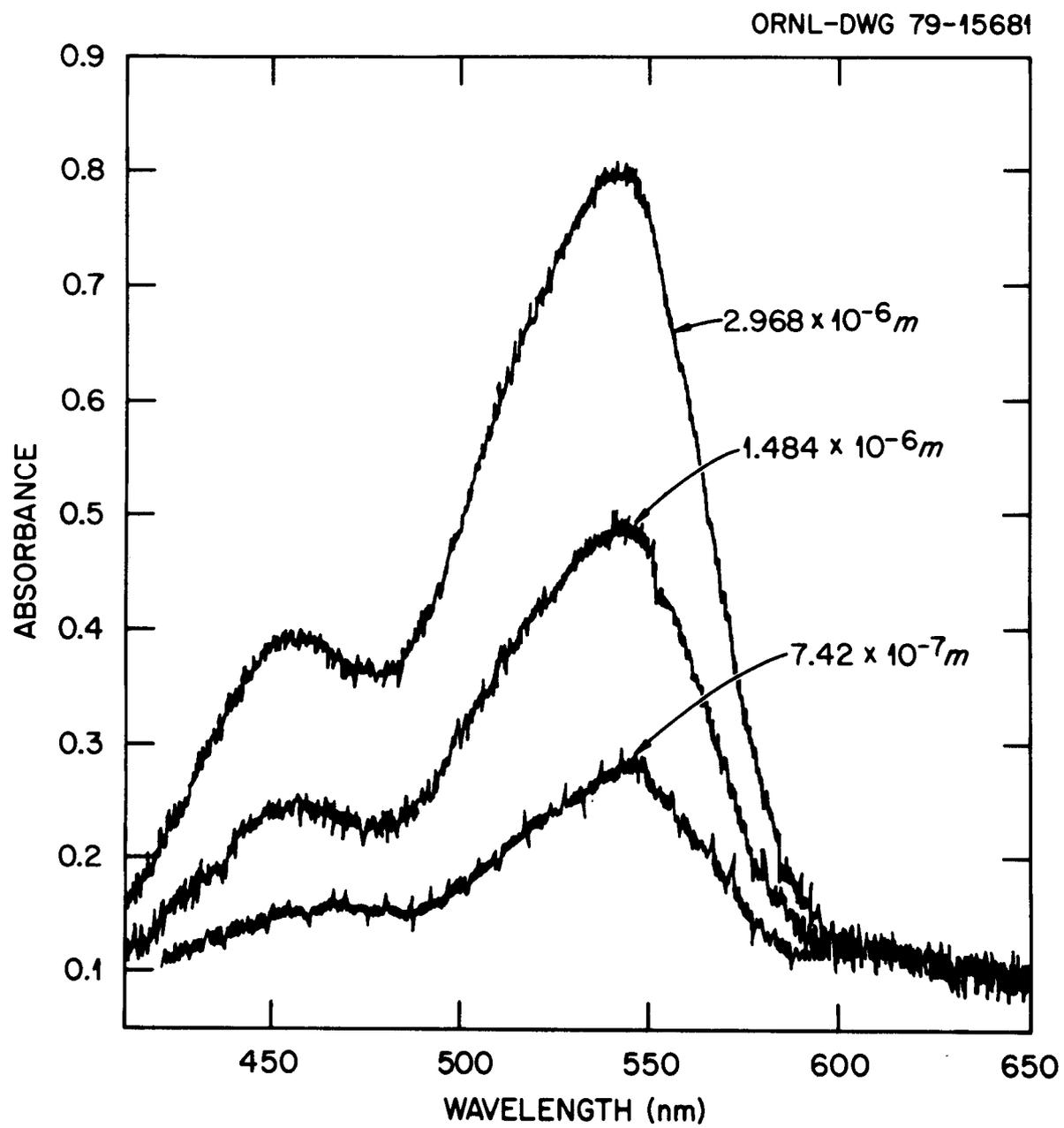


Fig. 3. Absorption Spectra of Al(III) Standards in the Region 400-650 nm.

Aluminum standards in the concentration range of  $10^{-7}$  m to  $10^{-8}$  m were prepared, added to the column, eluted with NaOH, and analyzed by the aluminon method. In each case 95-100% of the original aluminum was found. However, a relatively large blank had to be subtracted for the aluminum in the NaOH and the reproducibility of this limited the precision of the method.

## 2.2 Sizing Gibbsite Crystals

2.2.1 Elutriation. The column we selected for use in our solubility studies required a substantial amount (75-100 g) of single crystal gibbsite. A crystal size range of 10-50  $\mu\text{m}$  was desirable to satisfy the need for a large surface area yet eliminate the possibility of the solubility being controlled by very fine material.

We first tried the elutriation method of particle separation as described by Beavers and Jones (1966). This procedure is based on a controlled flow through several vessels shaped like separatory funnels; the liquid leaves the top of one vessel and enters the bottom of the next one. Each subsequent vessel is larger than the preceding one, thus, at constant flow, particles have a longer time to settle in each subsequent vessel.

Several attempts were made to obtain a particle size range of 10 to 50  $\mu\text{m}$  but were not successful. One problem was that the particles seemed to stick together or agglomerate in the liquid and settle.

2.2.2 Mechanical Seiving. Several grades of  $\text{Al}(\text{OH})_3$  were kindly supplied by Alcoa for our experiments. We selected Alcoa series C-331 because this grade contains low amounts of iron, sodium oxide, and silica and because the average crystal size of this grade is approximately 10  $\mu\text{m}$ . This material was sized by means of a sonic sifter (manufactured by Allen-Bradley Co.), a mechanical sifter which utilizes a trapped column of air to agitate particles on sieves. The rims of the screens fit together to form a solid outer shell; this allows rubber diaphragms on each end of the column to be pulsed by a vibrator. The motion of the

diaphragm causes the air column inside to continuously agitate particles on the screens.

