HYDROLYSIS OF ALUMINUM SULPHATE

SOLUTIONS AT HIGH TEMPERATURES

BY

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Dipl. Ing. (Chemical Engineering)
University of Belgrade, 1963

A THESIS SUBMITTED IN PARTIAL FULFILMENT

OF THE REQUIREMENTS FOR THE DEGREE

OF MASTER OF APPLIED SCIENCE

In the Department

of

METALLURGY

We accept this thesis as conforming to the

required standard

THE UNIVERSITY OF BRITISH COLUMBIA

February 1971

ABSTRACT

Normal and acid aluminum sulphate solutions containing about 6.0 gr/l of aluminum and up to 50 gr/l $SO_4^=$ were hydrolyzed until equilibrium was reached in the temperature region 125-250°C. Under the equilibrium conditions the only stable solid phase observed in equilibrium with a liquid phase of various compositions was basic aluminum sulphate with nominal formula $3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O$. A small portion of the ternary diagrams for the system $Al_2O_3-SO_3-H_2O$ at 225°C and 250°C was constructed. A mixture of aluminum sulphate and other metal sulphates, K_2SO_4, Na_2SO_4, Li_2SO_4, $FeSO_4$ and $CuSO_4$ i.e. was hydrolyzed at 225°C in order to find the effect of these salts on hydrolysis.

The overall hydrolysis reaction was found to occur according to the chemical equation:

$$6Al^{+++} + 4HSO_4^- + 14H_2O \longrightarrow 3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O + 14H^+$$
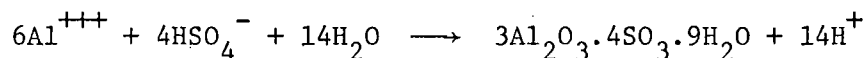
The equilibrium constants at 125, 150, 175, 200, 225 and 250°C were determined.

Finally a mechanism for the hydrolysis of aluminum sulphate was proposed.

ACKNOWLEDGEMENT

The author wishes to express sincere thanks to Dr. E. Peters for
his continuing guidance and interest in this project. His thanks is
extended to fellow graduate students, particularly Mr. D. Jones and the
technical staff of the Department of Metallurgy for their helpful
discussions and assistance.

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1. INTRODUCTION

The aluminum industry was the first to use a pressure hydro-
metallurgical process (The Bayer process) on a large scale. Caustic
soda solutions are used to dissolve aluminum from bauxites and alumina
is separated. Even though caustic solutions are not very selective
and the Bayer process is limited to low silica ores, alumina is produced
commerically only by this process. This has imposed on the aluminum
industry the task of transportation of bauxties over a long distance
because the producing countries do not have bauxites of their own.
The production of aluminum in countries such as Canada and the
United States is today very sensitive to the availability of bauxites
from foreign countries.

With a desire to recover aluminum from clay minerals, processes
have been considered,from time to time, that are applicable to common
North American clays for the domestic production of alumina. Such
processes might also be useful in the treatment of certain mine waters
from copper dump leaching, which contain dissolved aluminum sulphate, among
other sulphate salts.

Any new process producing alumina must compete in price with the
Bayer process. This limits new leaching processes to cheap reagents.
Sulphuric acid is the favourite reagent considered for alternate

alumina production processes and an acid process developed by C.S.I.R.O.[*]
has been found to produce aluminum sulphate solutions which can be
hydrolysed to yield basic aluminum sulphate.

Most of the work in hydrolysis has been done with basic aluminum
sulphate solutions, or solutions containing alkali metal sulphates
and under "process conditions". Because of this there is practically
no data on equilibrium hydrolysis available in the literature.

Some equilibrium hydrolysis work was carried out on the $Fe_2O_3-SO_3-H_2O$
system. With some exceptions $Al_2O_3-SO_3-H_2O$ and $Fe_2O_3-SO_3-H_2O$ systems
precipitate similar compounds during hydrolysis.

The separation of basic aluminum sulphate salts from aluminum
sulphate solutions is not well understood either from a kinetic or
thermodynamic point of view. This work is concerned with hydrolysis
reactions of aluminum sulphate solutions that occur in the temperature
range 125-250°C, and attempts were made to study both precipitation
rates and the final equilibria.

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[*] Commonwealth Scientific and Industrial Research Organization -
Melbourne

2. A REVIEW OF THE LITERATURE

It is generally known that above a temperature which is a characteristic of the metal ion involved, a sulphate salt becomes less soluble as the temperature is further increased.

E.T. Carlson and C.S. Simons[1] have reported the necessity of temperature increase from 200 to 275°C to achieve selective extraction of nickel and cobalt from laterite ore. At 200°C, even though nickel and cobalt sulphate solubility was high enough to give good recoveries, the selectivity was rather poor because of the high solubility of aluminum and iron sulphates. They noticed that the $SO_3:Al_2O_3$ ratio in the residue was about 1:1 and suggested that Al_2O_3 and SO_3 exist in it as a compound.

2.1   The $Fe_2O_3-SO_3-H_2O$ System

At elevated temperatures ferric sulphate solutions hydrolyze to precipitate ferric oxide or basic salts. Posnjak and Merwin[2] have studied the $Fe_2O_3-SO_3-H_2O$ system at temperatures up to 200°C. At 200°C only three solid phases exist in equilibrium with various compositions of the liquid phase. Fe_2O_3 is in equilibrium with dilute solutions of ferric sulphate. The stable phase in equilibrium with a somewhat higher concentration of sulphuric acid in solution is a basic salt of the composition $Fe_2O_3 \cdot 2SO_3 \cdot H_2O$. Finally, at high concentrations
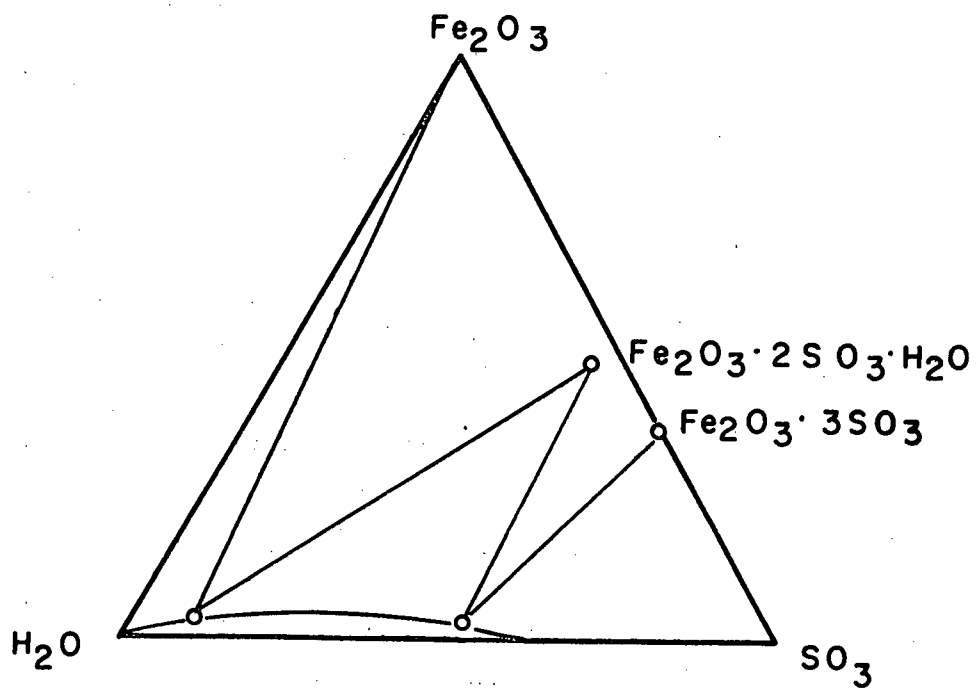
Fig.I. $Fe_2O_3 - SO_3 - H_2O$ SYSTEM
AT 200 C°
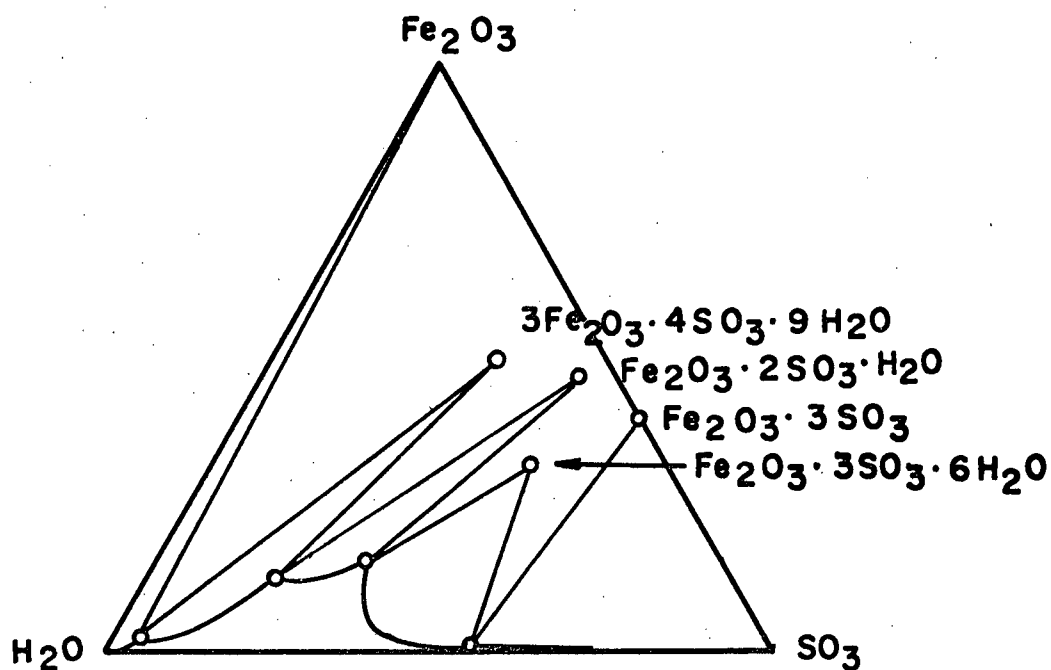
Fig. 2 . Fe$_2$O$_3$- SO$_3$- H$_2$O SYSTEM
AT 140 C°

of sulphuric acid in solution the stable phase is the normal salt, $Fe_2O_3 \cdot 3SO_3$ (Fig. 1).

With decreasing temperature the isotherms become more complicated and at 140°C, there are five solid phases in equilibrium with different compositions of the liquid phase (Fig. 2). With further decrease in temperature the equilibrium isotherms become still more complicated. At 130°C, ferric oxide monohydrate replaces the anhydrous ferric oxide, and at 110°C anhydrous ferric sulphate disappears and two acid salts are stable ($Fe_2O_3 \cdot 4SO_3 \cdot 3H_2O$ and $Fe_2O_3 \cdot 4SO_3 \cdot 9H_2O$).

2.2   The Al_2O_3-SO_3-H_2O System

P.T. Davey and T.R. Scott[3] have studied the Al_2O_3-SO_3-H_2O system under process conditions in order to determine the optimum conditions for production of alumina. Their experiments approached equilibrium to varying degrees. Solutions with initial SO_3:Al_2O_3 ratio less than 3.0 and high in aluminum content were hydrolyzed at temperatures of 100-220°C. In this temperature range the only stable phase observed, in equilibrium with various liquid phases, was basic aluminum sulphate of the nominal formula $3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O$. At these temperatures, the precipitated phase was in equilibrium with acid solutions of aluminum sulphate. Only a limited number of experiments were performed for periods of time long enough to reach the equilibrium. The equilibrium saturation curve for this system at 220°C is given in Fig. 3. This saturation curve was obtained by hydrolyzing aluminum sulphate solutions with initial SO_3:Al_2O_3 ratio less than 3.0.
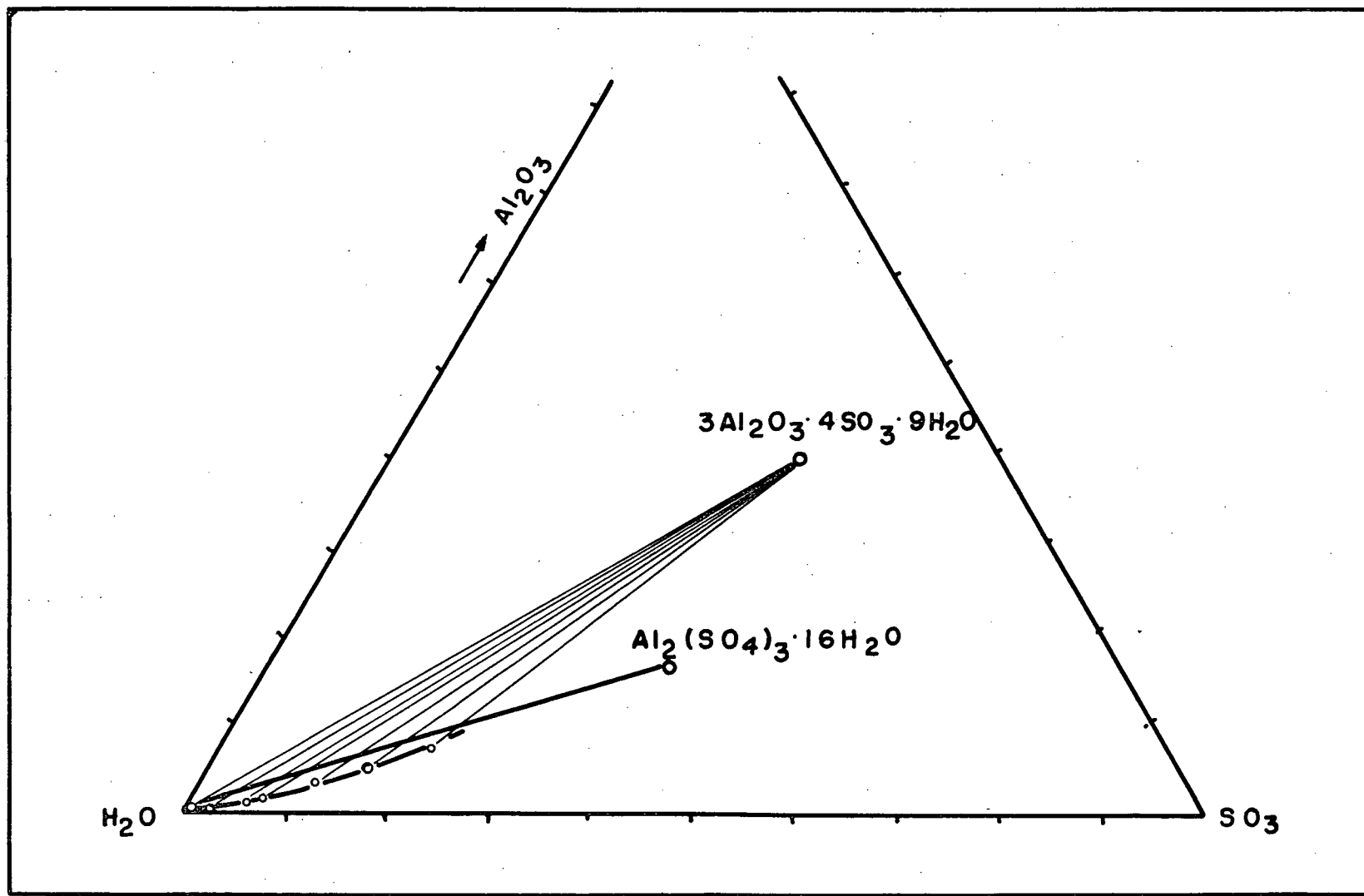
Fig. 3. $Al_2O_3 - SO_3 - H_2O$ SYSTEM AT 220 C°

Basset and Goodwin[4] have studied the system Al_2O_3-SO_3-H_2O at 25°C at this temperature concentrated solutions of aluminum sulphate can be crystallized to yield either hydrated aluminum sulphate $Al_2(SO_4)_3 \cdot 16H_2O$ or the basic salt $Al_2O_3 \cdot 2SO_3 \cdot 11H_2O$ depending on SO_3:Al_2O_3 ratio of the initial solution. These crystalline materials tend to occlude mother liquor and are readily soluble in water, which makes it difficult to remove impurities by washing without redissolving a substantial amount of the solid phase.

T.R. Scott et al.[5-9] have proposed an acid process for recovery of aluminum from ores low in bauxite content and high in silica. The stages of the new process are described as follows:

a. <u>Digestion</u> Recycled liquor containing aluminum sulphate is used to recover extra aluminum from an ore at 180°C.

b. <u>Modification</u> A liquor from the digestion stage is treated with fresh bauxite to give a solution of basic aluminum sulphate with SO_3:Al_2O_3 ratio less than 3.0.

c. <u>Reduction</u> Modified liquor is treated with sulphur dioxide to reduce soluble iron to the ferrous state at 100°C.

d. <u>Hydrolysis</u> Reduced liquor is hydrolyzed at 220°C in the absence of oxygen to produce basic aluminum sulphate.

e. <u>Calcination</u> Basic aluminum sulphate is heated, preferrably in stages at 1200 °C-1300°C, to yield the required α-alumina and a mixture of sulphurous gases for recycling.

J.L. Henry and G.B. King[10] have studied the system Al_2O_3-SO_3-H_2O

at 60°C. At this temperature two basic salts were found to be in equilibrium with solutions of aluminum sulphate having an $SO_3:Al_2O_3$ ratio very close to 3.0. The salt $Al_2O_3.2SO_3.11H_2O$ is in equilibrium with solutions of pH about 2.5 and $Al_2O_3.SO_3.6H_2O$ is in equilibrium with solutions of pH 2.5-3.20. At very low concentrations of free sulphuric acid in solution normal aluminum sulphate is the stable phase at 60°C.

R.A. Chaves, V.V. Kavelin and B.P. Sobolev[11] have studied the side reactions occurring in the sulphuric acid process for extracting nickel and cobalt from Cuban laterites and have revealed the presence of the following compounds: hematite $\alpha-Fe_2O_3$, boehmite $\gamma-Al_2O_3.H_2O$, aluminochromite $Fe(CrAl)_2O_4$, basic iron sulphate $Fe_2O_3.2SO_3.H_2O$, basic aluminum sulphate $3Al_2O_3.4SO_3.9H_2O$ and hydroniojarosite $3Fe_2O_3.4SO_3.9H_2O$.

The largest amount of basic aluminum sulphate is formed in the autoclave where the preheated pulp at 250°C mixes with concentrated sulphuric acid,indicating very high reaction rate at this temperature.

Beside aluminum and ferric sulphate salts, other trivalent and quadrivalent metal sulphates can be hydrolyzed.[12] At room temperature violet-coloured chromium sulphate solutions are stable, but at high temperatures these are converted into green complexes in solution. When $SO_3:Cr_2O_3$ ratio in the initial solution is less than 3.0 hydrolyzed chromic oxide is precipitated but only at temperatures higher than 180°C.

Even at high temperatures solutions of lanthanum sulphate do not hydrolyze readily below pH 7.

Vanadium is almost completely precipitated even in the presence of free sulphuric acid to yield V_2O_5. In the absence of oxygen at $100°C$, the solutions are stable, but precipitate V_2O_4 at temperatures above $200°C$.

Scandium could be separated from rare earths provided that the solubility product of the scandium compound was exceeded at the temperature and in the solutions used.

Indium can be separated from zinc electrolysis liquors under the same conditions as for scandium.

Titanium and zirconium sulphates hydrolyze readily without recourse to autoclave conditions.

2.3   The $M_2O-Al_2O_3-SO_3-H_2O$ System[*]

Under otherwise the same conditions, the presence of alkali metal sulphates will increase the hydrolysis yield of a basic salt from aluminum sulphate solutions. V.S. Sazhin, A.K. Zapolskii and N.N. Zaklarova[13] have studied the influence of ammonium, sodium, and potassium sulphates on hydrolysis of aluminum sulphate solutions. The degree of hydrolysis was increased in the following series: $(NH_4)_2SO_4 <$ $Na_2SO_4 < K_2SO_4$.