We first screened the gibbsite crystals through a 150  $\mu\text{m}$  screen, then through a 38  $\mu\text{m}$  screen and finally through a 10  $\mu\text{m}$  screen. The yield from the 10  $\mu\text{m}$  screening was 1-2 grams over an 8-hour period. Although this is a slow process, all the gibbsite used in our column work was sized in this manner. Microscopic examination confirmed that indeed all of our material was in the range of 10-40  $\mu\text{m}$ . The BET surface area was 0.65  $\text{m}^2/\text{g}$ .

### 2.3 pH Measurements

The pH was measured with a Corning combination electrode from which the bridge solution was replaced with 1 m NaCl. The standard solution for calibration of a 801A Orion pH meter used to make the potential measurements was 0.001 m HCl in 1 m NaCl. Therefore, the definition of pH is  $(-\log m_{\text{H}^+})$  rather than the common NBS definition,  $-\log a_{\text{H}^+}$ . The electrode was held in a flow-through tube for some of the measurements. In others a thermostatted sample of solution was measured batch-wise.

### 2.4 Columns and Apparatus

For the high and low pH runs a column was fabricated using 1.27 cm 316 stainless steel pipe with a platinum liner. The liner was rolled from platinum sheet and welded, then inserted inside the stainless tubing and flared over each end. Machined Teflon fittings contacted the platinum on each end of the column and were held in place by stainless steel nuts. The column was 1.3 cm in diameter and 40 cm long. The Teflon fitting at the lower end of the column contained a filter disk of porous Teflon pressed into a recess. This porous Teflon prevented material from the column entering the samples.

The sized gibbsite crystals, described in the previous section, were added to the column as a slurry in deionized  $\text{H}_2\text{O}$ . This procedure

took several days since the water passed very slowly through the Teflon frit at the bottom of the column. The dead volume at the top of the column was about 8 ml. In all the experiments flow rates of about 0.5 ml/hr to 2 ml/hr were used and the solutions were gravity fed.

For the near neutral pH runs a Teflon column was fabricated to replace the platinum lined column. This column was slightly smaller internally than the previous column and used Teflon feed exit lines. The exit line was connected to a glass apparatus which contained a glass electrode and could be immersed in a water bath. The pH of the sample exiting the column was continuously monitored with an Orion 801A pH meter. The water bath used to contain the electrode apparatus was the same one used to circulate water through the column jacket, thus both the column and the pH glass electrode were always at the same temperature.

Gibbsite removed from the platinum lined column was equilibrated with 500 cc of 1 m NaCl solution. The pH of the solution had initially been adjusted to 8.1 but after one week (the solution was periodically stirred and the pH measured), the pH was 7.24 and appeared stable. Some liquid was decanted and the remainder used to slurry the  $\text{Al}(\text{OH})_3$ . The Teflon column was filled with this slurry and the liquid allowed to drain through the column until it was completely filled with crystalline gibbsite.

After observing the flow through the column, it was placed inside a 5 cm glass water jacket equipped with metal flanges. The water jacket was then connected to a Haake Model FS external circulating water bath. A mixture of ethylene glycol and  $\text{H}_2\text{O}$  was used for the thermostating fluid. The Teflon fittings on each end of the column exited at the metal flanges on both ends of the water jacket and a water tight seal was made with swagelok fittings.

All feed solution containers, entrance lines, exit lines, and sample containers were polyethylene or Teflon. The feed solution container as well as the sample collector was fitted with Ascarite traps to reduce  $\text{CO}_2$  contamination.

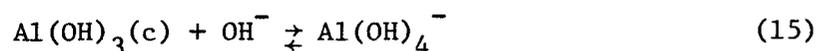
## 3. RESULTS AND OBSERVATIONS

## 3.1 High pH

We initially attempted to use 0.005 m NaOH feed solution but because of the low aluminum content and CO<sub>2</sub> contamination decided to increase the base concentrations. In the A-Run the feed solution was 1 m NaCl and 0.01055 m in NaOH; data from this run are shown in Table II. At the end of Run A we switched to a neutral feed solution containing 1 molal NaCl (pH ~ 6.5). After approximately 110 grams of feed solution had passed through the column, the Al concentration dropped below our detection limit ( $1.0 \times 10^{-6}$ , at the time) and the pH of the samples varied between 7 and 8.5.

The next run (C-Run) was made using a feed solution with the following compositions: Na<sup>+</sup>-0.8931 m, Cl<sup>-</sup>-0.7959 m, Al(OH)<sub>4</sub><sup>-</sup>, 0.01876 m, and OH<sup>-</sup>-0.07836 m (I = 0.89 m). We added the aluminum to the feed solution since we expected a rather high concentration in our samples. Stoichiometrically this was the same as starting with a solution of 0.7959 m NaCl and 0.09712 m NaOH. The data from this run are shown in Table III. We do not know the source of the scatter shown by the data in Fig. 4.

These data were analyzed in terms of the equilibrium



for which the quotient,  $Q_{s14}^b$ , is given by

$$Q_{s14}^b = \frac{[\text{Al(OH)}_4^-]}{[\text{OH}^-]} = \frac{m_{\text{Al}}}{m_{\text{OH}^-} - m_{\text{Al}}} \quad (16)$$

where the brackets represent species molalities and  $m_{\text{Al}}$  and  $m_{\text{OH}}$  represent stoichiometric molalities.

Table II. SOLUBILITY OF GIBBSITE IN 1 m NaCl  
CONTAINING 0.01055 m NaOH

$$Q_{s14}^b = \frac{m_{Al}}{m_{NaOH}^* - m_{Al}}$$

Sample Number	t(°C)	$m_{Al}$ Molality	$m_{NaOH}^* - m_{Al}$	$-\log Q_{s14}^b$
45	59.45	$1.936 \times 10^{-3}$	$8.614 \times 10^{-3}$	.648
46	59.45	$1.952 \times 10^{-3}$	$8.598 \times 10^{-3}$	.644
47	59.45	$1.982 \times 10^{-3}$	$8.568 \times 10^{-3}$	.636
48	59.45	$2.135 \times 10^{-3}$	$8.415 \times 10^{-3}$	.628
49	59.45	$2.006 \times 10^{-3}$	$8.544 \times 10^{-3}$	.629
50	59.45	$2.003 \times 10^{-3}$	$8.547 \times 10^{-3}$	.630
51	59.45	$2.011 \times 10^{-3}$	$8.539 \times 10^{-3}$	.628
54	90.12	$3.831 \times 10^{-3}$	$6.719 \times 10^{-3}$	.244
55	90.12	$3.512 \times 10^{-3}$	$7.038 \times 10^{-3}$	.302
56	90.12	$3.652 \times 10^{-3}$	$6.898 \times 10^{-3}$	.276
57	90.12	$3.673 \times 10^{-3}$	$6.877 \times 10^{-3}$	.272
58	90.12	$3.673 \times 10^{-3}$	$6.877 \times 10^{-3}$	.272
60	74.20	$2.685 \times 10^{-3}$	$7.865 \times 10^{-3}$	.467
61	74.20	$3.140 \times 10^{-3}$	$7.410 \times 10^{-3}$	.373
63	48.69	$1.548 \times 10^{-3}$	$9.002 \times 10^{-3}$	.764
64	48.69	$1.584 \times 10^{-3}$	$8.966 \times 10^{-3}$	.753
65	48.69	$1.548 \times 10^{-3}$	$9.002 \times 10^{-3}$	.764
67	24.20	$0.935 \times 10^{-3}$	$9.615 \times 10^{-3}$	1.012
68	24.20	$0.894 \times 10^{-3}$	$9.656 \times 10^{-3}$	1.033

\* Starting concentration before dissolution of gibbsite.

Table III. SOLUBILITY OF GIBBSITE IN NaCl  
(I = 0.89 m) and 0.09712 m NaOH

$$Q_{s14}^b = \frac{m_{Al}}{m_{NaOH} - m_{Al}}$$

Sample Number	t(°C)	$m_{Al}$ Molality	$m_{NaOH} - m_{Al}$	$-\log Q_{s14}^b$
4	30.45	$8.62 \times 10^{-3}$	$8.85 \times 10^{-2}$	1.011
5	30.45	$8.59 \times 10^{-3}$	$8.86 \times 10^{-2}$	1.013
6	30.39	$8.62 \times 10^{-3}$	$8.85 \times 10^{-2}$	1.011
7	30.39	$8.80 \times 10^{-3}$	$8.84 \times 10^{-2}$	1.002
9	49.61	$1.60 \times 10^{-2}$	$8.12 \times 10^{-2}$	.706
10	49.62	$1.60 \times 10^{-2}$	$8.12 \times 10^{-2}$	.706
11	49.61	$1.57 \times 10^{-2}$	$8.15 \times 10^{-2}$	.715
12	49.61	$1.69 \times 10^{-2}$	$8.03 \times 10^{-2}$	.677
13	49.62	$1.69 \times 10^{-2}$	$8.03 \times 10^{-2}$	.677
16	60.60	$2.09 \times 10^{-2}$	$7.63 \times 10^{-2}$	.562
17	60.60	$2.05 \times 10^{-2}$	$7.67 \times 10^{-2}$	.573
19	90.06	$3.59 \times 10^{-2}$	$6.13 \times 10^{-2}$	.232
20	90.20	$3.69 \times 10^{-2}$	$6.03 \times 10^{-2}$	.213
21	90.20	$3.59 \times 10^{-2}$	$6.13 \times 10^{-2}$	.232
23	75.99	$2.69 \times 10^{-2}$	$7.03 \times 10^{-2}$	.417
24	75.99	$2.68 \times 10^{-2}$	$7.04 \times 10^{-2}$	.419
25	75.99	$2.67 \times 10^{-2}$	$7.05 \times 10^{-2}$	.422
28	44.89	$1.27 \times 10^{-2}$	$8.45 \times 10^{-2}$	.823
29	44.93	$1.26 \times 10^{-2}$	$8.46 \times 10^{-2}$	.827
32	25.5	$9.08 \times 10^{-3}$	$8.80 \times 10^{-2}$	.986
33	25.7	$8.37 \times 10^{-3}$	$8.68 \times 10^{-2}$	1.016
35	25.95	$7.74 \times 10^{-3}$	$8.94 \times 10^{-2}$	1.062
37	44.63	$1.22 \times 10^{-2}$	$8.50 \times 10^{-2}$	.843
38	44.60	$1.22 \times 10^{-2}$	$8.50 \times 10^{-2}$	.843
39	44.60	$1.32 \times 10^{-2}$	$8.39 \times 10^{-2}$	.803
41	75.56	$2.57 \times 10^{-2}$	$7.14 \times 10^{-2}$	.444
42	75.56	$2.60 \times 10^{-2}$	$7.12 \times 10^{-2}$	.437
45	49.95	$1.39 \times 10^{-2}$	$8.32 \times 10^{-2}$	.777
46	49.95	$1.40 \times 10^{-2}$	$8.31 \times 10^{-2}$	.774
47	49.98	$1.43 \times 10^{-2}$	$8.28 \times 10^{-2}$	.763
48	50.00	$1.43 \times 10^{-2}$	$8.28 \times 10^{-2}$	.763
50	60.50	$1.89 \times 10^{-2}$	$7.82 \times 10^{-2}$	.616
51	60.51	$1.86 \times 10^{-2}$	$7.85 \times 10^{-2}$	.625
52	60.52	$1.83 \times 10^{-2}$	$7.88 \times 10^{-2}$	.634