S. Bretsznajder, J. Boczar, J. Piskorski and J. Porowski[14] have studied the hydrolysis of aluminum sulphate solutions with addition of sodium hydroxide at $179-285°C$ for $0-240$ min. The precipitated solid phase was found to be $Na_2O.3Al_2O_3.4SO_3.7H_2O$. Excess sodium hydroxide

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[*] M_2O = alkali oxide; $M \equiv Li$, Na, K, NH_4

greatly increased the yield. Higher temperature and more dilute solutions gave higher yields. There was little change in yield for periods longer than 30 min.

A.K. Zapolskii et al.[15-18] studied the effect of potassium sulphate from 0-167.5 gr/ℓ K_2SO_4 on hydrolysis of aluminum sulphate solution containing 308 gr/ℓ $Al_2(SO_4)_3$ at 170-250°C. The degree of hydrolysis sharply increased at all temperatures for K_2SO_4 concentration from 0-1 mole/ℓ. Further increase in K_2SO_4 concentration had little influence on hydrolysis. In the absence of K_2SO_4 basic aluminum sulphates of constant composition ($3Al_2O_3 \cdot 4SO_3 \cdot 7H_2O$) were formed. Potassium alunite $K_2[Al_6(SO_4)_4(OH)_{12}]^*$ was preferentially formed at 230-250°C from solutions containing 1 mole of K_2SO_4, or more, per mole of $Al_2(SO_4)_3$. At temperatures 170-190°C a less basic salt $K_2SO_4 \cdot 3Al_2O_3 \cdot 4SO_3 9H_2O$ was observed. The system $Na_2O-Al_2O_3-SO_3-H_2O$ was studied at 200°C under process conditions in order to determine the conditions for recovery of alumina from ores.[19] The precipitated compound was found to have a formula very close to $Na_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$.

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* $K_2[Al_6(SO_4)_4(OH)_{12}] = K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$.

3. EXPERIMENTAL

3.1   Experimental Technique

A shaking autoclave (Fig. 4) made of zirconium was used for all
hydrolysis experiments. The autoclave was placed in an aluminum
block containing five heaters (100 W. each) to provide good heat
distribution. The temperature was controlled by a 71 model "Thermis-
temp" temperature controller to within ± 0.1 °C. The temperature
controller was used with a YS1-602 sensing probe with a range of 80 to
250°C, and was independently calibrated against a precision mercury
thermometer in oil for each temperature used. The calibration curve
is shown in Fig. 5.

In the low pressure region the pressure in the system was
monitored by a transducer and recorded by a "Heath" servo-recorder.
For the high pressure region, a pressure gauge was used. A calibration
curve for the transducer is shown in Fig. 6. The variation of pressure
with temperature is given in Fig. 7. The heating time varied with
temperature and this variation is shown in Fig. 8.

For each run, the autoclave was filled with 75 ml of solution
leaving about 30 cc of gas volume in the autoclave.
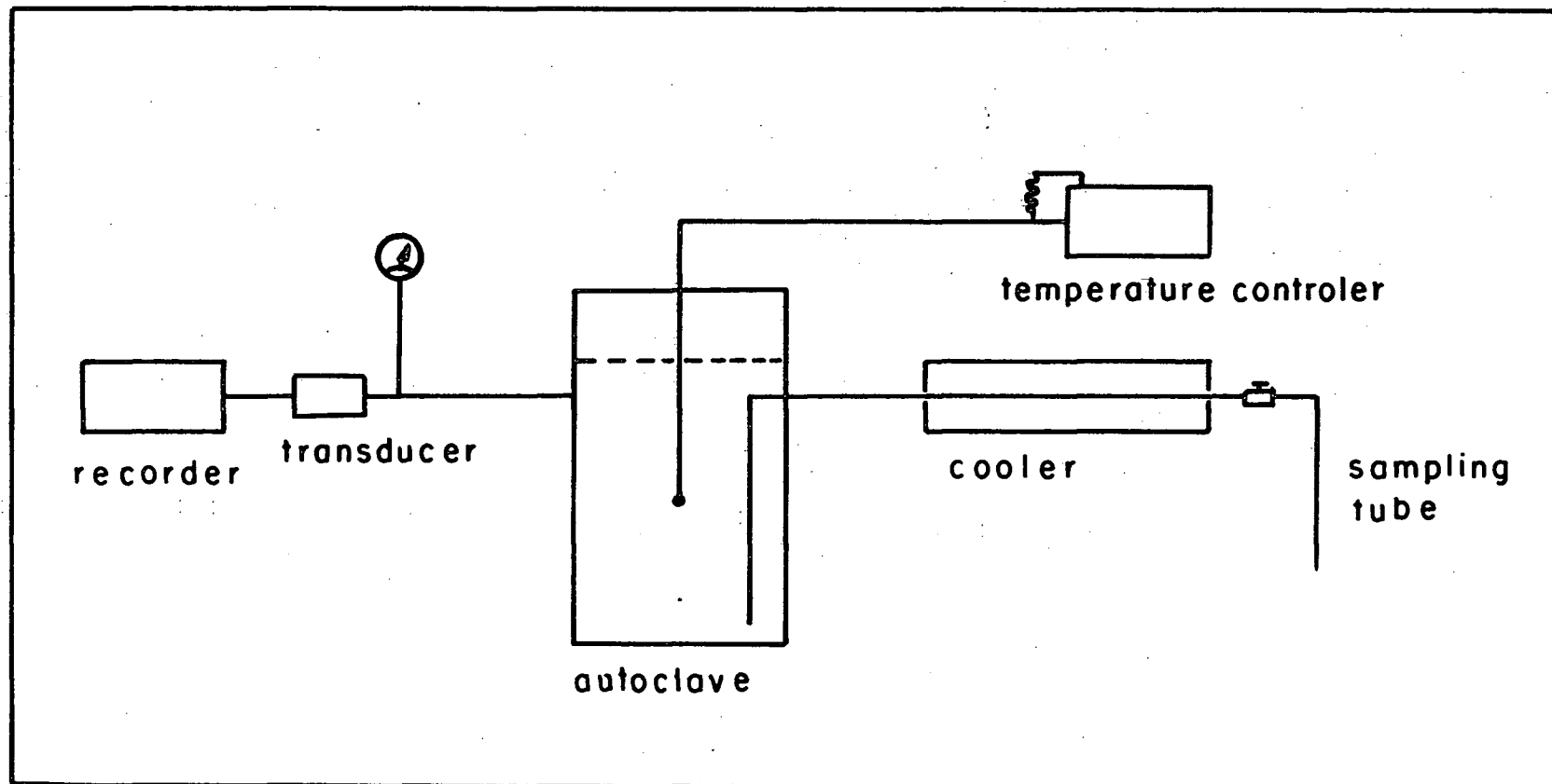
Fig. 4. EXPERIMENTAL APARATUS
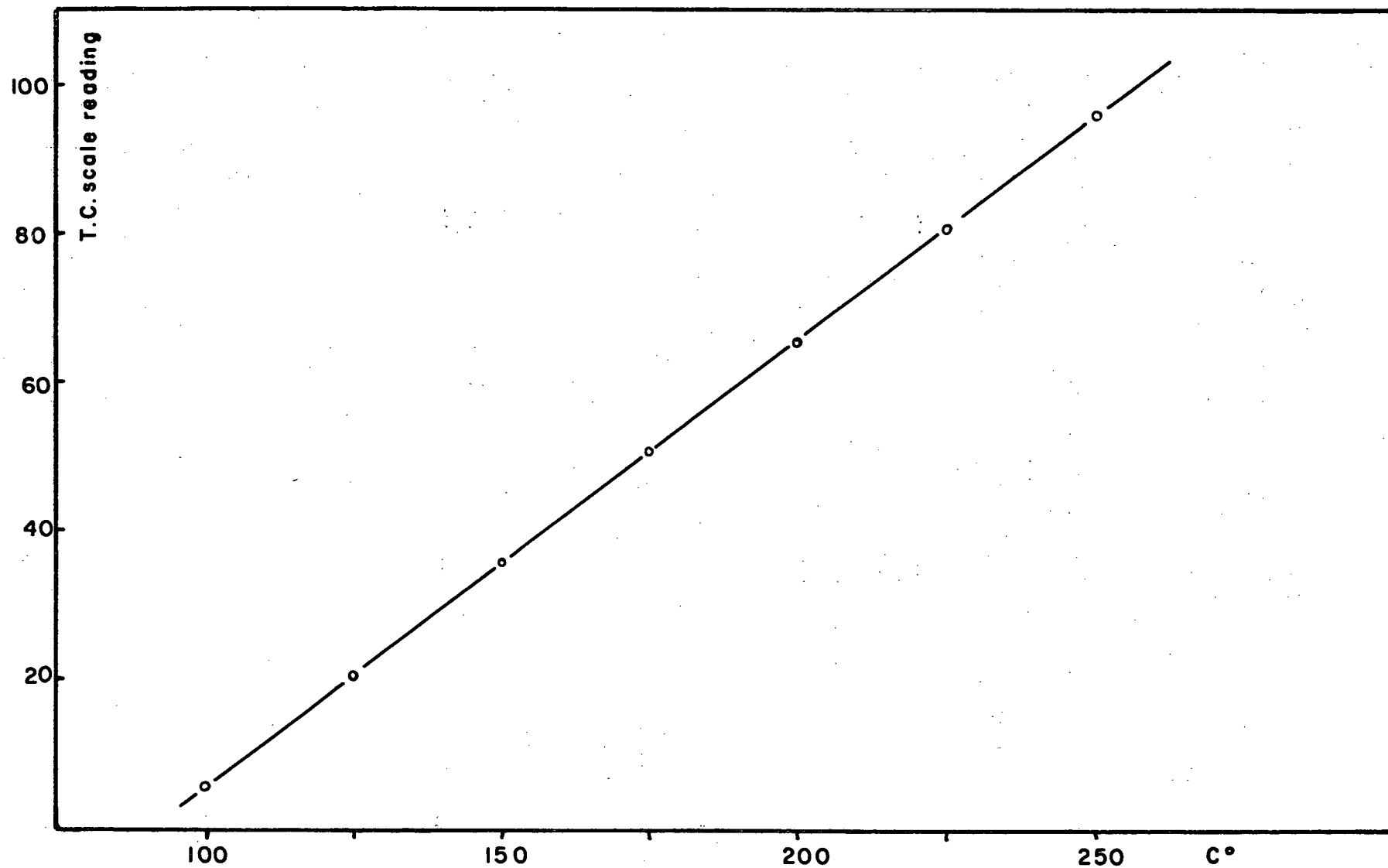
Fig. 5. Y.S.I.-602 THERMISTOR CALIBRATION
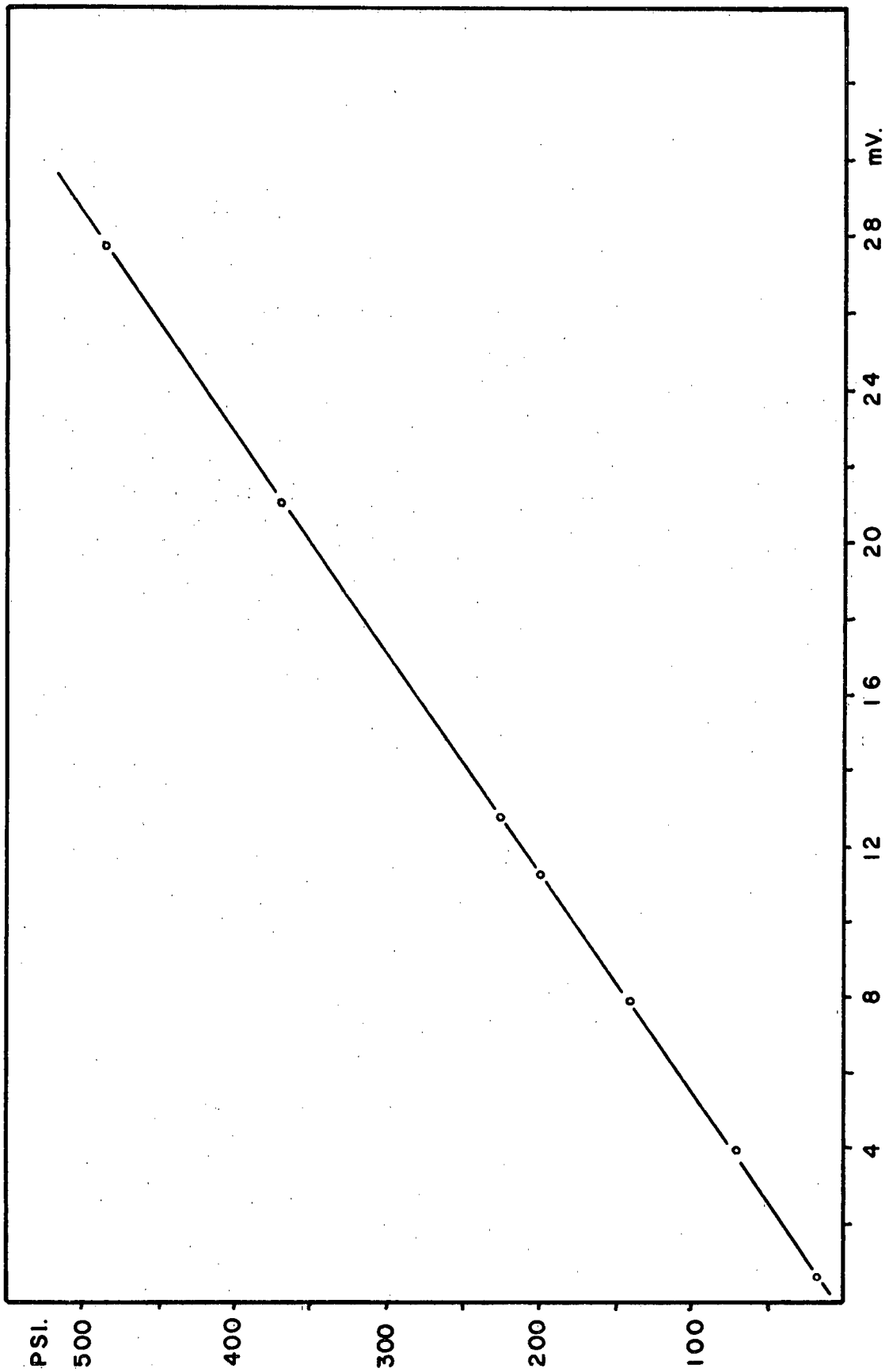
Fig. 6. TRANSDUCER CALIBRATION
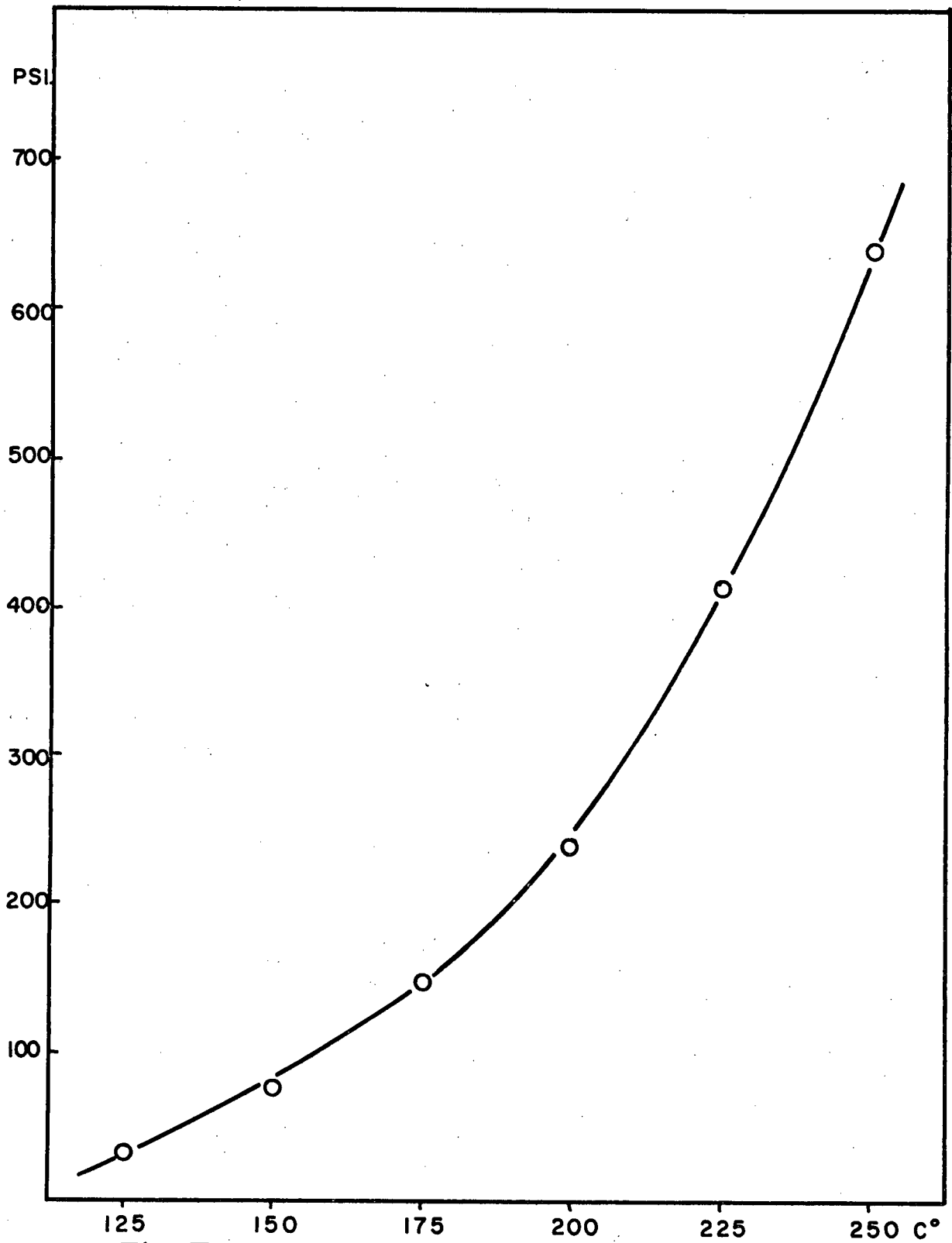
Fig. 7. PRESSURE DEPENDANCE ON TEMPERATURE
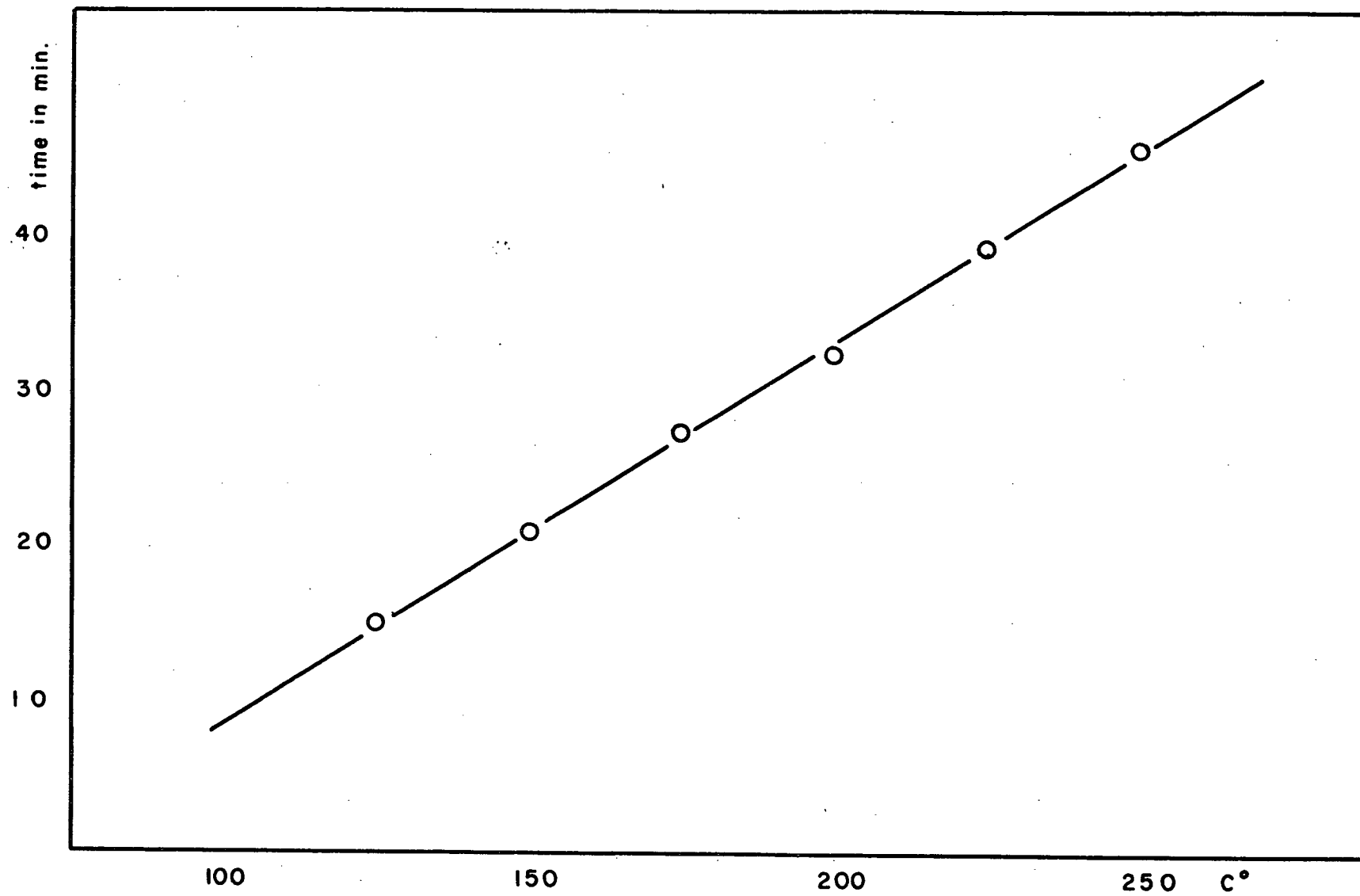
Fig. 8. HEATING TIME TO .REACH THE TEMPERATURE

Samples of hydrolyzed solution were taken from the cooling system and the sampling time was between 2 and 3 minutes depending on temperature.   To make sure that the samples represented the solution from the autoclave, the first 3 ml of solution from the sampling tube were discarded.