ORNL-DWG 79-15679

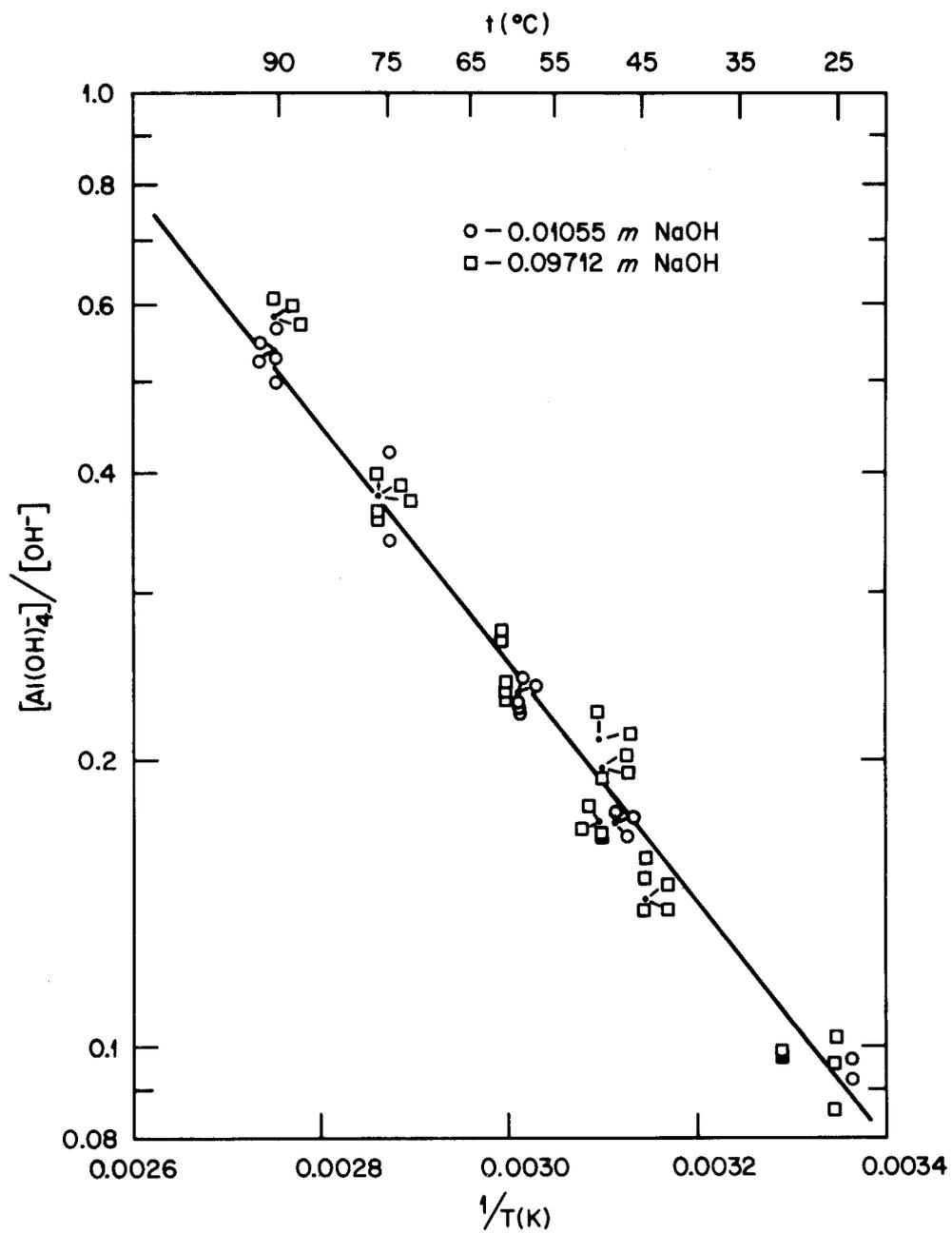


Fig. 4. The Ratio  $[Al(OH)_4^-]/[OH^-]$  at Equilibrium with Two Concentrations of NaOH in Column Experiments from 25 to 90°C.

A least-squares fit of the data of Tables II and III using unit weights gives

$$\log Q_{s14}^b = 3.3766 - 1326.4/T \quad (17)$$

with an agreement factor of 0.035. The standard error for  $\log Q_{s14}^b$  computed from the standard errors of the coefficients in Eq. 17 and their correlation coefficient is 0.01. (We should note here that an error was made in the composition of the feed solution in Run C so that the ionic strength was 0.89 m instead of the intended 1 m. However, this small difference in ionic strength is expected to have a very small effect on  $Q_{s14}^b$  where  $\Delta z^2$  is zero.)

The thermodynamic quantities calculated from Eq. 17 are:  $\Delta H_{s14}^b$  is  $6.07 \pm 0.12$  kcal/mole and  $\Delta S_{s14}^b$  is  $15.45 \pm 0.37$  cal °K<sup>-1</sup> mole<sup>-1</sup> (errors are one  $\sigma$ ).

### 3.2 Low pH

In the low pH runs the feed solution was 1 m NaCl with the pH adjusted to the desired level with HCl. Figure 5 shows the effluent pH during this run as a function of quantity of sample. A total of over 1,400 ml of feed solution (pH = 3.0) was passed through the column before the sample pH dropped below 6.0. Even then, the pH of the column effluent dropped only to ~ 4.0 and after 700 ml more of feed solution had passed through the column, the pH of the sample was down to ~ 3.7. The aluminum concentration in all samples was an order of magnitude higher than those estimated by Baes and Mesmer (1976) (Fig. 2).

The problem with dilute feed solutions seems to be associated with the inability to convert the surface of all the gibbsite to a uniform pH. We checked this supposition by titrating a slurry of gibbsite. The slurry contained 150 ml of 1 molal NaCl solution and 11 grams of gibbsite (38-75  $\mu$ m crystal size). Titrations were made starting at pH 10 and titrating to pH 3 with standard HCl and then back to pH 10