Immediately after the sample was taken it was filtered and its pH measured. Most of the hydrolysis product was precipitated on the autoclave walls and remained inside after the liquid was removed. The autoclave was then cooled with running water to room temperature and opened.

The precipitate was removed from the autoclave walls mechanically by shaking the autoclave with glass balls and a few milliliters of distilled water. After being filtered and washed, the precipitate was dried for 24 hrs at 105°C.

After the solid phase was removed the autoclave was washed with sodium hydroxide solution and then successively with dilute sulphuric acid and water. To evaporate the residual water, it was then heated and again allowed to cool to room temperature.

3.2   Materials Used

Aluminum sulphate, crystal, reagent, B&A,

$Al_2(SO_4)_3 \cdot 18H_2O$; M.W. 666.45
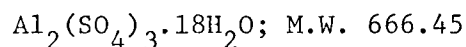
Maximum Limit of Impurities

Insoluble	0.005%
Free acid (H_2SO_4)	0.20%
Chloride (Cl)	0.002%
Arsenic (As)	0.00005%

Heavy metals (as Pb) 0.001%

Iron (Fe)   0.002%

Substances not precipitated
by NH_4OH as sulphates 0.20%

Lithium sulphate, granular reagent B & A

$Li_2SO_4 \cdot H_2O$ M.W. 127.96

Maximum Limit of Impurities

    Insoluble   0.010%

    Chloride (Cl)   0.002%

    Nitrate (NO_3)   0.001%

    Heavy metal (as Pb) 0.0005%

    Iron (Fe)   0.0002%

    Potassium (K)   0.05%

    Sodium (Na)   0.10%

Potassium sulphate, crystal, reagent B & A

K_2SO_4 M.W. 174.27

Maximum Limit of Impurities

    Insoluble   0.005%

    Chloride (Cl)   0.001%

    Nitrogen Compounds   0.005%
    (as N)

    Arsenic (As)   0.00005%

    Calcium, Magnesium
    and R_2O_3 precipitate 0.020%

    Heavy metals (as Pb) 0.0005%

    Iron (Fe)   0.0002%

    Sodium (Na)   0.005%

Sodium sulphate, anhydrous, granular reagent B & A

Na_2SO_4 M.W. 142.05

Maximum Limit of Impurities

Insoluble	0.010%
Loss on ignition	0.50%
Chloride (Cl)	0.002%
Nitrogen compounds as (N)	0.0005%
Arsenic (As)	0.0001%
Calcium, magnesium and R_2O_3 precipitate	0.010%
Heavy metals (as Pb)	0.0005%
Iron (Fe)	0.0005%

Ferrous sulphate, crystal, reagent B & A

$FeSO_4 \cdot 7H_2O$ M.W. 278.03

Maximum Limit of Impurities

Insoluble	0.005%
Chloride (Cl)	0.001%
Phosphate (PO_4)	0.001%
Copper (Cu)	0.005%
Ferric Iron (Fe^{+++})	0.01%
Manganese (Mn)	0.05%
Substances not precipitated by NH_4OH	0.050%
Zinc (Zn)	0.005%

Cupric sulphate, granular crystals, B.D.H. reagent

$CuSO_4 \cdot 5H_2O$ M.W.   249.69

Alkalies (suphated)   not more than 0.5%

Chloride (Cl)   not more than 0.005%

Iron (Fe)   not more than 0.08%

Aluminum "AnalaR"   B.D.H.

Al   M.W. 26.98

Acid insoluble matter   passes test

Iron (Fe)   0.004%

Copper (Cu)   0.005%

Silicon (Si)   0.01%

Total nitrogen (N)   0.002%

3.3   Preparation of Solutions for Hydrolysis

The aluminum sulphate solution was prepared by dissolving hydrated aluminum sulphate $Al_2(SO_4)_3 \cdot 18H_2O$ in distilled water. A solution of approximately 6.0 gr/ℓ of aluminum was made having $SO_3:Al_2O_3$ ratio of about 3.0, and a pH of 3.10. The solution was filtered before it was used for hydrolysis. Solutions of the lowest pH (pH = 0.70) used in this work were prepared by dissolving $Al_2(SO_4)_3 \cdot 18H_2O$ in dilute sulphuric acid. Any solution between these two limits (pH = 0.70 and pH = 3.10) was prepared by mixing selected ratios of the two.

Solutions containing alkaline metal sulphates and divalent metal sulphate salts were prepared by mixing the solution of the corresponding salt with aluminum sulphate solution.

Solutions of normal aluminum sulphate were discarded after 7 days of

storage. Aluminum sulphate solutions containing excess sulphuric acid
were kept for a few weeks. Solutions containing alkaline metal
sulphates were prepared just before using them.

3.4   Chemical Analysis

Initial and final solutions were analyzed for aluminum, sulphate,
and added metal ions. The pH of the solutions was measured before
and after hydrolysis.

The sulphate content was determined by precipitation as $BaSO_4$.
Aluminum was determined[20] by complexing with EDTA* and then back
titrating the excess EDTA with zinc sulphate using dithizone** as
an indicator and 1 M CH_3COOH-1 M CH_3COONH_4 solution as a buffer.
Standard aluminum sulphate solution was made from "Analar" aluminum
by dissolving it in sulphuric acid.

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* disodium salt of ethylene diamine

$$Na-OOCH_3C \diagdown \diagup CH_3COOH$$
$$NH_2-NH_2$$
$$HOOCH_3C \diagup \diagdown CH_3COONa$$
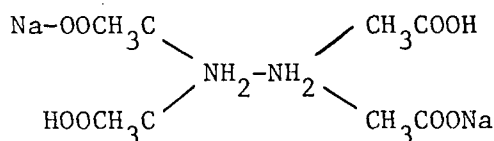
** diphenylthiocarbazone
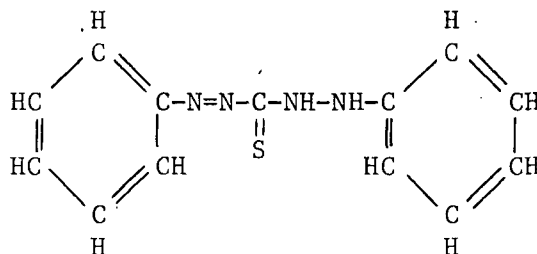
Divalent iron in the aluminum sulphate solution was analyzed by titrating Fe^{++} with $Ce(HSO_4)_4$ to oxidize it to Fe^{+++} using 1,10-orthophenanthroline[*] ferrous sulphate (Ferroin) as an indicator. In this case the aluminum content of the solution was determined from the difference in EDTA used to titrate both iron and aluminum.

Copper and aluminum sulphate solution was analyzed by titrating liberated I_2 with $Na_2S_2O_3$ to determine the copper content.[**] The aluminum content was determined from the difference in EDTA used to titrate both copper and aluminum.

The precipitated phase was also analyzed for aluminum and sulphate. The solid phase is soluble in strong sulphuric acid and strong sodium hydroxide, and therefore the same methods as for the solutions were used for analysis. Water content was taken as the difference between the total weight and the aluminum and sulphate content. Li, Na and K content was determined by the "EEL" flame photometer.

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[*]
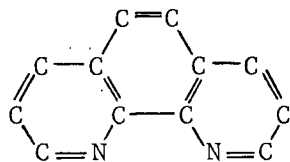
$[Fe(C_{12}H_8N_2)_3]^{++}$ cation; red colour

[**] $\quad 4I^- + 2Cu^{++} \rightleftharpoons 2CuI + I_2$

$\quad\quad I_2 + 2S_2O_3^= \rightleftharpoons 2I^- + S_4O_6^=$
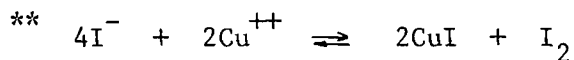
4. RESULTS AND DISCUSSION

The intention of the work presented in this thesis was to study the change in equilibrium hydrolysis of aluminum sulphate solutions with temperature, sulphuric acid concentration and other cations. It is generally known that the amount of precipitated phase is determined by the concentration of aluminum and sulphate in the initial solution for a given temperature.[3] In the present work the concentration of aluminum in the initial solution was not varied in order to make it possible to establish the effect of other factors. Results obtained are discussed under the following classifications:

4.1 The effect of temperature on hydrolysis of aluminum sulphate solutions.

4.2 The effect of sulphuric acid concentration on hydrolysis of aluminum sulphate solutions.

4.3 The equilibrium constants

4.4 Ternary diagrams for the $Al_2O_3-SO_3-H_2O$ system.

4.5 Mechanism of the hydrolysis of aluminum sulphate.

4.6 The effect of alkali metal sulphates on hydrolysis of aluminum sulphate.

4.7 The effect of divalent metal sulphates on hydrolysis of aluminum sulphate solutions.

4.8 Application of the hydrolysis process.

4.1 The Effect of Temperature on Hydrolysis of Aluminum Sulphate Solutions

At ordinary temperatures, concentrated solutions of aluminum sulphate will only crystallize a basic salt if the $SO_3:Al_2O_3$ ratio in the initial solution is less than 3.0.

S. Bretsznajder[14] has obtained normal aluminum sulphate from clay (calcined at 770-820°C for 1 hr) by leaching it with dilute sulphuric acid for 10-12 hrs at 80°C and cooling the filtrate to crystallize the normal aluminum sulphate hydrate. It was reported by T.R. Scott[3] that at temperatures higher than 110°C hydrolysis of aluminum sulphate solutions with initial $SO_3:Al_2O_3$ ratio less than 3.0 precipitates crystalline material "basic aluminum sulphate" (B.A.S.). This compound is related to the mineral alunite, having a formula expressed as $3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O$ with a theoretical composition as follows: Al_2O_3 = 38.8%; SO_3 = 40.6%; H_2O = 20.6%.

The temperature effect on hydrolysis was determined by hydrolyzing dilute solutions of aluminum sulphate with initial $SO_3:Al_2O_3$ ratio of about 3.0 in the temperature range 125-250°C. Retention time in these experiments was as long as 16 hrs. The equilibrium was determined from the hydrolysis curves when there was no further change in the aluminum concentration with prolonged time.

4.1.1 Hydrolysis of Aluminum Sulphate Solutions at 125°C

Hydrolysis experiments at this temperature were done with unfiltered solutions of pH = 3.10. Results obtained were not reproducible. When the same solutions were filtered, and then hydrolyzed, results were more uniform. Hydrolysis yields at equal time intervals were less for

filtered solutions, and, in both cases, not sufficient for chemical analysis. For times which were long enough to establish equilibrium, hydrolysis yields were almost the same for both the filtered and the unfiltered solutions, thus suggesting that a nucleation process plays an important role in the kinetics of the reaction at this temperature. Results of the analysis of hydrolyzed solutions are shown in Table 1 and Fig. 9.

Table 1. Hydrolysis of aluminum sulphate solutions at 125°C.[*]

Time at 125°C hrs	Al in sol. gr/ℓ	SO_4 in sol. gr/ℓ	Al prec. gr/ℓ	SO_4 prec. gr/ℓ	pH	SO_3/Al_2O_3 in the prec.
1.00	6.09	–	0.01	–	2.98	–
3.00	5.89	–	0.21	–	2.53	–
5.00	5.80	31.70	0.30	0.70	2.24	1.31
6.00	5.69	31.33	0.41	1.07	1.80	1.47
7.00	5.68	31.34	0.42	1.06	1.80	1.41
12.50	5.76	31.30	0.34	1.10	1.78	1.82
13.75	5.65	31.38	0.45	1.02	1.79	1.27
16.50	5.68	31.38	0.42	1.02	1.78	1.36

[*] Starting solution: 32.40 ± 0.3 gr/ℓ $SO_4^=$
6.10 ± 0.05 gr/ℓ Al
pH = 3.10

Fig. 9. HYDROLYSIS OF ALUMINIUM SULPHATE AT 125 C°

4.1.2   Hydrolysis of Aluminum Sulphate Solutions at 150°C

Filtered solutions of aluminum sulphate with initial $SO_3:Al_2O_3$

ratio of about 3.0 were hydrolyzed at 150°C for different times.

Results obtained are presented in Table 2 and Fig. 10. From Fig. 10

equilibrium seems to be reached in 6.0 hrs and the $SO_3:Al_2O_3$ ratio

of the precipitated compound remains unchanged with prolonged times.

The amount of precipitated compound was not sufficient for chemical

analysis but the X-ray diffraction pattern indicated that basic

aluminum sulphate existed at this temperature (see Appendix III-A).

Table 2. Hydrolysis of aluminum sulphate solutions at 150°C[*]

Time at 150°C	Al in sol.	$SO_4^=$ in sol.	Al prec.	SO_4 prec.	pH	$SO_3:Al_2O_3$
hrs	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ		in the prec.
1.00	5.28	30.44	0.82	1.96	1.67	1.34
2.00	5.07	29.96	1.03	2.44	1.55	1.33
3.00	4.84	-	1.26	-	1.45	-
4.00	4.76	-	1.34	-	1.45	-
6.00	4.64	28.65	1.46	3.75	1.40	1.44
10.00	4.64	28.60	1.46	3.80	1.38	1.46
16.00	4.65	28.64	1.45	3.46	1.44	1.34

[*] Starting solution: 32.40 gr/ℓ $SO_4^=$

6.10 gr/ℓ Al

pH = 3.10

Fig.10. HYDROLYSIS OF ALUMINIUM SULPHATE AT 150 C°

time in hrs.

4.1.3 Hydrolysis of Aluminum Sulphate Solutions at 175°C

Filtered solutions of aluminum sulphate with initial $SO_3:Al_2O_3$

ratio of about 3.0 were hydrolyzed at 175°C and results obtained are

presented in Table 3 and Fig. 11. The precipitated phase has a ratio

of $SO_3:Al_2O_3$ of about 1.32 (calculated from Fig. 11) corresponding to

the ratio of basic aluminum sulphate. Analysis of the solid phase

confirmed the presence of the basic aluminum sulphate (see Appendix

II. for Chem. Anal. and Appendix III-B for X-ray diff. patterns.).

Table 3. Hydrolysis of aluminum sulphate solutions at 175°C[*]

Time at 175°C	Al in sol.	$SO_4^=$ in sol.	Al prec.	SO_4 prec.	pH	$SO_3:Al_2O_3$ in the prec.
hrs.	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ		
1.00	4.45	28.53	1.54	3.87	1.30	1.32
2.00	3.96	27.26	2.14	5.14	1.27	1.35
4.00	3.68	26.76	2.42	5.64	1.18	1.31
6.00	3.56	26.39	2.54	6.01	1.15	1.33
10.00	3.55	26.40	2.55	6.00	1.15	1.32
16.30	3.50	26.40	2.60	6.00	1.15	1.30

[*] Starting solution: 32.40 gr/ℓ $SO_4^=$
6.10 gr/ℓ Al
pH = 3.10

Fig.II. HYDROLYSIS OF ALUMINIUM SULPHATE AT 175 C°
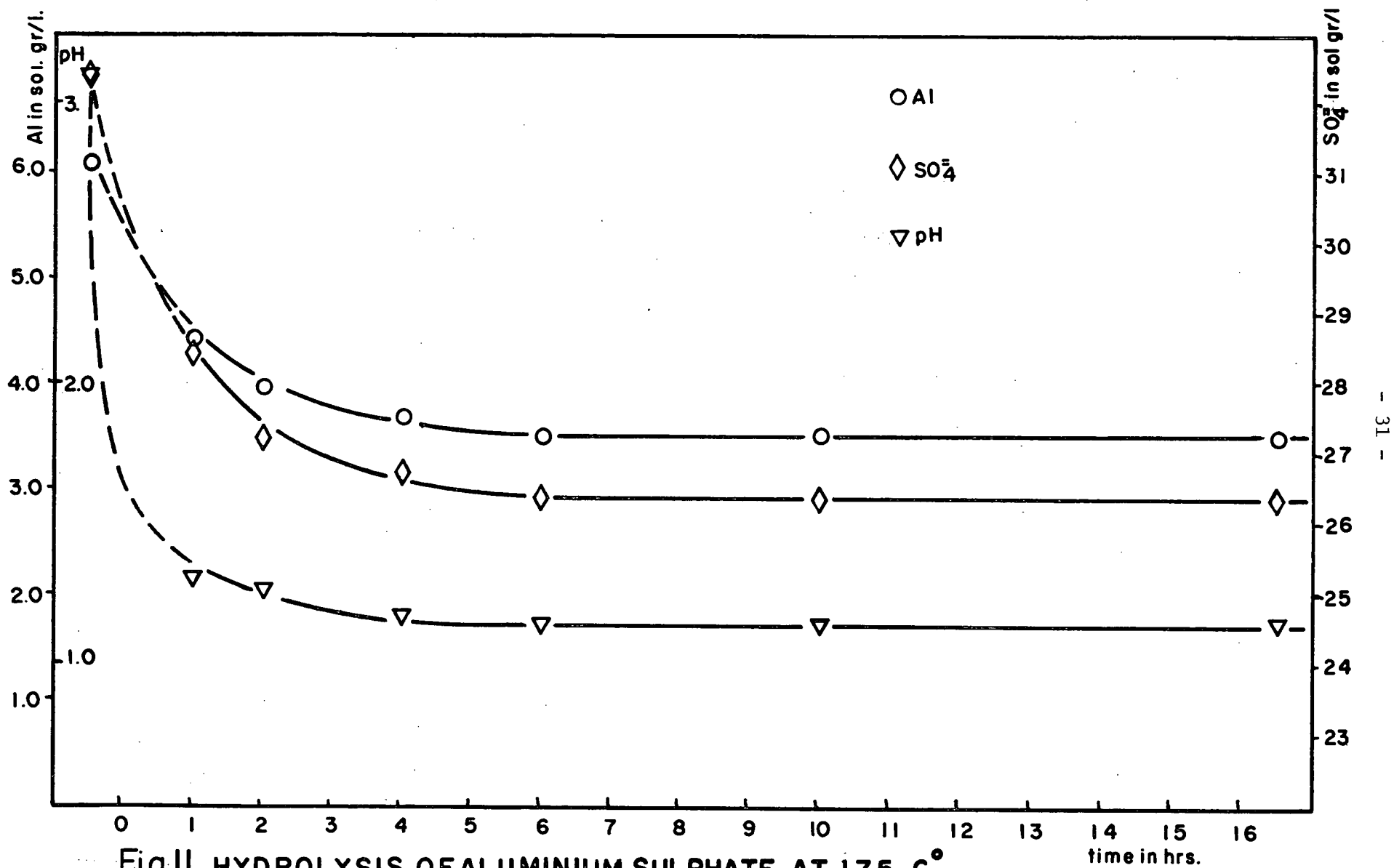
4.1.4   Hydrolysis of Aluminum Sulphate Solutions at 200°C

Solutions with intial $SO_3:Al_2O_3$ ratio of about 3.0 were hydrolyzed at 200°C for as long as 18 hrs. Results obtained are shown in Table 4 and Fig. 12. The equilibrium hydrolysis yield is higher than at 175°C. The $SO_3:Al_2O_3$ ratio of the precipitated compound calculated from Fig. 12 is about 1.31.   Analysis of solid phase shows that the precipitated compound is the basic aluminum sulphate (see Appendix II for Chem. anal. and Appendix III-C for X-ray diff. pattern).

Table 4. Hydrolysis of aluminum sulphate solutions at 200°C[*]

Time at 200°C	Al in sol.	$SO_4^=$ in sol.	Al prec.	SO_4 prec.	pH	$SO_3:Al_2O_3$
hrs.	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ		in the prec.
1.00	3.30	25.78	2.80	6.62	1.07	1.33
2.00	3.01	24.98	3.09	7.42	1.03	1.35
4.00	2.71	24.32	3.39	8.08	0.99	1.34
6.00	2.51	23.91	3.59	8.49	0.98	1.33
6.45	2.51	23.89	3.59	8.51	0.98	1.33
18.00	2.40	23.65	3.70	8.75	0.98	1.33

[*] Starting solution: 32.40 gr/ℓ $SO_4^=$

6.10 gr/ℓ Al

pH = 3.10
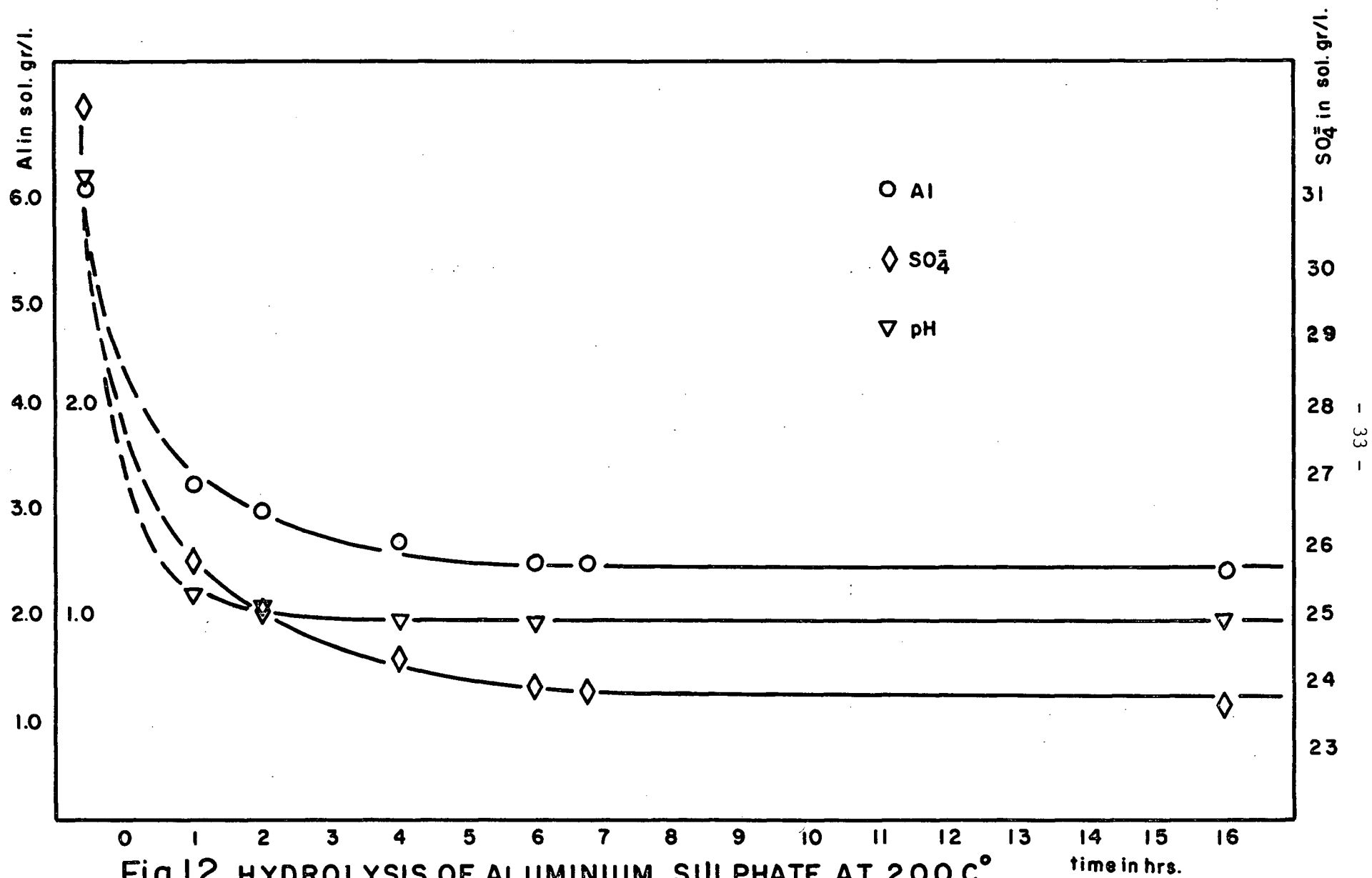
Fig.12. HYDROLYSIS OF ALUMINIUM SULPHATE AT 200 C°

4.1.5   Hydrolysis of Aluminum Sulphate Solutions at 225°C

Filtered solutions of aluminum sulphate with initial SO_3:Al_2O_3 ratio of about 3.0 were hydrolyzed at 225°C and results obtained are shown in Table 5 and Fig. 13. Hydrolysis yields are very high. The precipitated phase has an SO_3:Al_2O_3 ratio 1.33 (calculated from Fig. 13). Analysis of the solid phase showed the composition of basic aluminum sulphate (see Appendix II for Chem. anal. and Appendix III-D for X-ray diff. pattern).

Table 5. Hydrolysis of aluminum sulphate solutions at 225°C[*]

Time at 225°C	Al in sol.	$SO_4^=$ in sol.	Al prec.	SO_4 prec.	pH	SO_3:Al_2O_3
hrs.	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ		in the prec.
1.00	1.89	22.45	4.21	9.95	0.89	1.33
1.00	1.88	22.35	4.22	10.05	0.92	1.34
2.00	1.80	22.31	4.30	10.09	0.92	1.32
2.00	1.73	21.55	4.37	10.85	0.89	1.39
3.00	1.65	21.96	4.45	10.44	0.88	1.32
5.00	1.58	21.40	4.52	11.00	0.89	1.37
8.40	1.44	21.36	4.66	11.04	0.85	1.33
16.00	1.48	21.63	4.54	10.77	0.85	1.33

[*]   Starting solution: 32.40 gr/ℓ $SO_4^=$
                            6.10 gr/ℓ Al
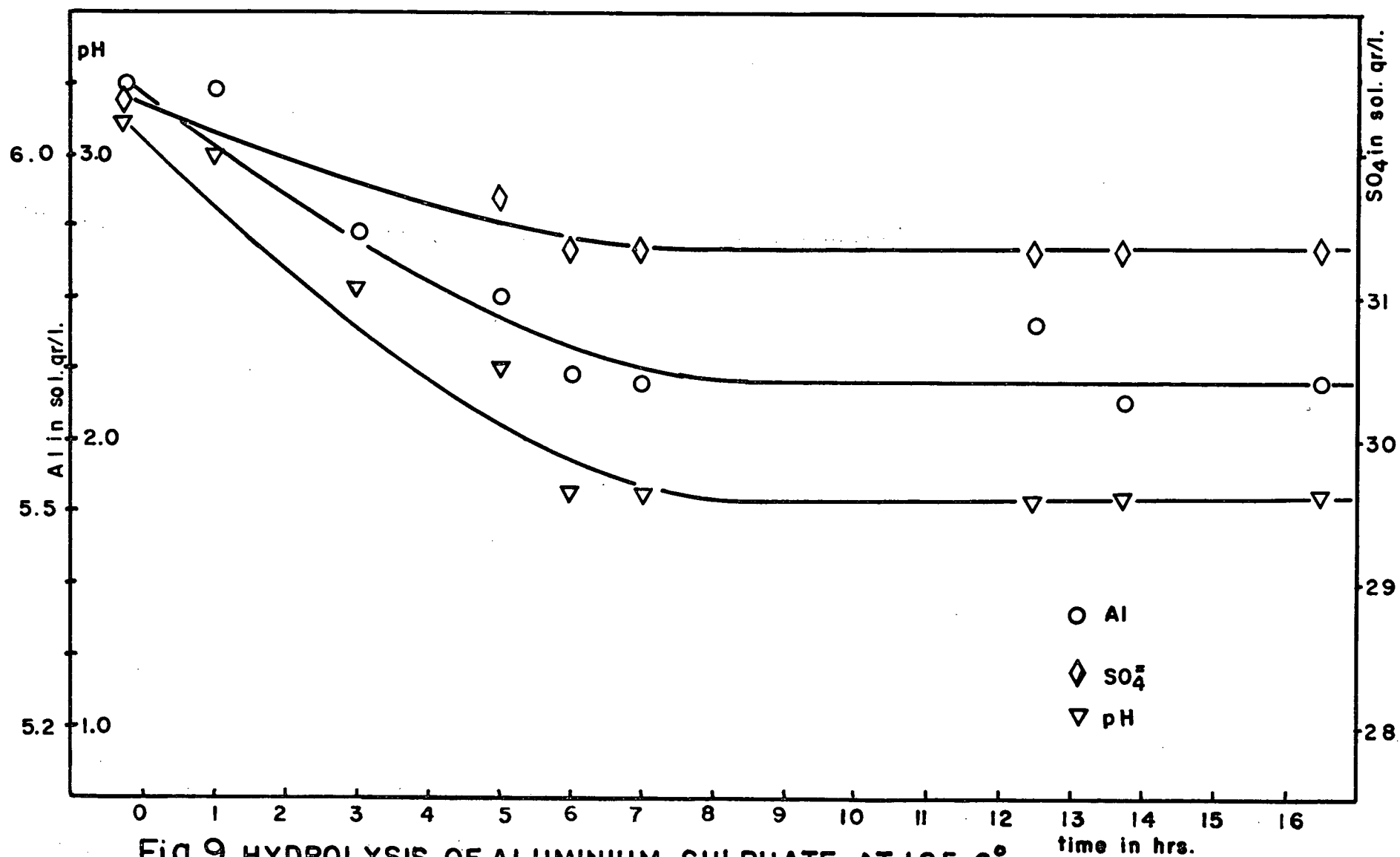   pH = 3.10

Fig.13. HYDROLYSIS OF ALUMINIUM SULPHATE AT 225 C°   time in hrs.

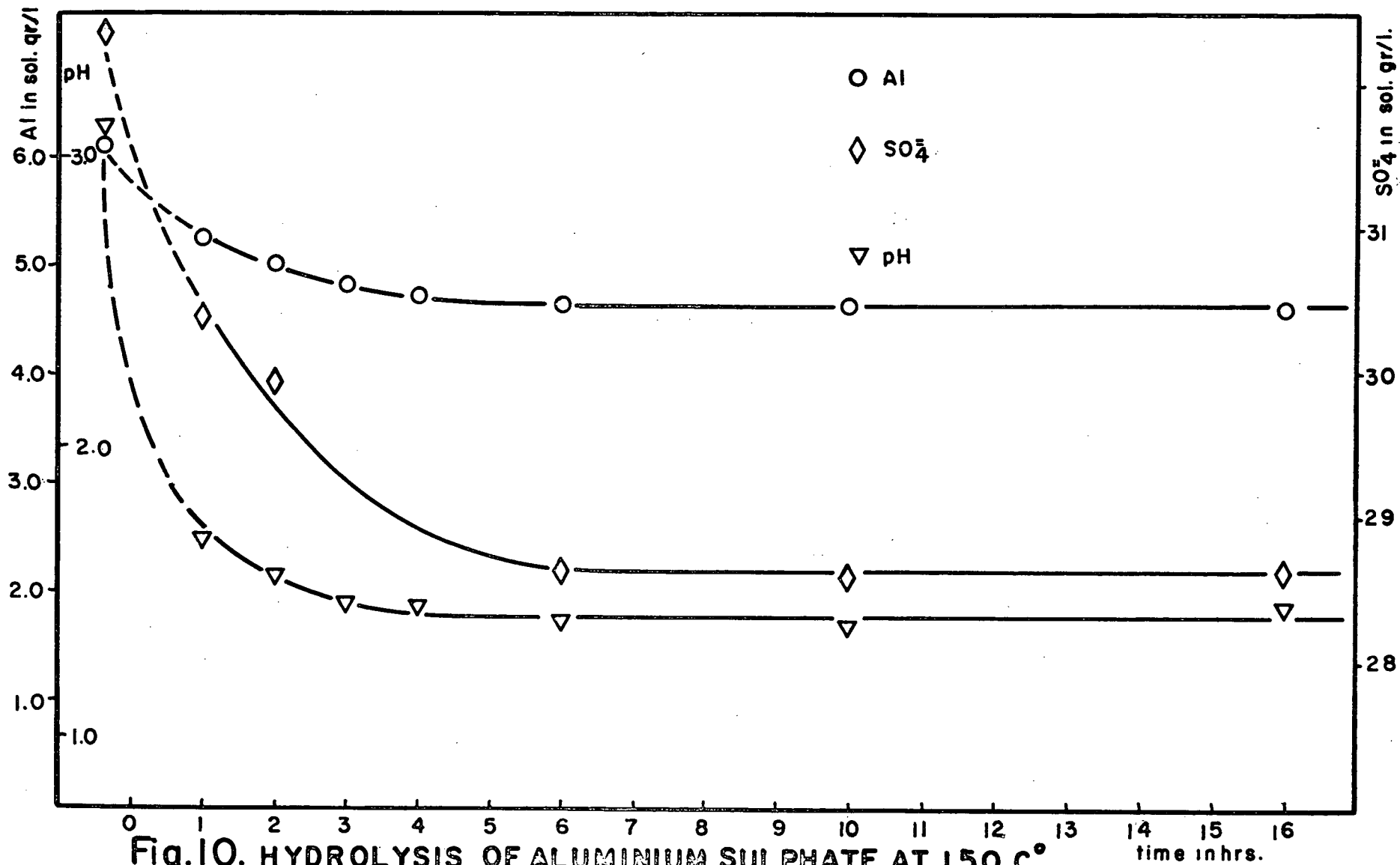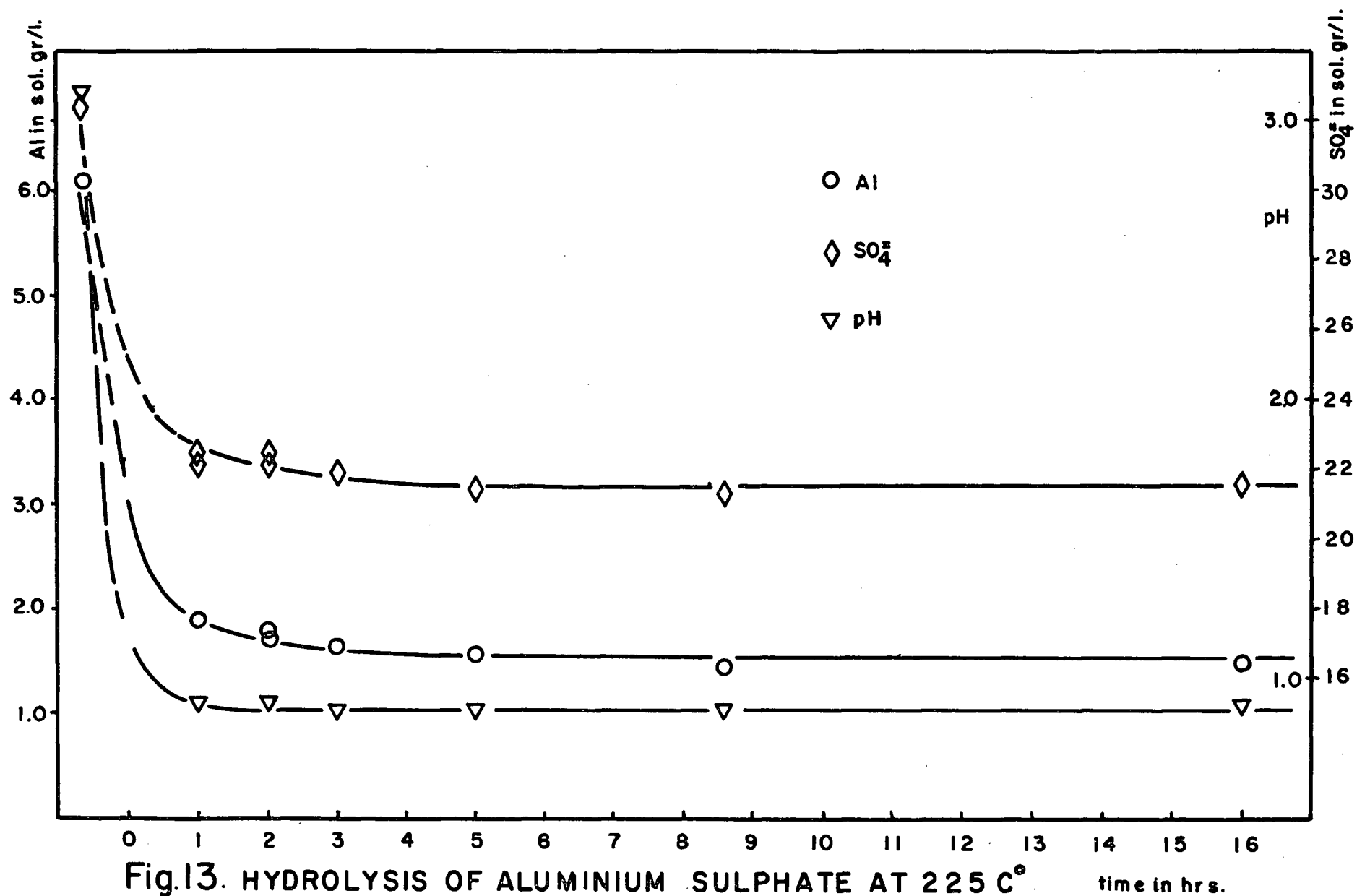#### 4.1.6 Hydrolysis of Aluminum Sulphate Solutions at 250°C

Filtered solutions of aluminum sulphate were hydrolyzed at 250°C and it was found that the amount of precipitated basic aluminum sulphate on heating the autoclave to this temperature was comparable to the amount of basic salt precipitated in 16 hrs at 225°C. This suggests that the reaction rate above 225°C must be very high. Results obtained at this temperature are shown in Table 6 and Fig. 14. The $SO_3:Al_2O_3$ ratio of the precipitated compound is 1.33. Analysis of the solid corresponds to the basic aluminum sulphate (see Appendix II for Chem. anal. and Appendix III-E for X-ray diff. pattern).