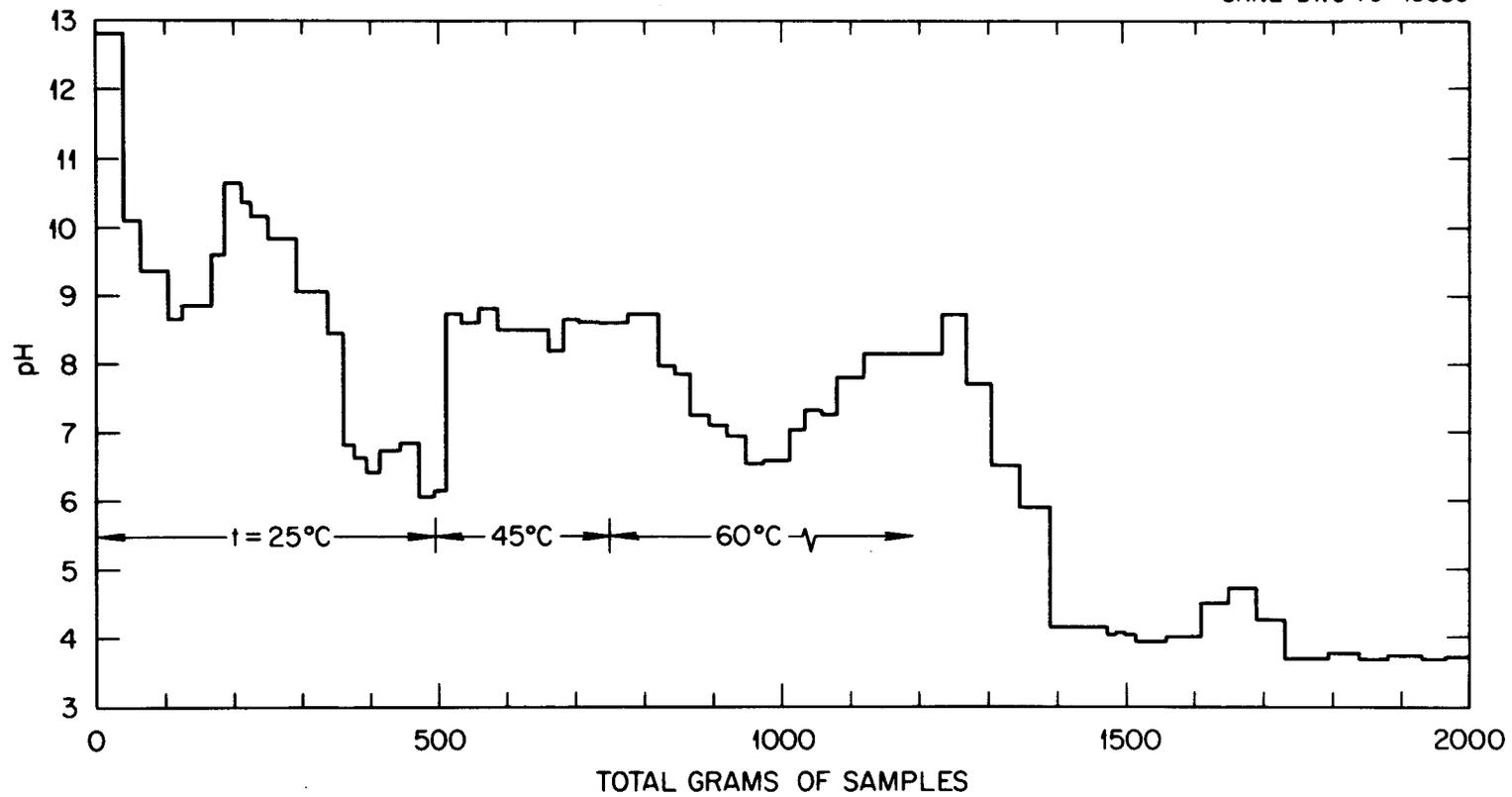
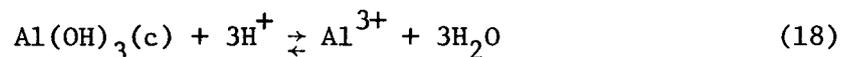


Fig. 5. Variation of Effluent pH from a Column Containing 75 g  $\alpha$ -Al(OH)<sub>3</sub> Using a Feed Solution of 1 m NaCl and 0.001 m HCl.

with standard NaOH. Two complete cycles were made in this manner. One of the titrations is shown in Fig. 6 which illustrates the large buffering capacity of gibbsite in this pH region. The consumption of hydrogen ions from pH 10 to 4.9 is likely due to the solid itself since the equilibrium solubility is very low in this region. The amount of acid consumed would be equivalent to the neutralization of one layer of hydroxide ions each occupying  $22\text{\AA}^2$  on the surface. Also, the small amount of hydrogen ions consumed at the lowest pH values indicates a non-equilibrium condition with respect to dissolved aluminum in this experiment.

The important consequence of this strong buffering by the solid hydroxides is that it is not possible to neutralize or transform the surface with dilute solutions of acid or base. It is particularly difficult to control the pH in equilibrations in the near neutral range for this reason using the column approach. It becomes necessary to remove the solid from the column, to adjust the pH with strong acid or base in a stirred vessel and then to refill the column. Once adjusted the pH of the column can control the pH of the feed solution. This was done in Run E in the next section.

Data taken from the end of Run D is shown in Fig. 7. If the assumption is made that no hydrolysis is occurring at pH of 3.7 (consistent with the results in the literature for 25°C), then an estimate can be made for the quotient for the equilibrium



These data give  $\log Q_{s10}$  of  $7.20 \pm 0.15$  at 60°C in 1 m NaCl. The scatter is unsatisfactory for a detailed analysis of the data and it may be due to non-equilibrium conditions in the column and to the inaccuracy of the pH measurements.