Table 6. Hydrolysis of aluminum sulphate at 250°C[*]

Time at 250°C	Al in sol.	$SO_4^=$ in sol.	Al prec.	SO_4 prec.	pH	$SO_3:Al_2O_3$
hrs.	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ		in the prec.
0.00	1.52	21.57	4.58	10.83	0.85	1.33
1.00	0.97	20.27	5.13	12.13	0.80	1.33
3.30	0.88	20.27	5.22	12.13	0.80	1.31
6.30	0.91	20.13	5.19	12.27	0.79	1.33

[*] Starting solution: 32.40 gr/ℓ $SO_4^=$
6.10 gr/ℓ Al
pH = 3.10
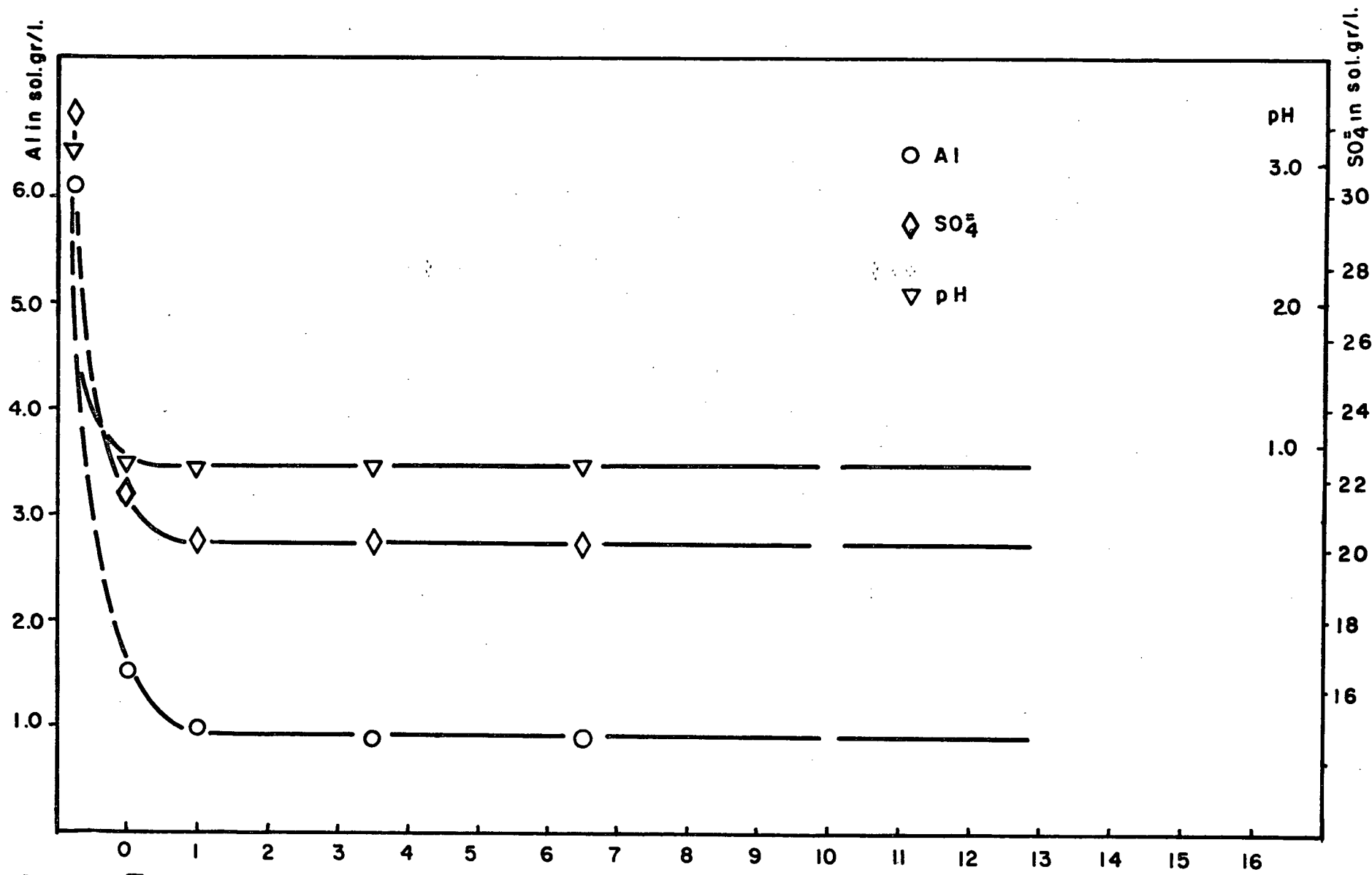
Fig. 14. HYDROLYSIS OF ALUMINIUM SULPHATE AT 250 C°

4.2   The Effect of Sulphuric Acid Concentration on Hydrolysis

         of Aluminum Sulphate Solutions

Most of the work on hydrolysis of aluminum sulphate was done on

solutions having initial $SO_3:Al_2O_3$ ratio less than 3.0. The reason

for this was to obtain high yields in a short time and at low tempera-

tures. If hydrolysis is to be used as a purification process for

leach solutions higher concentrations of sulphuric acid would be

expected. In the work presented in this thesis a series of experiments

with solutions containing about 6.0 gr/ℓ aluminum and different

concentrations of sulphuric acid was done. Hydrolysis curves in the

previous part were used to determine the retention time for the two

temperatures 225°C and 250°C. These two temperatures were chosen because

of the high yields at short times   with solutions having an $SO_3:Al_2O_3$

ratio of about 3.0.

4.2.1   Hydrolysis of Aluminum Sulphate Solutions with Initial

         $SO_3:Al_2O_3$ Ratio > 3.0 at 250°C

Filtered solutions with excess sulphuric acid were hydrolyzed at

250°C for 4 hrs. The highest $SO_3:Al_2O_3$ ratio used in this set of

experiments was about 4.63. Results obtained are shown in Table 7 and

Fig. 15. As the concentration of excess acid in the initial

solution was increased the amount of precipitated basic aluminum

sulphate decreased.
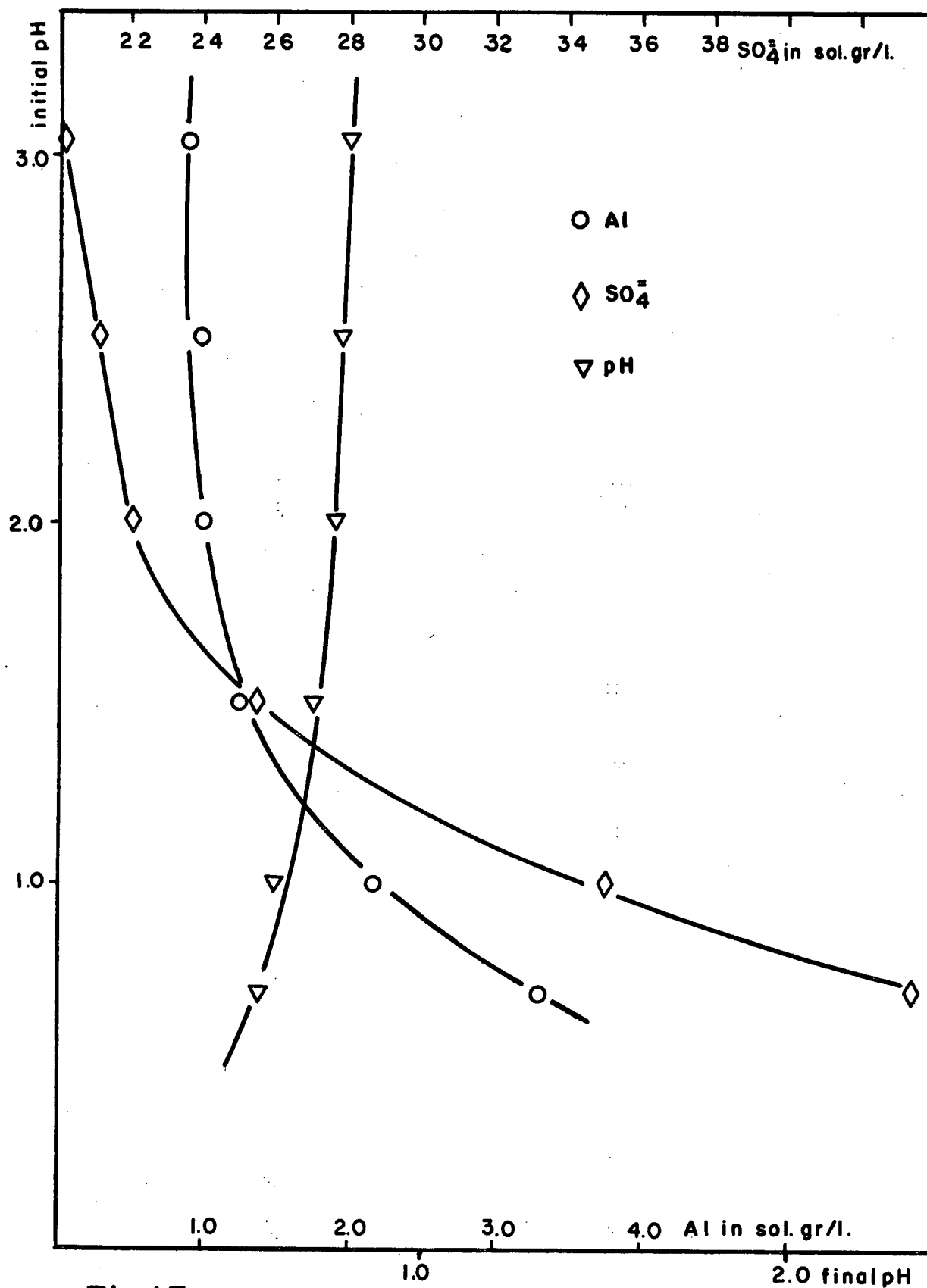
Fig.15. HYDROLYSIS OF ACID ALUMINIUM
SULPHATE AT 250 C°

Table 7. The effect of excess sulphuric acid on hydrolysis of
aluminum sulphate at 250°C.

pH initial	$SO_4^=$ init. gr/ℓ	Al in sol. gr/ℓ	$SO_4^=$ in sol. gr/ℓ	Al prec. gr/ℓ	SO_4 prec. gr/ℓ	pH final
0.70	50.08	3.31	43.43	2.79	6.65	0.56
1.00	44.26	2.17	34.97	3.93	9.29	0.60
1.50	37.05	1.25	25.45	4.85	11.60	0.70
2.00	34.08	1.00	22.05	5.10	12.03	0.76
2.50	33.21	0.98	21.13	5.12	12.08	0.78
3.10	32.40	0.91	20.13	5.19	12.27	0.80

4.2.2 Hydrolysis of Aluminum Sulphate Solutions with Initial $SO_3:Al_2O_3$ Ratio > 3.0 at 225°C

Filtered solutions of aluminum sulphate were hydrolyzed at 225°C for 6 hrs. Initial solutions used in this set of experiments were the same as solutions used at 250°C. Hydrolysis yields increased with increasing pH of the initial solution. Results obtained from this set of experiments are presented in Table 8 and Fig. 16.
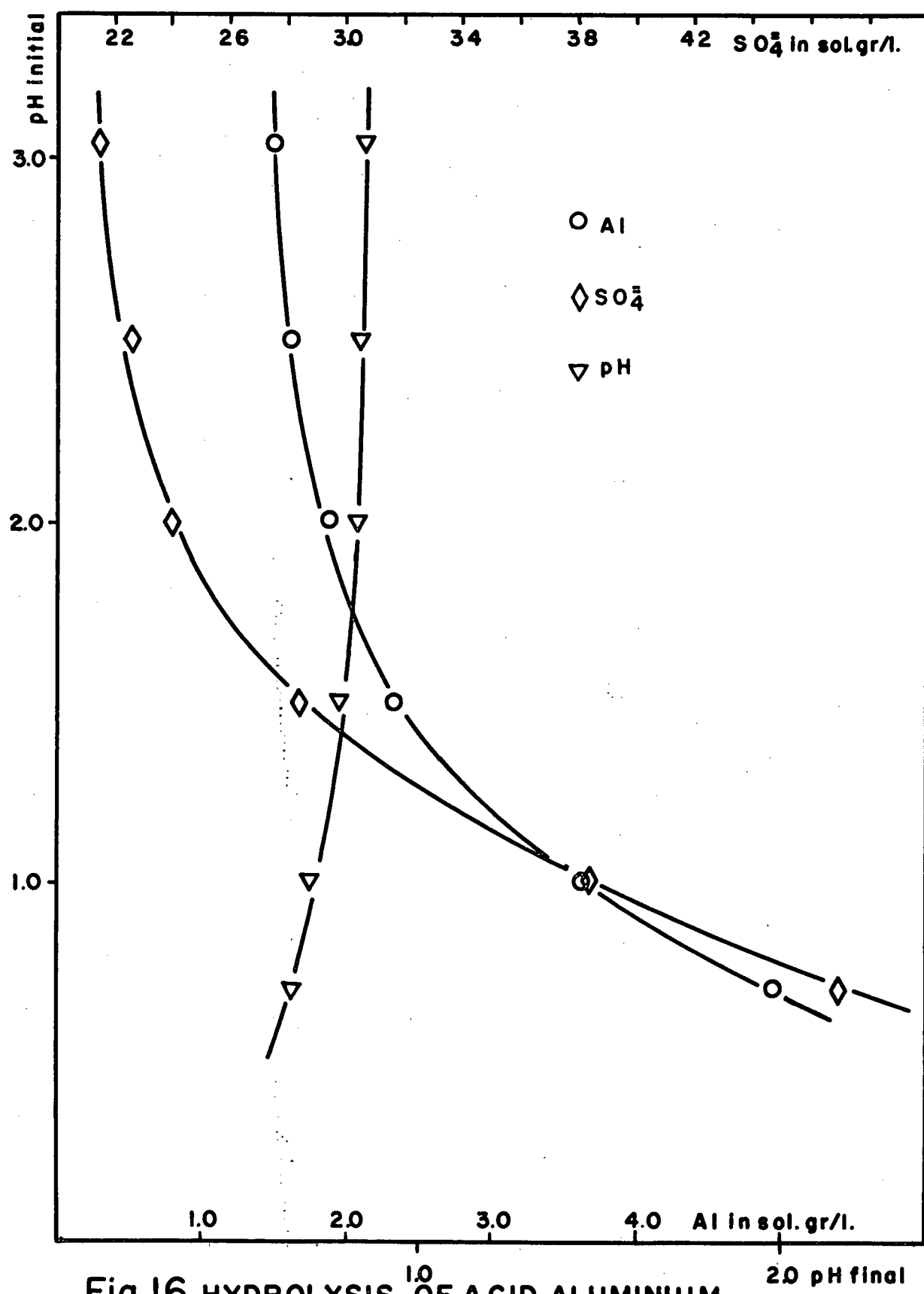
Fig. 16. HYDROLYSIS OF ACID ALUMINIUM
SULPHATE AT 2 25 C°

Table 8. The effect of excess sulphuric acid on hydrolysis of

aluminum sulphate at 225°C.

pH initial	$SO_4^=$ init. gr/ℓ	Al in sol. gr/ℓ	$SO_4^=$ in sol. gr/ℓ	Al prec. gr/ℓ	$SO_4^=$ prec. gr/ℓ	pH final
0.70	50.08	4.94	47.04	1.16	3.04	0.65
1.00	44.26	3.62	38.35	2.48	5.91	0.70
1.50	37.05	2.33	28.37	3.77	8.68	0.78
2.00	34.08	1.87	24.10	4.23	9.98	0.83
2.50	33.21	1.63	22.60	4.47	10.61	0.84
3.10	32.40	1.50	21.52	4.60	10.88	0.85

4.3 The Equilibrium Constants

Application of the phase rule to the system Al_2O_3-SO_3-H_2O requires

that at constant temperature, a solution composition exists which is

invariant when in equilibrium with two solid phases, e.g. $Al_2O_3 \cdot nH_2O$ and

$3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O$ (B.A.S. - the most basic salt).

If the starting solution has a composition below this point,

the first phase to precipitate is always the oxide, but the solution

composition will change in the direction of the invariant point until

the basic salt also precipitates. The location of the invariant

point P (Fig. 17) will change with the temperature.
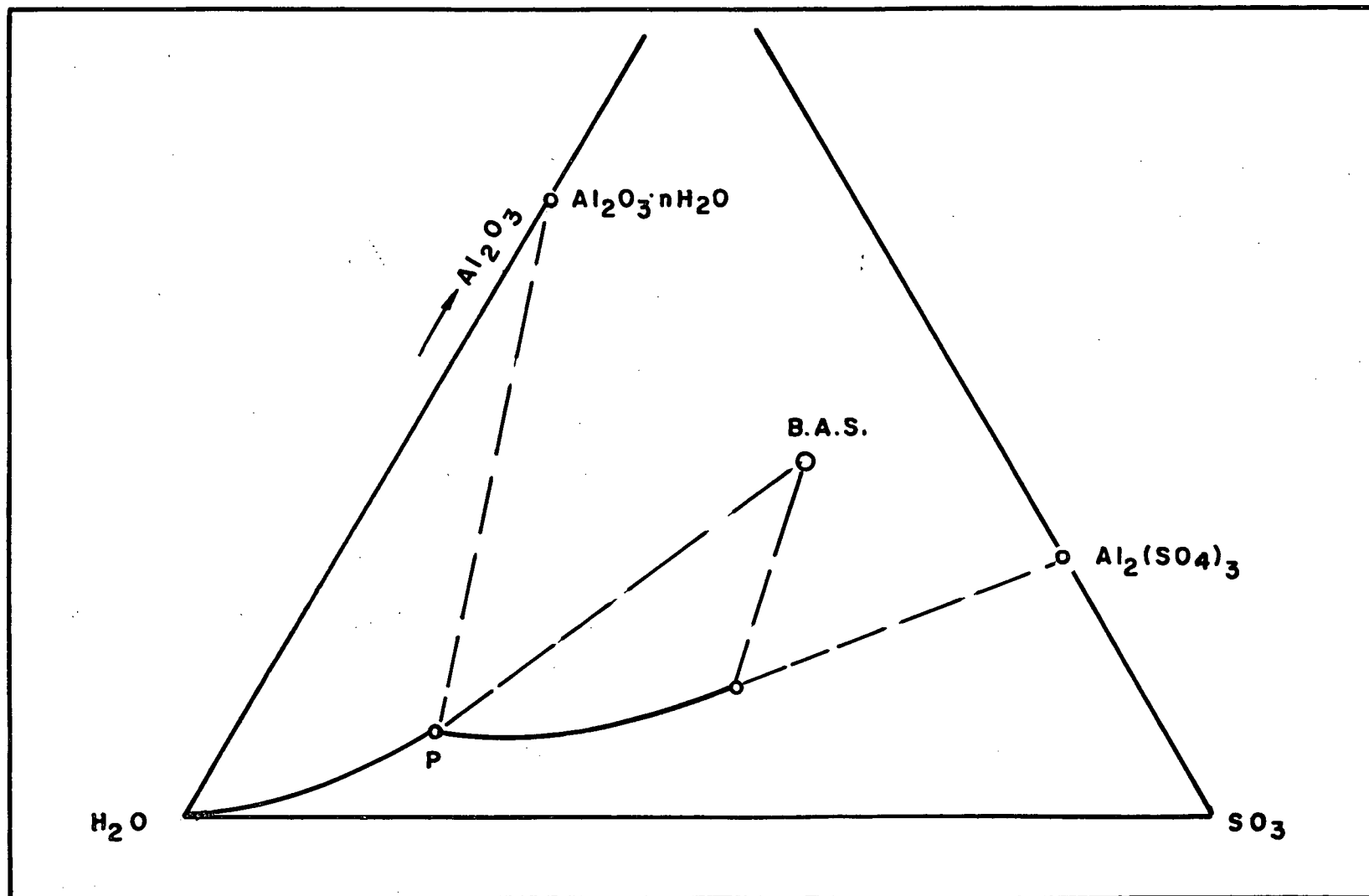
Fig.17. PHASE DIAGRAM OF THE $Al_2O_3-SO_3-H_2O$ SYSTEM

If the solution composition is below the invariant point P at the temperature T and above the invariant point at any temperature higher than T, then the oxide will precipitate in the early stages of heating and at later stages the basic salt will precipitate while the oxide will tend to redissolve. Eventually the oxide may completely disappear if the composition of the solution is such that it is above the invatiant point. In the work of T.R. Scott, a second phase $(Al_2O_3 \cdot nH_2O)$ was not observed because the hudrolysis was carried out at high concentrations of aluminum in solutions and it can only be expected to precipitate from dilute solutions of basic aluminum sulphate.

The X-ray diffraction patterns did not show the presence of Al_2O_3 in the solid phase and therefore it can be concluded that the solution composition is above the invariant point where only one phase exists in equilibrium with the liquid phase. The X-ray diffraction pattern of the precipitate obtained at $125^{\circ}C$, was very poor so that no conclusion about the presence of aluminum oxide could be made. If there is only one solid phase in equilibrium with liquid phase at all temperatures from $125^{\circ}C$ up to $250^{\circ}C$, then the same hydrolysis reaction should occur. For such a reaction, the slope of a plot of log [equilibrium constant] vs. $1/T^{\circ}K$ should be linear.

R.G. Robins[21] has reported values for the second dissociation constant of sulphuric acid up to about $200^{\circ}C$ which are in good agreement with the values calculated from the correspondence principle. Values of these constants are given in Table 9. The presence of aluminum sulphate will shift the equilibrium to the left in the reaction $4SO_4^- \rightleftharpoons H^+ + SO_4^=$. Therefore only HSO_4^- ions will exist in solution. Assuming that aluminum sulphate is completely dissociated, and that only HSO_4^- ion can exist

Table 9. Equilibrium constants for the reaction $HSO_4^- \underset{\leftarrow}{\rightarrow} H^+ + SO_4^=$

T°C	125	150	175	200	225	250
log K	-3.53	-3.89	-4.40	-4.72	-5.95	-6.05

in solution in the temperature range 125-250°C the hydrolysis reaction can be written as:

$$6Al^{+++} + 4HSO_4^- + 14H_2O \rightleftharpoons 3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O + 14H^+ \qquad (1)$$
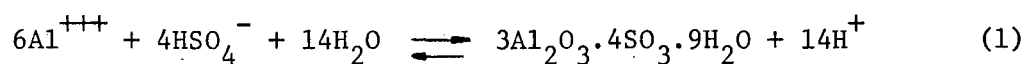
The equilibrium constant for this reaction can be expressed as:

$$K = \frac{[H^+]^{14}}{[Al^{+++}]^6 [HSO_4^-]^4} \qquad (2)$$

An expression for the variation of the equilibrium constant K with temperature is derived by combining

$$-\Delta G° = RT \ln K \qquad (3)$$

and

$$\left[\frac{\partial}{\partial T} \left(\frac{\Delta G°}{T}\right)\right]_P = -\frac{\Delta H°}{T^2} \qquad (4)$$

Therefore

$$\left(\frac{\partial \ln K}{\partial T}\right)_P = \frac{d \ln K}{dT} = \frac{\Delta H°}{RT^2} \qquad (5)$$

assuming that $\Delta H°$ is virtually independent of temperature. Equation (5) can be also written as

$$\frac{d \ln K}{d\ 1/T} = -\frac{\Delta H°}{R} \tag{6}$$

Thus, if $\ln K$ is plotted against $1/T$ the slope of the curve at any point is equal to $-\Delta H°/R$. From the expression for the equilibrium constant (2) it follows that

$$-\log K = 14pH + 6 \log [Al^{+++}] + 4 \log [HSO_4^-] \tag{7}$$

The pH of the hydrolyzed solutions was measured at room temperature and as such it is different from the pH at which the reaction occurs. The change in the dissociation constant of water (Table 10) is such that the pH of the solution should decrease with increasing temperature.

Table 10. Hydrolysis constant of water

T C°	25	60	100	150	200	250	300	350
$-\log K$	14.0	13.05	12.21	11.65	11.30	11.18	11.19	11.33

True pH value at any temperature can be defined thermodynamically but it cannot be easily measured. The pH change which occurs in heating or cooling an electrolyte solution is due to the hydrolysis and change in activity of all ions in solution. Assuming that the pH of hydrolyzed solutions remains unchanged with temperature the equilibrium constant for the hydrolysis reaction can be calculated at each temperature.

Results of the equilibrium hydrolysis of normal aluminum sulphate

solutions in the temperature range 125-250°C are presented in Table

11 and Fig. 18. Results in Table 7 and Table 8 were also used to

calculate the equilibrium constants for hydrolysis of aluminum

sulphate solutions with excess sulphuric acid. Calculated values of

log K   are presented in Table 12.

Table 11. Equilibrium hydrolysis of normal aluminum sulphate in the
temperature range 125-250°C.

Temp.	Aluminum in sol.	Sulphate in sol.	pH
°C	gr/ℓ	gr/ℓ	
125	5.68	31.35	1.78
150	4.65	28.65	1.42
175	3.50	26.40	1.15
200	2.45	23.80	0.98
225	1.46	21.60	0.85
250	0.90	20.20	0.79

Table 12. Values of log K for the hydrolysis of aluminum sulphate
solutions with excess sulphuric acid at 225°C and 250°C

Init. pH	0.70	1.00	1.50	2.00	2.50	3.10
log K_{225}	-3.43	-2.96	-2.42	-2.16	-1.93	-1.77
log K_{250}	-1.00	0.00	0.513	0.503	0.374	0.35
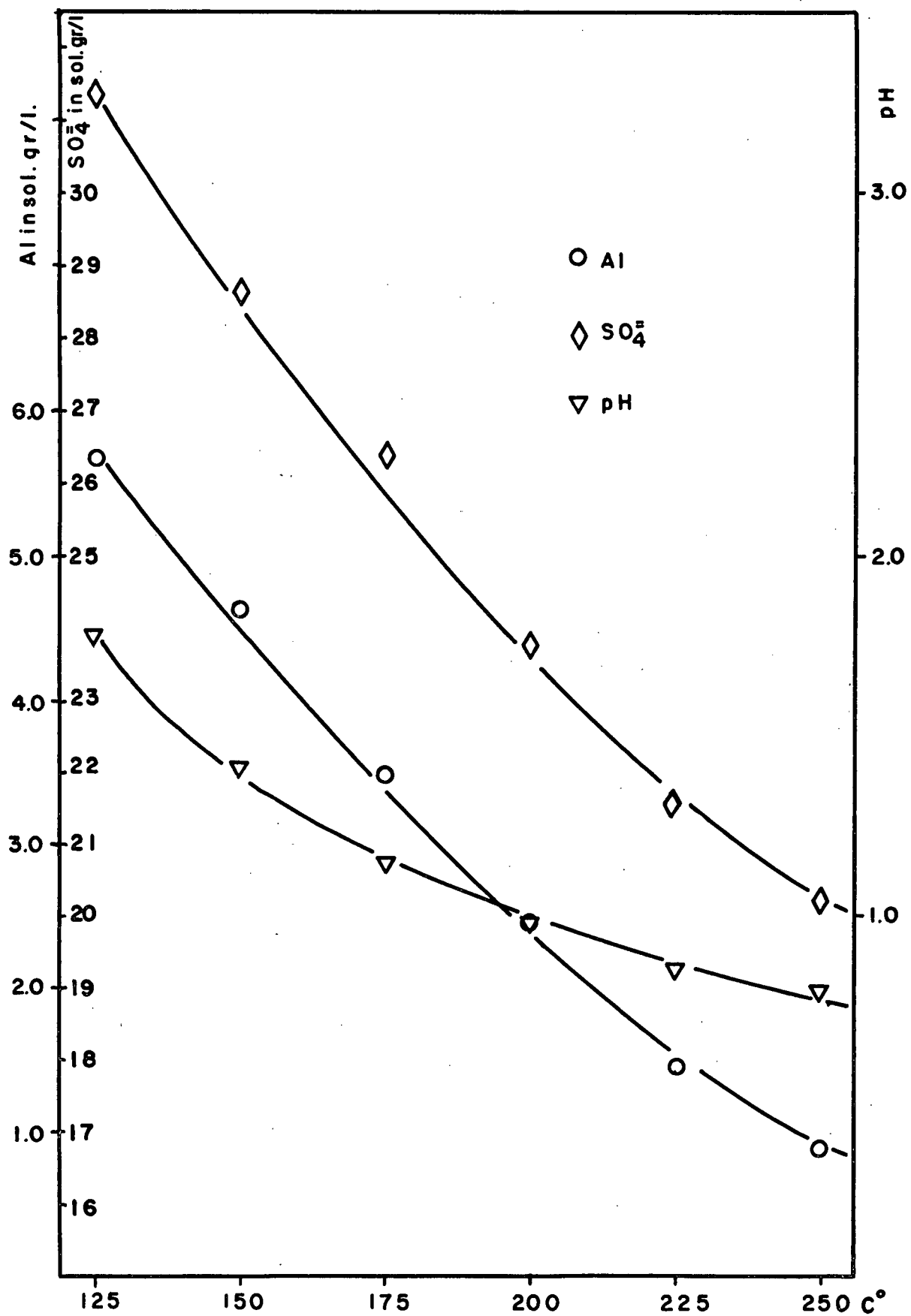
Fig.18. EQUILIBRIUM HYDROLYSIS

Mean equilibrium constants for 225°C and 250°C were calculated from Table 12 and were found to be:

$$\log K_{225°C} = -2.44 \qquad K = 3.62 \times 10^{-3}$$
$$\log K_{250°C} = 0.302 \qquad K = 2.0$$

Table 13 presents the equilibrium constants for hydrolysis reaction of aluminum sulphate in the temperature range 125-250°C.

Table 13. Equilibrium constants for the hydrolysis reaction of aluminum sulphate

$1/T \times 10^4$	log K	$1/T°K$	T°C
25.10	−18.92	1.2×10^{-19}	125
23.60	−13.20	6.3×10^{-14}	150
22.30	− 8.63	2.3×10^{-9}	175
21.10	− 5.05	8.9×10^{-6}	200
20.05	− 2.44	3.6×10^{-3}	225
19.10	+. 0.302	2.0	250

Since the plot of log K against 1/T gives a straight line (Fig. 19) it is most probable that there is only one solid phase in equilibrium with the liquid phase. Therefore the solution composition is above the invariant point P (Fig. 17) at all temperatures.
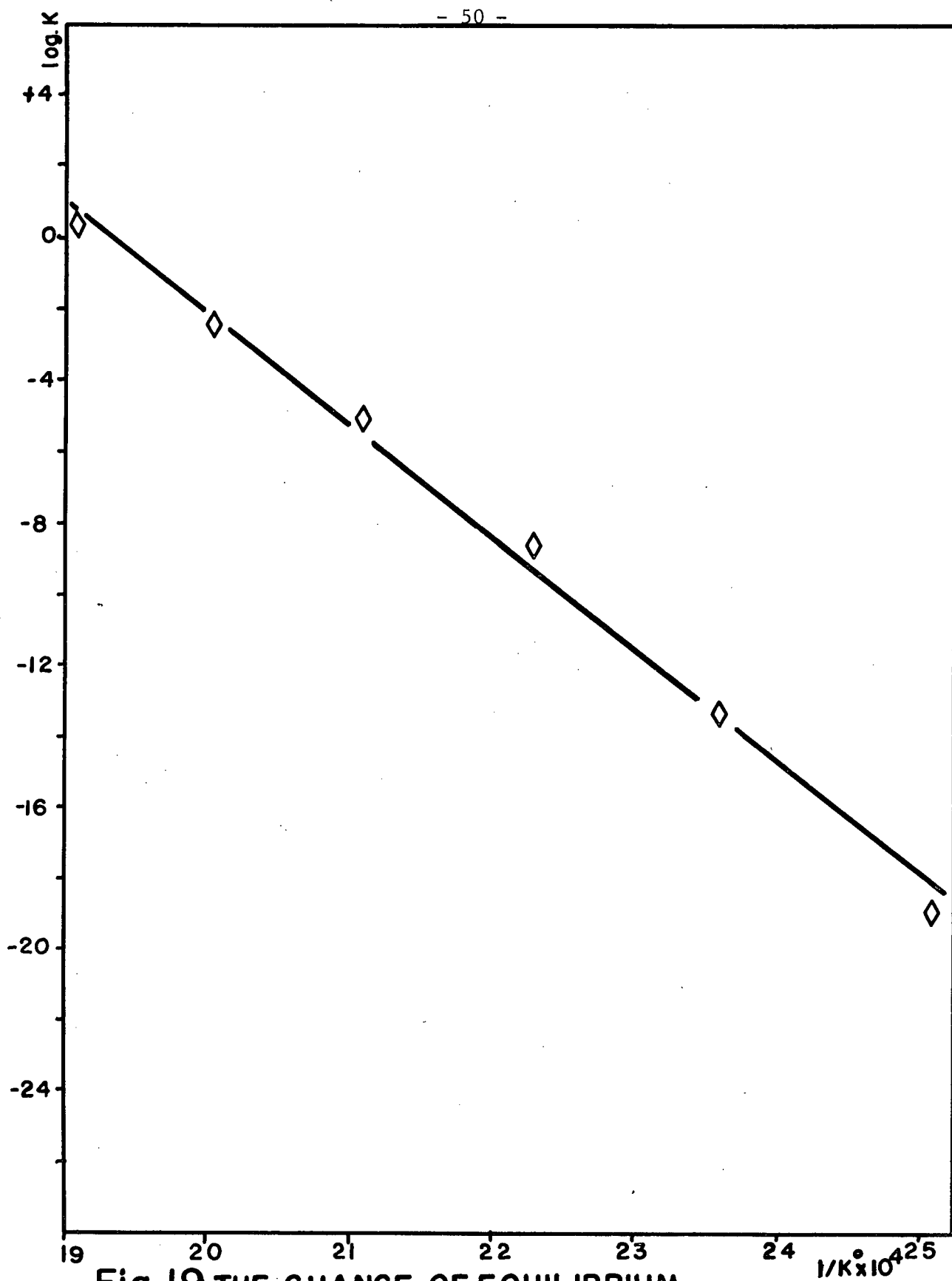
Fig. 19. THE CHANGE OF EQUILIBRIUM
CONSTANT WITH TEMPERATURE

4.4   Ternary Diagrams for the System $Al_2O_3-SO_3-H_2O$

Some data is available on the hydrolysis of basic aluminum sulphate at temperatures up to 220°C,[3] but no useful data is available on hydrolysis of acid aluminum sulphate solutions. Experimental data from Section 4.2 was used to calculate the equilibrium liquid composition in acid aluminum sulphate solutions at 225 and 250°C. Ternary diagrams were constructed for the water corner of the $Al_2O_3-SO_3-H_2O$ system at 225 and 250°C. Tables 14 and 15 show the composition of the initial and final solutions at 250 and 225°C.

Table 14. Solution composition at 250°C

	Starting liq. comp. wt %			Equil. liq. comp. wt %		
	Al_2O_3	SO_3	H_2O	Al_2O_3	SO_3	H_2O
1	1.12	4.10	94.78	0.51	3.52	95.98
2	1.12	3.59	95.29	0.40	2.84	96.76
3	1.12	3.00	95.88	0.23	2.07	97.70
4	1.12	2.77	96.11	0.184	1.79	98.03
5	1.12	2.69	96.20	0.18	1.72	98.10
6	1.12	2.64	96.24	0.168	1.63	98.20

Table 15. Solution composition at 225°C

	Starting liq. comp. wt %			Equil. liq. comp. wt %		
	Al_2O_3	SO_3	H_2O	Al_2O_3	SO_3	H_2O
1	1.12	4.10	94.78	0.91	3.81	95.28
2	1.12	3.59	95.29	0.66	3.11	96.23
3	1.12	3.00	95.88	0.43	2.31	97.26
4	1.12	2.77	96.11	0.345	1.96	97.69
5	1.12	2.69	96.20	0.30	1.84	97.86
6	1.12	2.64	96.24	0.276	1.75	97.97

The data from Tables 14 and 15 are presented graphically in Fig. 20
and 21. The intersection of the initial and final liquid composition
lines suggests the possibility of the presence of a second phase in
the system at 250 and 225°C. The second phase is probably a normal
aluminum sulphate but it could not be detected in any of the experiments
from the X-ray diffraction patterns of the solid. Although a number of
experiments with solutions of the composition corresponding to the points
A_1 and A_2 in Fig. 20 and 21 were done, the presence of a second phase
could not be unambiguously proven.