### 3.3 Neutral pH

Equilibrations were made by pH adjustment of the bed in a batch titration as discussed above. The first samples from the Run E were

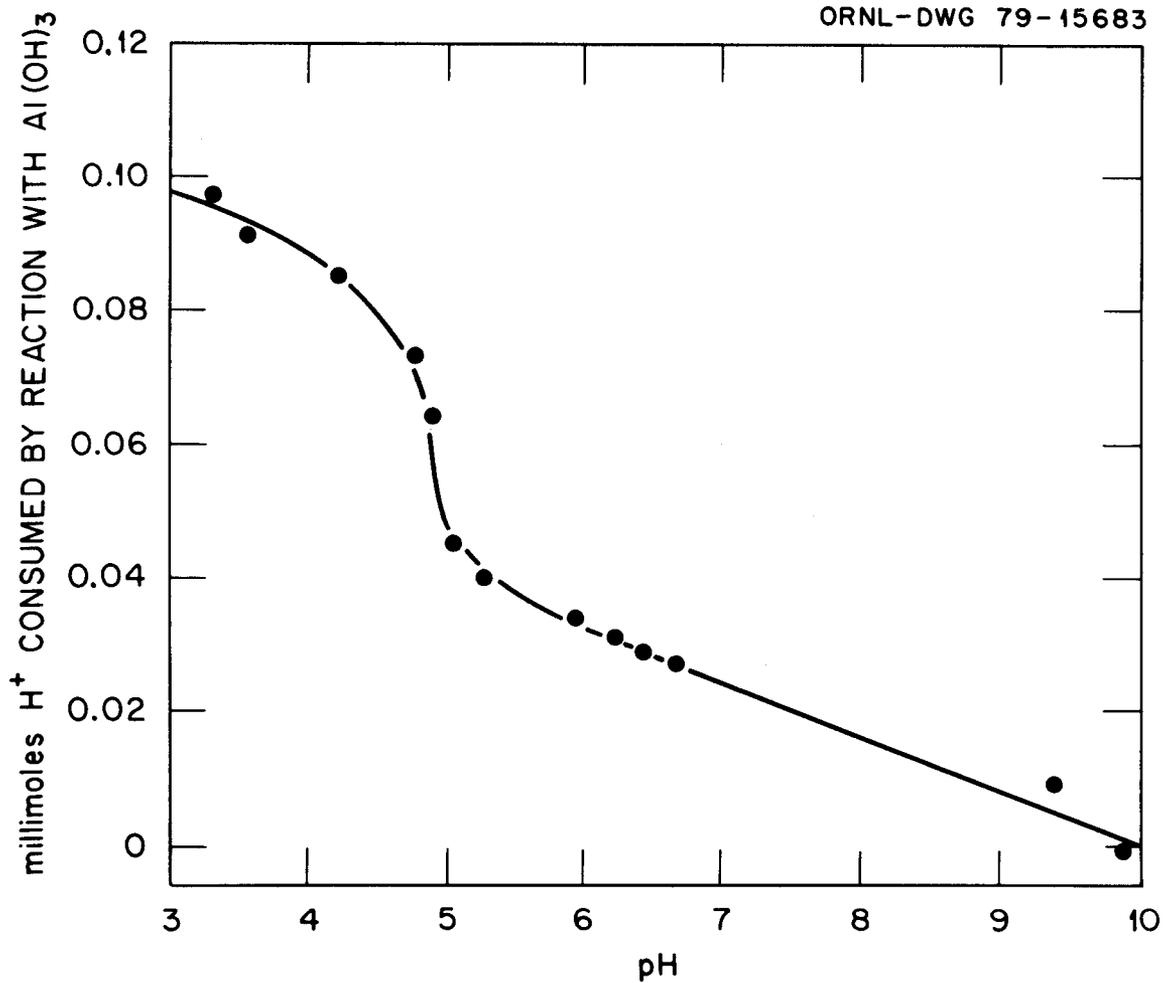


Fig. 6. Titration of 11 g of  $\alpha$ -Al(OH)<sub>3</sub> in 150 ml of 1 m NaCl with HCl to Observe the Consumption of H<sup>+</sup>. The amount consumed between pH 10 and 4.9 appears to be due to the solid itself.