Acid aluminum sulphate solutions (compositions A_1 and A_2 - Figs.
20 and 21) were hydrolysed for predetermined times, and solution samples
were taken. The autoclave and the remaining material was cooled to room
temperature, and the resulting solution was analyzed. From the difference
in solution compositions, the SO_3:Al_2O_3 ratio of the re-dissolved
precipitate was calculated. It was
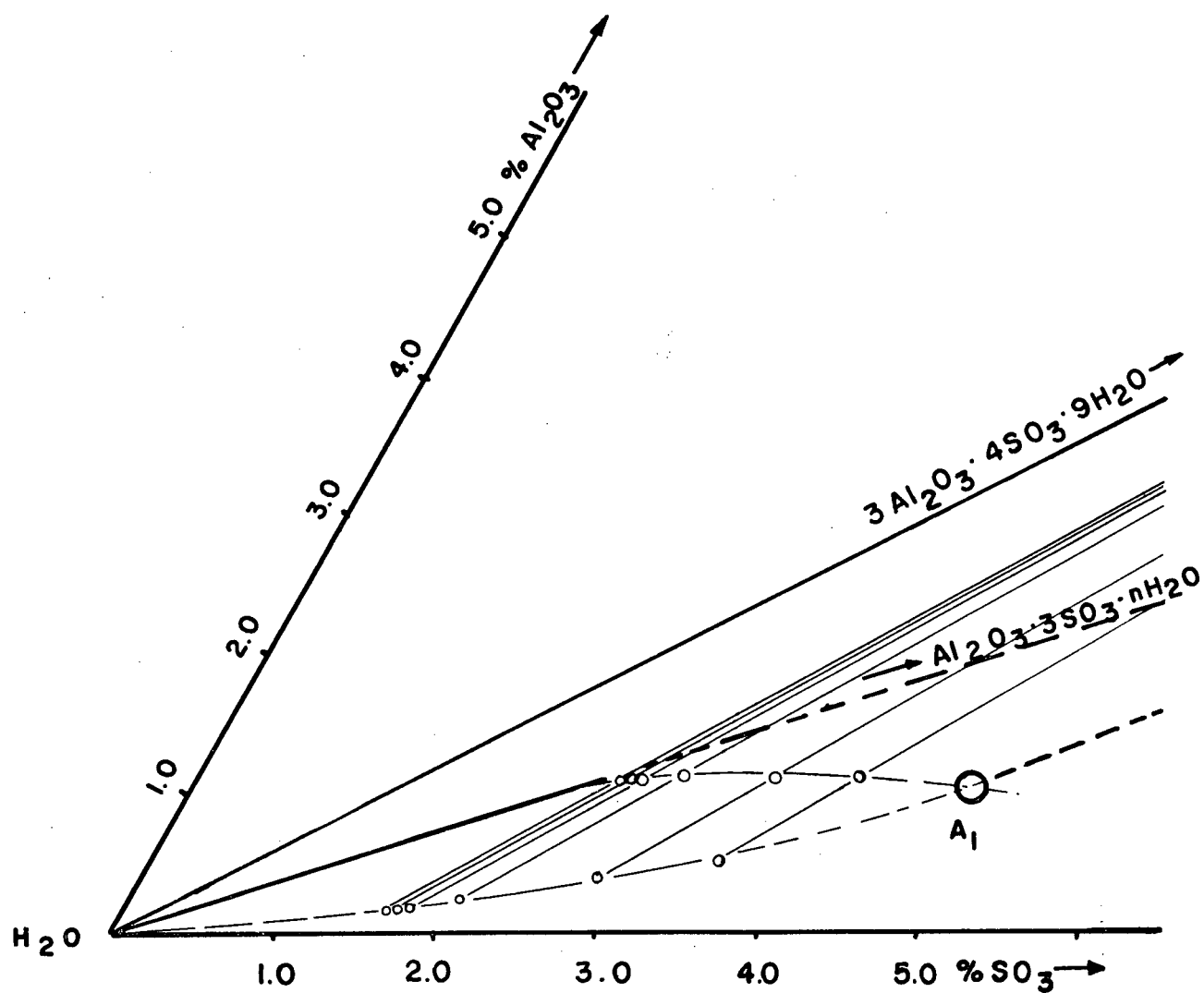
Fig. 20. $Al_2O_3 - SO_3 - H_2O$ SYSTEM AT 250 C°
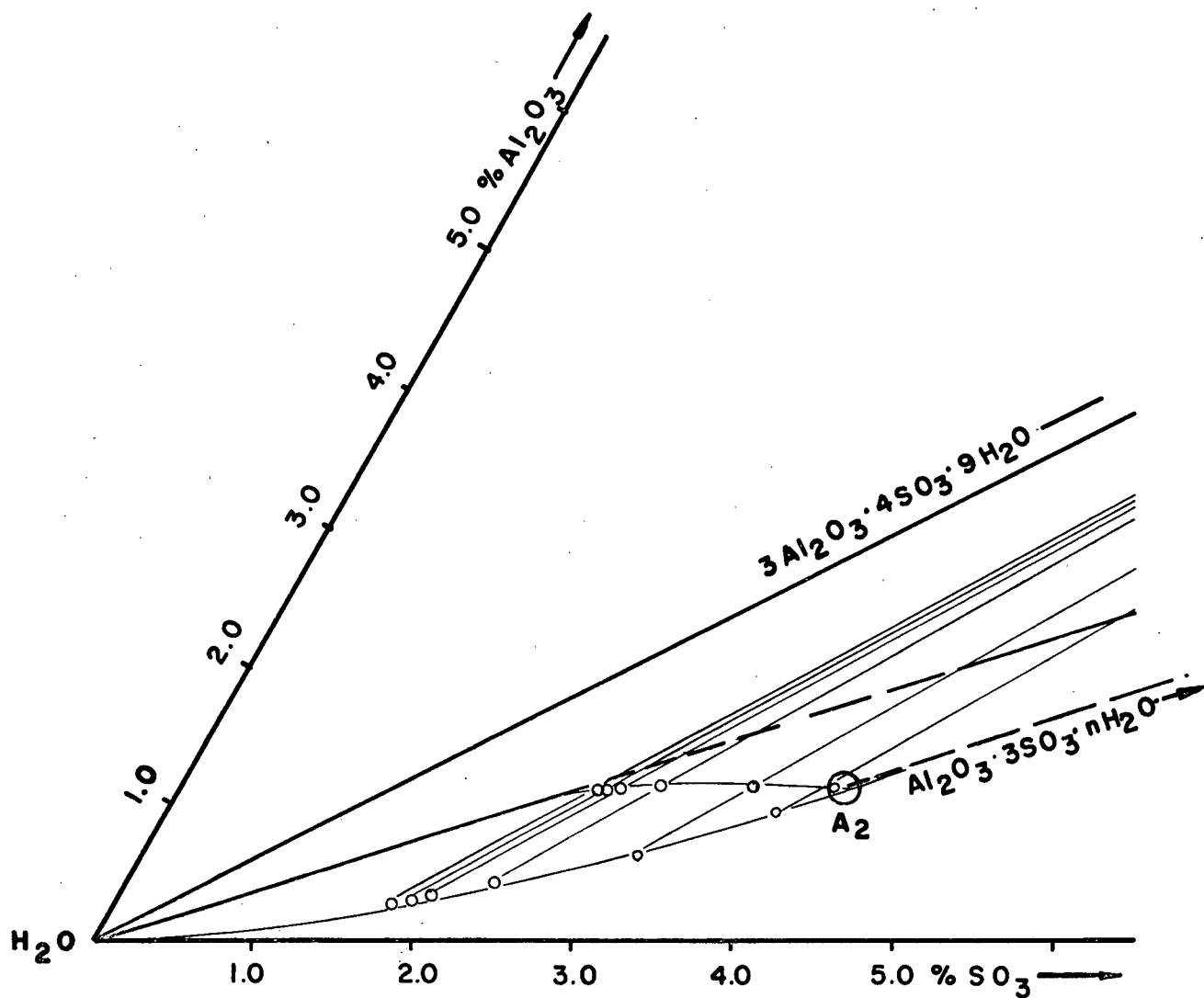
Fig. 21. $Al_2O_3 - SO_3 - H_2O$ SYSTEM AT 225C°

found to be slightly increased but it was far from the $SO_3:Al_2O_3$ ratio of a normal salt.

4.5   Mechanism of the Hydrolysis of Aluminum Sulphate

In aqueous solutions aluminum sulphate is at least partially dissociated into its constituents.

$$Al_2(SO_4)_3(aq) \rightleftharpoons 2Al^{+++} + 3SO_4^{=} \tag{8}$$
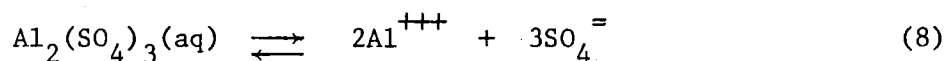
The Al^{+++} ion in solution will react with H_2O to give:

$$Al^{+++} + H_2O \longrightarrow Al(OH)^{++} + H^{+} \tag{9}$$
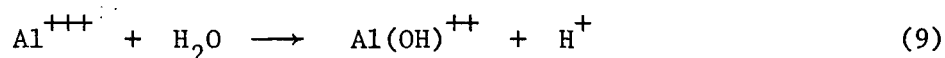
The concentration of $Al(OH)^{++}$ in solution will depend on the concentration of Al^{+++} and H^{+} in the intial solution. $Al(OH)^{++}$ cation in solution reacts with HSO_4^{-} ion to give the basic aluminum sulphate:

$$6Al(OH)^{++} + 4HSO_4^{-} + 8H_2O \longrightarrow 3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O + 8H^{+} \tag{10}$$
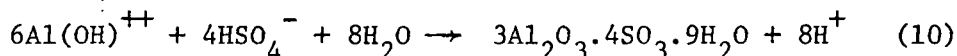
The equilibrium constant for reaction (9) was reported by Helgeson[22] and it is $10^{-4.75}$ for dilute solutions. Because of the change in the dissociation constant of water with temperature this constant will change, and become more and more positive as the temperature is increased. Helgeson gives the equilibrium constant values for the reaction:

$$Al(OH)^{++} \rightleftharpoons Al^{+++} + OH^{-} \tag{11}$$
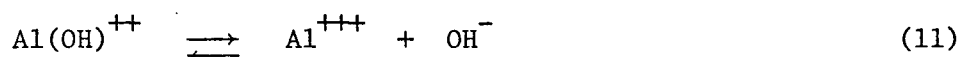
Reaction (9) is simply a combination of reaction (11) and

$$H_2O \; \rightleftharpoons \; H^+ \; + \; OH^- \hspace{4cm} (12)$$

Knowing the equilibrium constants at temperatures up to 300°C

for reactions (11) and (12) the equilibrium constant for reaction (9)

can be calculated from the relation:

$$\log K_9 \; = \; \log K_{12} \; - \; \log K_{11}$$

Calculated values for K_9 are given in Table 16.

Table 16. Equilibrium constants for reaction $Al^{+++} \; + \; H_2O \; \rightleftharpoons$

$Al(OH)^{++} \; + \; H^+$

Temp °C	25	50	60	100	150	200	250	300
log K	-4.75	-3.87	-3.53	-2.26	-0.84	+0.63	+1.97	+3.31

Precipitation reaction (10) is a fast reaction as can be seen from the

precipitation curves at high temperatures where it reaches equilibrium

during the heating period.

4.6   The Effect of Alkali   Metal Sulphates on Hydrolysis of

         Aluminum Sulphate at 225°C

When sulphates of Li, Na or K are present in aluminum sulphate

solutions during hydrolysis, corresponding alunites of the general form

$M_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$ are precipitated instead of basic aluminum

sulphate. Since the solubility of these compounds is less than the

solubility of basic aluminum sulphate ("Hydrogen Alunite") the

hydrolysis yields are higher and very close to 100%.

P.T. Davey and T.R. Scott[3] have reported complete precipitation

of aluminum in 30 min. at 220°C from solutions with initial $SO_3:Al_2O_3$

ratio of 2.87. The ratio of $K_2SO_4:Al_2(SO_4)_3$ calculated on the basis

of aluminum present in starting solution was 2.16. The precipitated

compound was of a composition corresponding to $K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$.

V.S. Sazhin, A.K. Zapolskii and N.N. Zakharova[13] have studied

hydrolysis of aluminum sulphate solutions having an initial molar

ratio of $K_2SO_4:Al_2(SO_4)_3$ of 0.33. Concentration of aluminum sulphate

in solution was 308 gr/ℓ (0.9 M), having $SO_3:Al_2O_3$ ratio of 3.0.

Such solutions were hydrolyzed for 1 hr in the temperature range

175-250°C. Maximum hydrolysis yield at 250°C was about 82%. Their

results show the presence of two solid phases. In the temperature

range 175-190°C, basic potassium-aluminum sulphates of the form

$K_2SO_4 \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O$ are precipitated. At temperatures higher

than 230°C, alunites are formed with the formula $K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$.

In the temperature range 190-230°C they have reported a mixture of the

two. In order to see the effect of alkali metal sulphates on

hydrolysis of dilute solutions of aluminum sulphate, solutions with

$M_2SO_4:Al_2(SO_4)_3$ ratio of about 0.5 containing 6.10 gr/ℓ aluminum with

$SO_3:Al_2O_3$ ratio of about 3.0 were hydrolyzed at 225°C until

equilibrium was established. M_2SO_4 corresponds to Li_2SO_4, Na_2SO_4 and

K_2SO_4.

4.6.1   The Effect of Lithium Sulphate on Hydrolysis of Aluminum

Sulphate at 225°C

Aluminum sulphate-lithium sulphate solution containing 6.12 gr/ℓ aluminum, 38.30 gr/ℓ $SO_4^=$ and 0.815 gr/ℓ lithium was hydrolyzed at 225°C until equilibrium was reached. The results obtained are presented in Table 17 and Fig. 22.

Table 17.   Hydrolysis of aluminum sulphate-lithium sulphate solution at 225°C[*]

Time at 225°C	Al^{+++} in sol	$SO_4^=$ in sol	Li^+ in sol	Al prec	$SO_4^=$ prec	Li prec	pH
hrs	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ	
0	1.74	27.87	0.44	4.38	10.43	0.375	0.82
1	1.29	26.71	0.40	4.83	11.59	0.415	0.78
2	1.16	26.48	0.39	4.96	11.82	0.425	0.75
3	1.07	26.36	0.39	5.05	11.94	0.425	0.71
3	1.11	26.36	0.39	5.01	11.94	0.425	0.73
5	1.05	26.37	0.39	5.07	11.93	0.425	0.72
8	1.05	26.36	0.39	5.07	11.94	0.425	0.72

[*]   Starting solution: 38.30 gr/ℓ $SO_4^=$
6.12 gr/ℓ Al
0.815 gr/ℓ Li
pH = 3.05
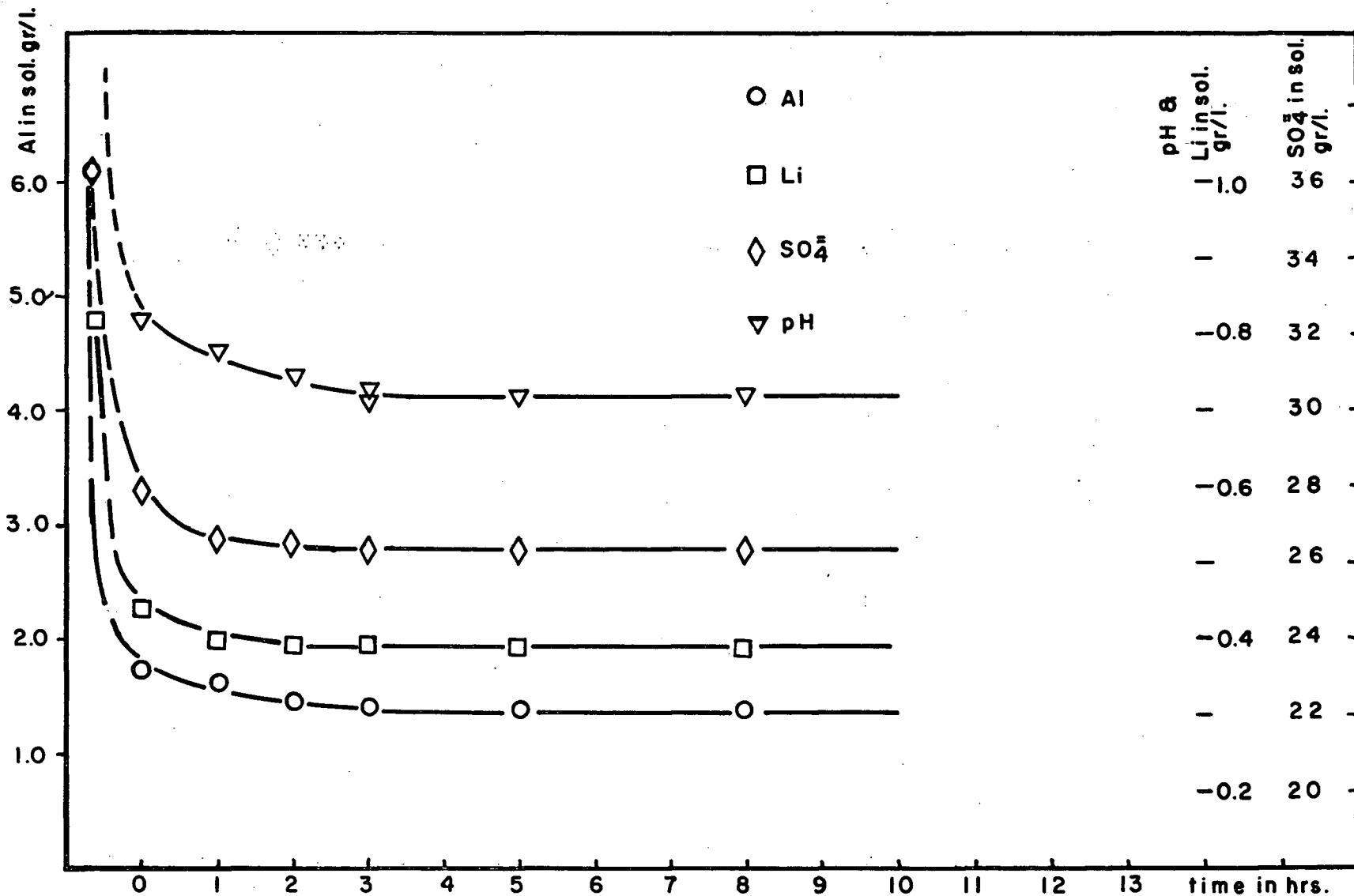
Fig. 22. HYDROLYSIS OF LITHIUM—ALUMINIUM SULPHATE
SOLUTION AT 225 C°

The precipitated compound was analyzed (see App. II) and its composition was found to be $Li_2O.3Al_2O_3.4SO_3.6H_2O$. In a four component system such as this, it is normal to have at least two solid phases in equilibrium with the liquid phase, but since the concentration of Li^+ ions in solution is high enough to precipitate all the aluminum present in the starting solution as lithium alunite, only one solid phase is precipitated. The X-ray diffraction pattern for both basic aluminum sulphate and basic lithium-aluminum sulphate is almost the same, so it is difficult to distinguish between the two (see App. III-K and III-E).

4.6.2 The Effect of Sodium Sulphate on Hydrolysis of Aluminum Sulphate at 225°C.

Aluminum sulphate-sodium sulphate solution containing 6.12 gr/ℓ Al^{+++}, 2.625 gr/ℓ Na^+ and 38.14 gr/ℓ $SO_4^=$ was hydrolyzed at 225°C. About 5.0 gr/ℓ of aluminum was precipitated while heating the system to 225°C. When the equilibrium was reached about 98% of the aluminum present in the initial solution was precipitated as a basic salt. The results obtained in this set of experiments are presented in Table 18 and Fig. 23. Analysis of precipitated solid phase shows the composition corresponding to $Na_2O.3Al_2O_3.4SO_3.6H_2O$ (see App. II). The X-ray diffraction pattern of this compound is the same as for basic aluminum sulphate and lithium alunite (see App. III-H).

Table 18. Hydrolysis of aluminum sulphate-sodium sulphate solution
at 225°C[*]

Time at 225°C	Al^{+++} in sol	$SO_4^=$ in sol	Na^+ in sol	Al prec	$SO_4^=$ prec	Na prec	pH
hrs	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ	
0	1.05	26.06	1.44	5.07	12.08	1.185	0.77
1	0.41	24.58	1.00	5.71	13.56	1.625	0.70
2	0.24	24.19	0.925	5.88	13.95	1.70	0.69
2	0.32	24.06	0.925	5.80	14.08	1.70	0.69
4	0.17	24.04	0.925	5.95	14.10	1.70	0.63
8	0.13	23.84	0.925	5.99	14.20	1.70	0.63

[*] Starting solution: 38.14 gr/ℓ $SO_4^=$

6.12 gr/ℓ Al

2.625 gr/ℓ Na

pH = 3.09

4.6.3. The Effect of Potassium Sulphate on Hydrolysis of Aluminum Sulphate at 225°C

Potassium sulphate-aluminum sulphate solution containing 6.12 gr/ℓ aluminum, 4.465 gr/ℓ potassium and 38.14 gr/ℓ $SO_4^=$ was hydrolyzed at 225°C. About 97% precipitation occurs in heating the system to 225°C. 100% precipitation occurs in only a few minutes at 225°C. Results obtained are presented in Table 19 and Fig. 24. The precipitated compound was analyzed and it was found to correspond to the formula $K_2O.3Al_2O_3.4SO_3.6H_2O$ (see App. II).
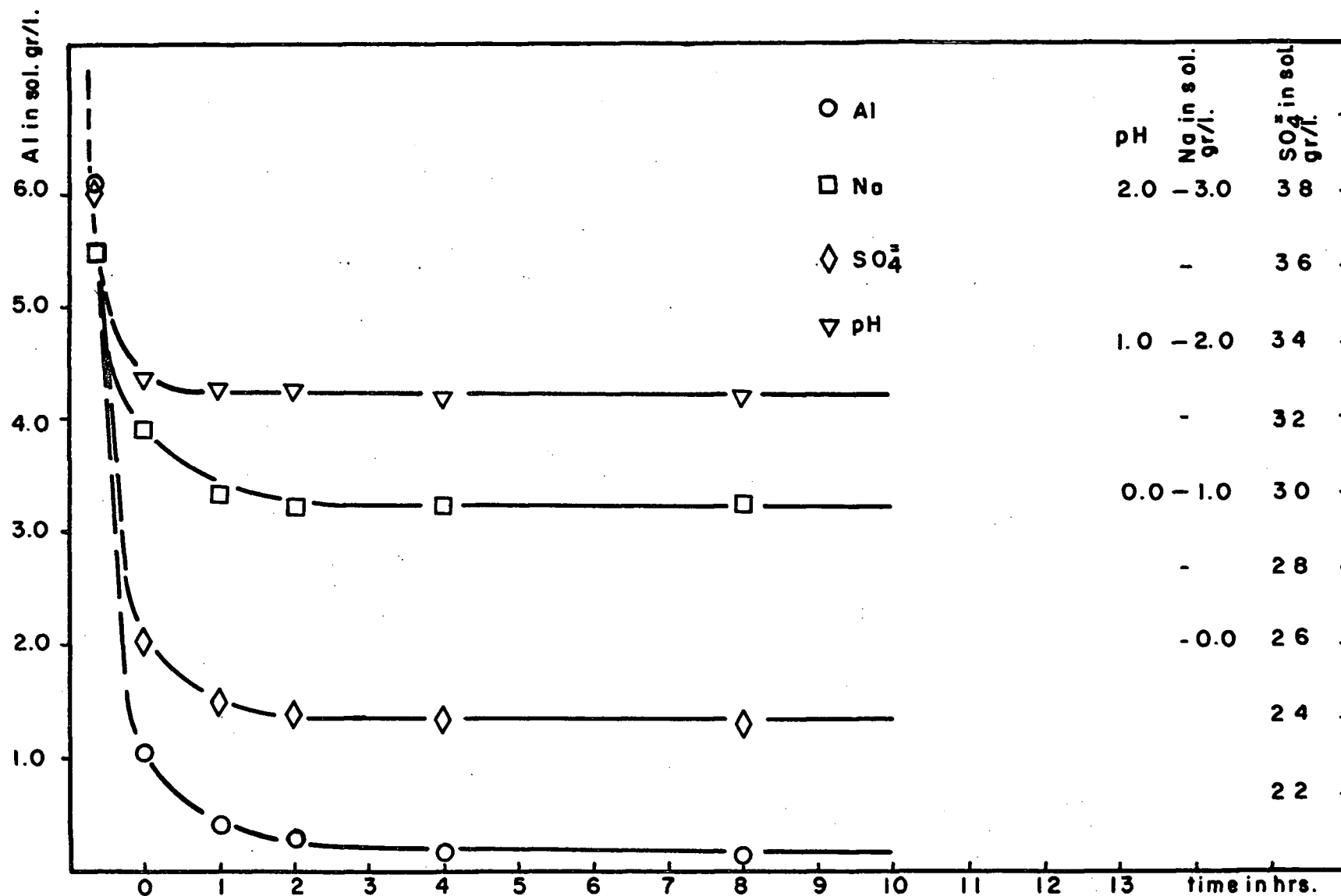
Fig. 23. HYDROLYSIS OF SODIUM—ALUMINIUM SULPHATE
SOLUTION AT 225 C°