ORNL-DWG 79-15682

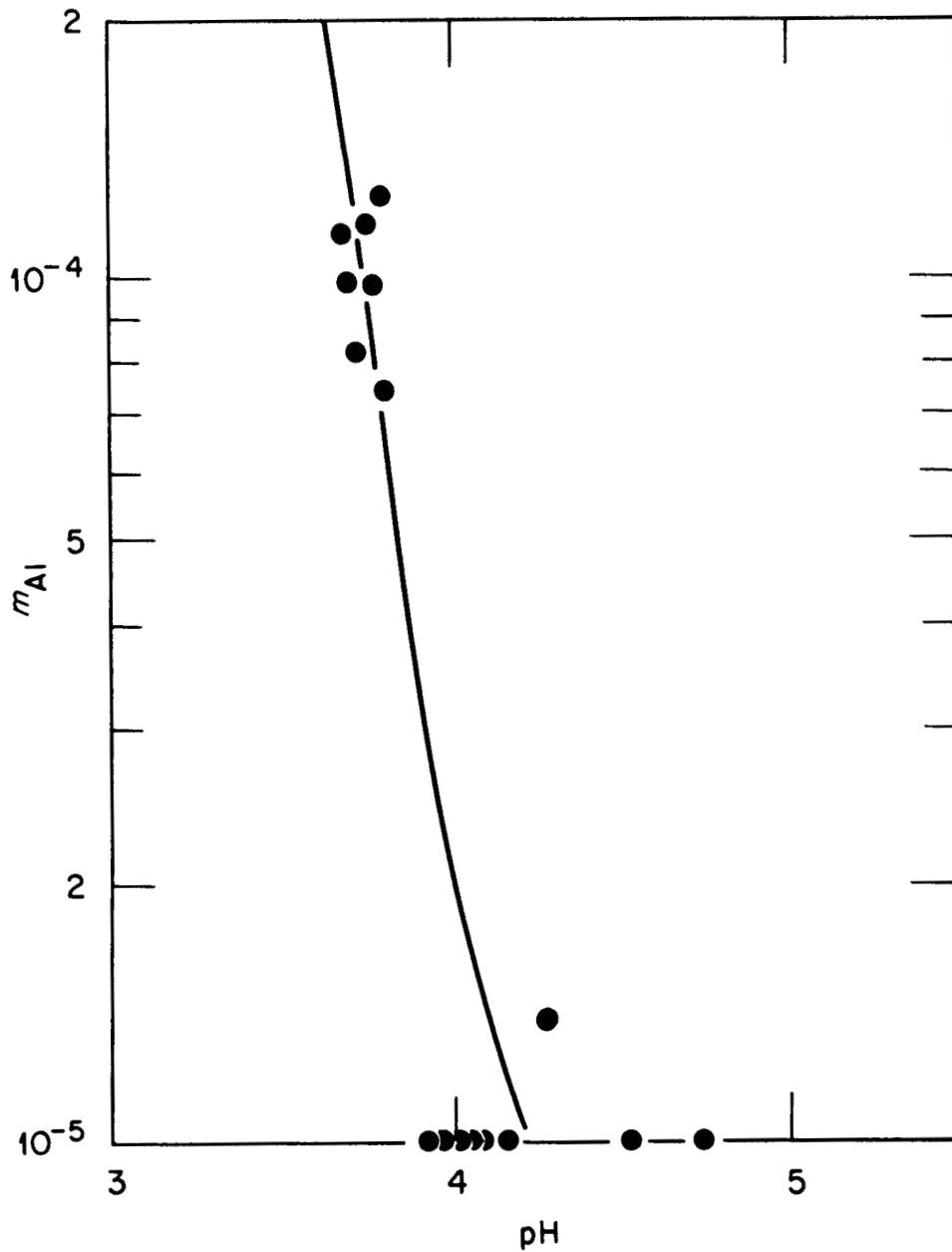


Fig. 7. Log  $m_{Al}$  vs pH Plot of the Data from the End of Run D at 60°C, i.e., where the effluent pH was most nearly equal to the pH of the feed solution. A value for  $\log Q_{s10}$  of  $7.20 \pm .15$  is obtained with the assumption of no hydrolysis at pH of 3.75.

analyzed in the conventional manner and the aluminum concentration was found to be below the detection limit (ca.  $10^{-6}$  m). At this time we began collecting large samples ( $\sim 200$  ml) and concentrating by ion-exchange. The concentration factor in the procedure was about twenty times but the precision suffered from the large blank due to the NaOH elutant. The results in Table IV are quite scattered and the solubility appears to be in the  $5 \times 10^{-7}$  to  $5 \times 10^{-8}$  m range near the minimum of the solubility. We consider that these results must be established with better precision to be satisfactory for defining the appropriate equilibrium quotients. At the higher temperatures the observed values of  $m_{Al}$  are lower than the  $Al(OH)_4^-$  as computed from Eq. 17. This is an impossible result and we are unable at this time to place limits on the uncertainties of the observations. More effort will continue to be made to establish the solubility in both the low pH and near neutral region. New approaches for the equilibrations, means of concentrating, and establishment of reversibility will be developed.

### 3.4 Comparison with Other Results

Our results in  $\log Q_{s14}^b$  in 1 m NaCl can be compared with the results of Russell et al. (1955) in NaOH solutions and with the results of Apps (1970) in very dilute solution. Figure 8 shows the logarithm of the solubility as a function of pH. The bold line is computed from the data in Table I for 25°C and ionic strength of unity. The solid lines in the basic region are computed from Eq. 17 for  $\log Q_{s14}^b$  and  $\log Q_w$  from Busey and Mesmer (1978). The agreement in the basic region amongst the various data sets is quite good when the differences in medium electrolyte and ionic strength are taken into account. The results of Russell et al. (1955) in 1 m NaOH are shown as short-dashed lines and the values for  $\log K_{s14}$  from Apps (1970) are shown as dotted lines. In the acidic region the solid line represents our results at 60°C in 1 m NaCl and the dashed lines represent the results of Singh (1974, 1976).

Our results in the near neutral region are not shown because the scatter of the data are yet too great to provide useful bases for assigning equilibrium constants.

Table IV. SUMMARY OF RESULTS IN THE NEAR NEUTRAL pH REGION

T	$m_{Al}$	pH	$[Al(OH)_4^-]$ (Eq. 17)
25°	$3.8 \times 10^{-8}$ m <5 $\times 10^{-8}$ m	$6.75 \pm 0.04$	$9.1 \times 10^{-9}$ m
45°	$4.4 \times 10^{-7}$ m	$6.45 \pm 0.25$	$3.7 \times 10^{-8}$ m
60°	<5 $\times 10^{-8}$ m	6.58	$1.9 \times 10^{-7}$ m
86.7°	$7.4 \times 10^{-7}$ m $9.0 \times 10^{-8}$ m	$6.8 \pm 0.1$	$2.3 \times 10^{-6}$ m

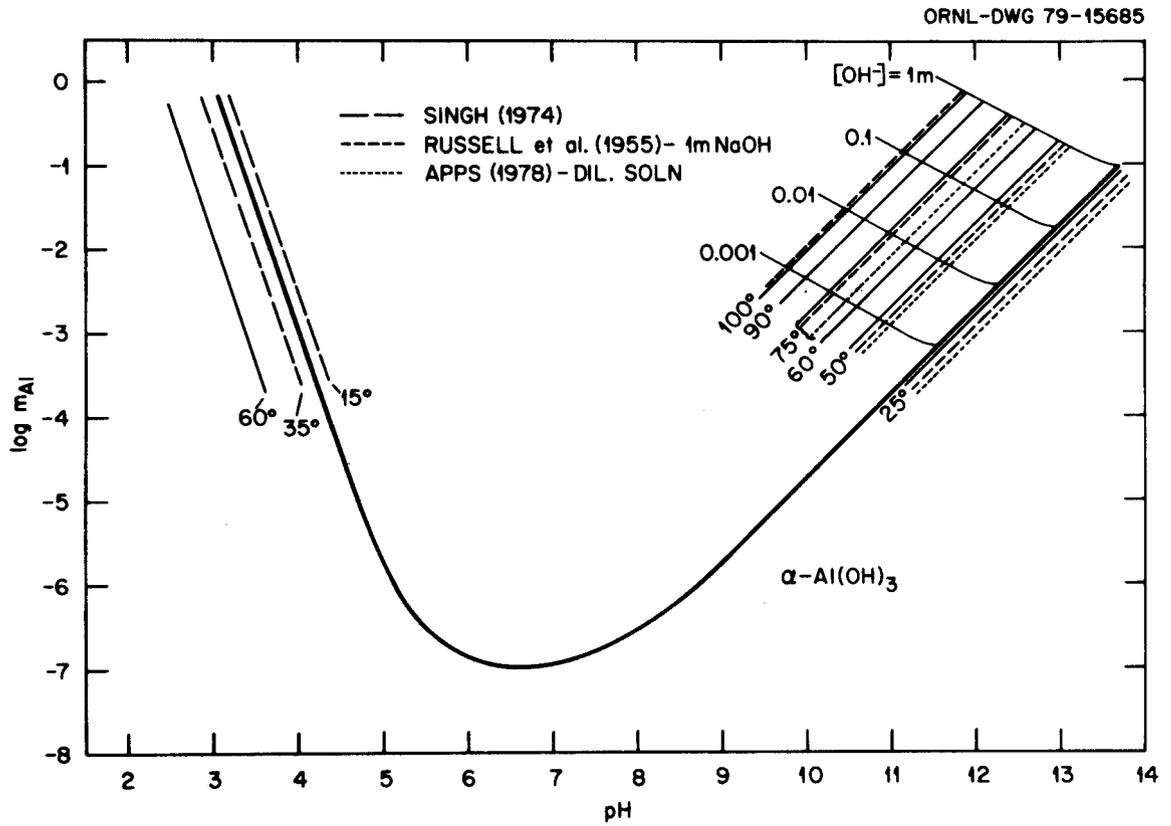


Fig. 8. Comparison of Results with Literature Data. The heavy curve is computed from data in Table I for 1 m NaCl and 25°C; the light lines - this work and the broken lines represent literature data.

## REFERENCES

- Apps, J. A., The Stability Field of Analcime, (Thesis) Harvard University, Cambridge, Mass., May, 1970.
- Baes, C. F., Jr., and R. E. Mesmer, The Hydrolysis of Cations, Wiley-Interscience, New York, 1976.
- Beavers, A. H. and R. L. Jones, *Soil Sci. Soc. Amer. Proc.* 30, 126 (1966).
- Busey, R. H. and R. E. Mesmer, *J. Chem. Engr. Data* 23, 175 (1978).
- Dryssen, D. and V. Tyrrell, *Acta. Chem. Scand.* 15, 393 (1961).
- Dryssen, D. and P. Lumme, *Acta. Chem. Scand.* 16, 1785 (1962).
- Enüstün, B. V. and J. Turkevich, *J. Amer. Chem. Soc.* 82, 4502 (1960).
- Freundlich, H., Colloid and Capillary Chemistry, Methuen, p. 154 (1926).
- Hsu, P. A., *Soil Sci.* 96, 230 (1963).
- Jayman, T.C.Z. and S. Sivasubramaniam, *Analyst* 99, 296 (1974).
- Kittrick, J. A., *Soil Sci. Soc. Amer. Proc.* 30, 596 (1966).
- Kraus, K. A., H. O. Phillips, and F. Nelson, Proceedings of the IAEA Conference, Copenhagen, September 1960, in "Radioisotopes in the Physical Sciences and Industry," Vol. III, 387 (1962).
- Ostwald, W., *Z. Phys. Chem.* 34, 495 (1900).
- Packter, A. and H. S. Dhillon, *Z. Phys. Chemie, Leipzig* 252, 249 (1973).
- Russell, A. S., J. D. Edwards, and C. S. Taylor, *J. Metals* 7, 1123 (1955).
- Schindler, P., "Heterogeneous Equilibria Involving Oxides, Hydroxides, Carbonates, and Hydroxide Carbonates," Advances in Chemistry Series, No. 67, p. 196 (1967).
- Singh, S. S., *Soil Sci. Soc. Amer. Proc.* 38, 415, 1974; *Soil Sci.* 121, 332 (1976).
- Wollaston, *Phil. Trans.* 103, 57 (1813).

## INTERNAL DISTRIBUTION

- |                                    |                      |
|------------------------------------|----------------------|
| 1-2. Central Research Library      | 21. O. L. Keller     |
| 3. ORNL Patent Office              | 22. K. A. Kraus      |
| 4. ORNL-Y-12 Technical Library     | 23. M. H. Lietzke    |
| Document Reference Section         | 24. W. L. Marshall   |
| 5. Laboratory Records, ORNL, RC    | 25. L. Maya          |
| 6-7. Laboratory Records Department | 26-30. R. E. Mesmer  |
| 8-12. C. F. Baes                   | 31. R. E. Meyer      |
| 13. E. G. Bohlmann                 | 32. M. T. Naney      |
| 14. J. H. Burns                    | 33. F. A. Posey      |
| 15. R. H. Busey                    | 34. A. J. Shor       |
| 16. C. Brunton                     | 35. R. A. Strehlow   |
| 17. F. W. Dickson                  | 36-40. F. H. Sweeton |
| 18. E. L. Fuller, Jr.              | 41. I. L. Thomas     |
| 19. H. F. Holmes                   | 42. A. Zucker        |
| 20. J. S. Johnson, Jr.             |                      |

## EXTERNAL DISTRIBUTION

43. John A. Apps, Energy and Environment Division, Lawrence Berkeley Laboratory, Berkeley, CA 94729
44. Paul Cohen, 3024 Beechwood Blvd., Pittsburgh, PA 15217
45. John Haas, U.S. Geological Survey, 959 National Center, Reston, VA 22092
- 46-48. B. F. Hitch, Kawecki-Berylco Industries, Research and Development Department, P.O. Box 567, Boyertown, PA 19512
49. C. S. Patterson, Furman University, Greenville, SC 29609
50. John E. Ricci, 17 Nolan Avenue, Yonkers, NY 10704
51. Assistant Manager, Energy Research and Development, DOE-ORO
- 52-228. Given distribution as shown in TID-4500 under Chemistry category (25 copies - NTIS)