Table 19. Hydrolysis of aluminum sulphate-potassium sulphate solution at 225°C[*]

Time at 225°C	Al in sol	$SO_4^=$ in sol	K in sol	Al prec	$SO_4^=$ prec	K prec	pH
hrs	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ	
0	0.21	24.06	1.61	5.91	14.08	2.855	0.69
1	0.00	23.54	1.51	6.12	14.60	2.955	0.67
2	0.00	23.56	1.51	6.12	14.58	2.955	0.66
3	0.00	23.54	1.51	6.12	14.60	2.955	0.66

[*] Starting solution: 38.14 gr/ℓ $SO_4^=$

6.12 gr/ℓ Al

4.465 gr/ℓ K

pH = 3.09

When alkali metal sulphate-aluminum sulphate solutions are hydrolyzed at 225°C only one solid phase is found to be in equilibrium with the liquid phase. The solid phase corresponds to the formula $M_2O.3Al_2O_3.4SO_3.6H_2O$. This is contrary to the results of V.S. Sazhin.[13] If there is any temperature limit in formation of $M_2O.3Al_2O_3.4SO_3.6H_2O$ it should be below 225°C and not 230°C. The most probable second phase in such mixed solutions would be the basic aluminum sulphate under the condition that there is insufficient M^+ present in the initial solution to precipitate all aluminum in the form of alunite.

The reaction for the hydrothermal precipitation of alunites can be written as

$$6Al^{+++} + 4HSO_4^- + 2M^+ + 12H_2O \rightleftharpoons M_2O.3Al_2O_3.4SO_3.6H_2O + 16H^+$$

(13)
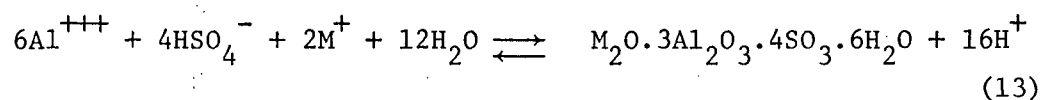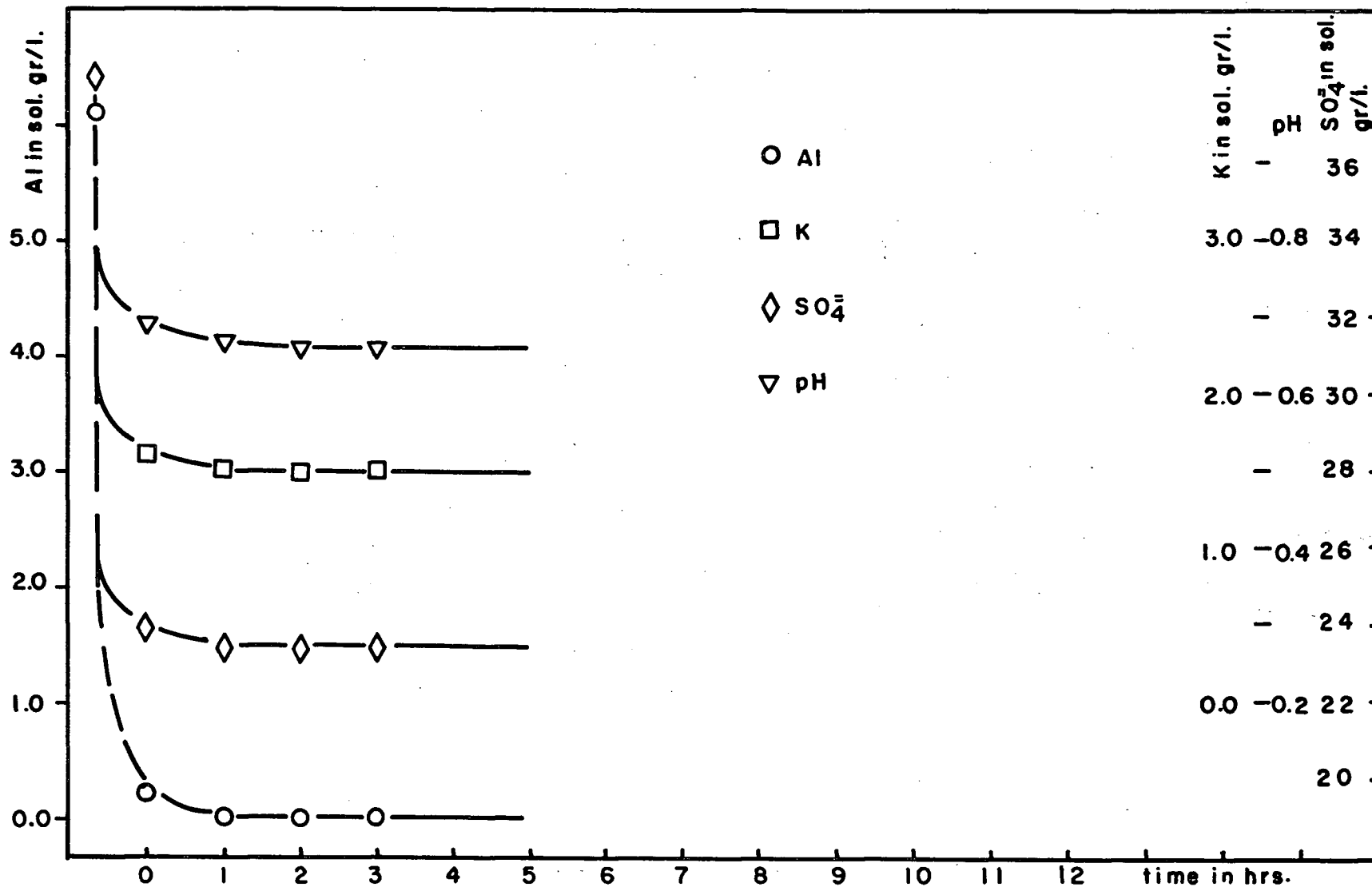
Fig. 24. HYDROLYSIS OF POTASSIUM—ALUMINIUM SULPHATE
SOLUTION AT 225 C°

The effect of alkali metal sulphate salts is such that the hydrolysis yields are increased in the following series K > Na > Li. This series is the same if the ionic radii of the Li, Na, and K are compared. Table 20 shows the ionic radii of the ions involved in this system. Fig. 25 shows the straight line relation between the ionic radii and precipitated amount of aluminum in heating the system to 225°C.

Table 20. Ionic radii of the ions involved in the system

Element	Type of Radius	Ionic radius A°	Al prec. %
H	1^+	0.00	48.00
Al	3^+	0.57	
Fe	3^+	0.67	
Li	1^+	0.68	71.80
Fe	2^+	0.80	60.50
Cu	2^+	0.80	61.40
Na	1^+	0.98	83.00
K	1^+	1.33	96.80

4.7   The Effect of Divalent Metal Sulphates on Hydrolysis of

        Aluminum Sulphate Solutions at 225°C

As a general rule, ions of divalent metals do not precipitate with basic aluminum sulphate. Many trivalent or quadrivalent metals precipitate as oxides, hydroxides or basic salts under the same
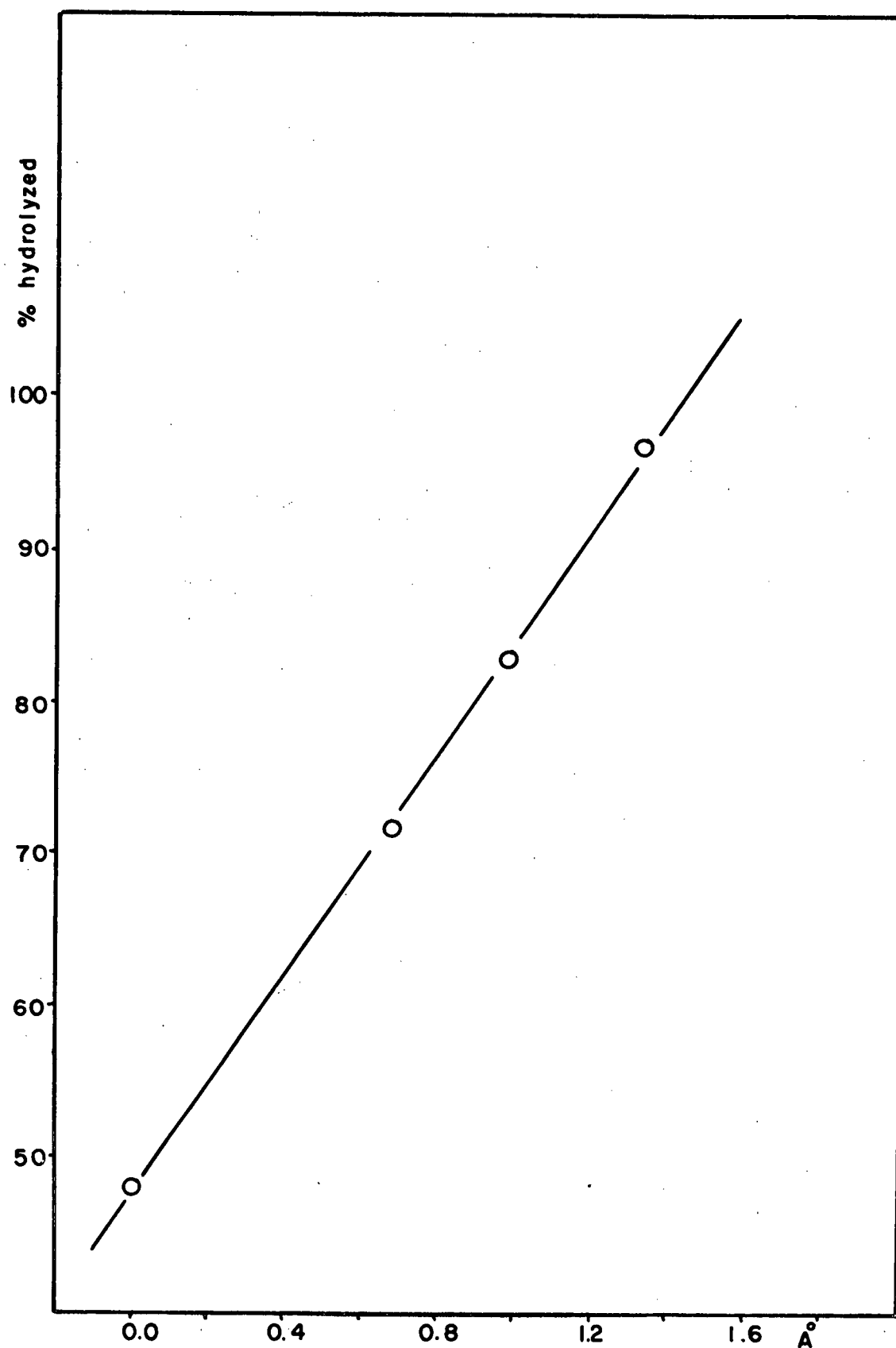
Fig. 25. HYDROLYSIS YELDS DEPENDANCE ON
IONIC RADII

conditions as for hydrolysis of aluminum sulphate. The effect of copper and iron was investigated at 225°C mostly because of their presence in many leach solutions.

4.7.1 The Effect of Copper Sulphate on Hydrolysis of Aluminum Sulphate Solutions at 225°C

A copper-sulphate-aluminum sulphate solution containing 6.10 gr/ℓ aluminum, 3.58 gr/ℓ copper and 37.92 gr/ℓ $SO_4^=$ was hydrolyzed at 225°C. There was practically no copper precipitation detected in these experiments. Results obtained are presented in Table 21 and Fig. 26.

Table 21. Hydrolysis of aluminum sulphate-copper sulphate solution at 225°C[*]

Time at 225°C	Al in sol	Cu in sol	SO_4 in sol	Al prec	Cu prec	SO_4 prec	pH
hrs.	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ	gr/ℓ	
0	2.35	3.56	29.02	3.75	0.02	8.90	0.94
1	1.48	3.58	26.92	4.62	0.00	11.00	0.85
2	1.23	3.57	26.32	4.87	0.01	11.60	0.82
4	1.12	3.56	26.06	4.98	0.02	11.86	0.82
6	1.10	3.58	26.06	5.00	0.00	11.86	0.82

[*] Starting solution: 6.10 gr/ℓ Al
3.58 gr/ℓ Cu
37.92 gr/ℓ $SO_4^=$
pH = 3.0
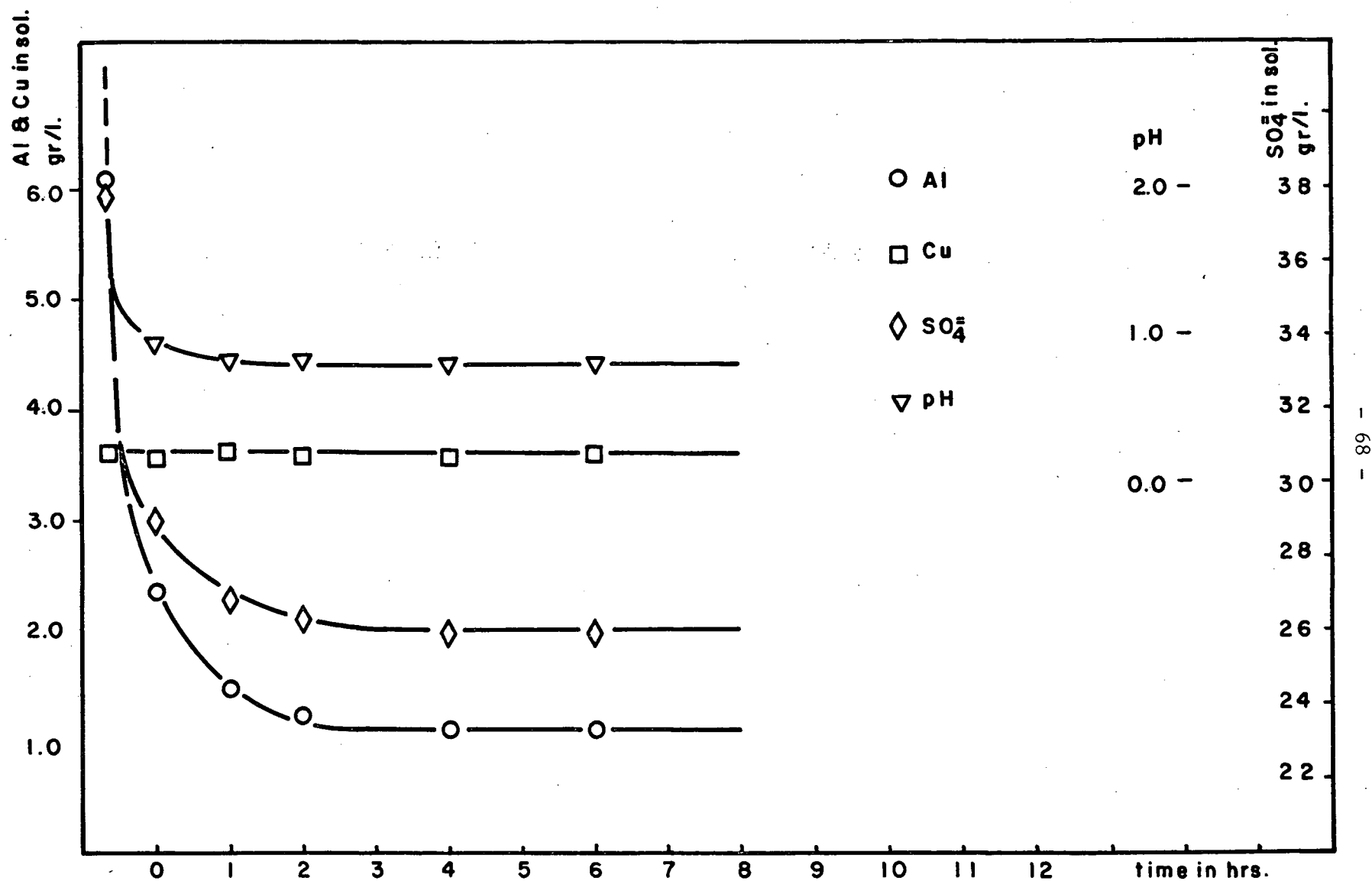
Fig. 26. HYDROLYSIS OF COPPER—ALUMINIUM SULPHATE
SOLUTION AT 225 C°

4.7.2   The Effect of Ferrous Sulphate on Hydrolysis of Aluminum

Sulphate Solutions at 225°C

A   ferrous sulphate-aluminum sulphate solution   containing

6.12 gr/ℓ aluminum, 3.26 gr/ℓ iron and about 38.29 gr/ℓ $SO_4^=$ was

hydrolyzed at 225°C.   Some iron was precipitated in the form of Fe_2O_3

due to atmospheric oxidation of ferrous iron.   Results

obtained in this set of experiments are presented in Table 22 and Fig.

27.   The increased precipitation of aluminum can be attributed to the

common ion effect.   The bivalent ions are not compatible with the

alunite lattice and do not tend to replace the hydrogen ions in basic

aluminum sulphate.   T.R. Scott[3] has reported that no contamination

of basic aluminum sulphate occurs in the presence of Mg, Cd, Zn and Ni

even at high concentrations.

Table 22.   Hydrolysis of aluminum sulphate-ferrous sulphate solution

at 225°C[*]

Time at 225°C hrs	Al in sol gr/ℓ	Fe in sol gr/ℓ	$SO_4^=$ in sol gr/ℓ	Al prec gr/ℓ	Fe prec gr/ℓ	$SO_4^=$ prec gr/ℓ	pH
0	2.42	2.69	29.44	3.70	0.57	8.85	0.97
1	1.57	2.68	27.48	4.55	0.58	10.81	0.82
2	1.40	2.69	27.04	4.72	0.57	11.25	0.80
4	1.15	2.66	26.42	4.97	0.60	11.87	0.82
6	1.12	2.69	26.40	5.00	0.57	11.89	0.80

[*]   Starting solution: 6.12 gr/ℓ Al;   3.26 gr/ℓ Fe;   38.29 gr/ℓ $SO_4^=$;

pH = 3.0
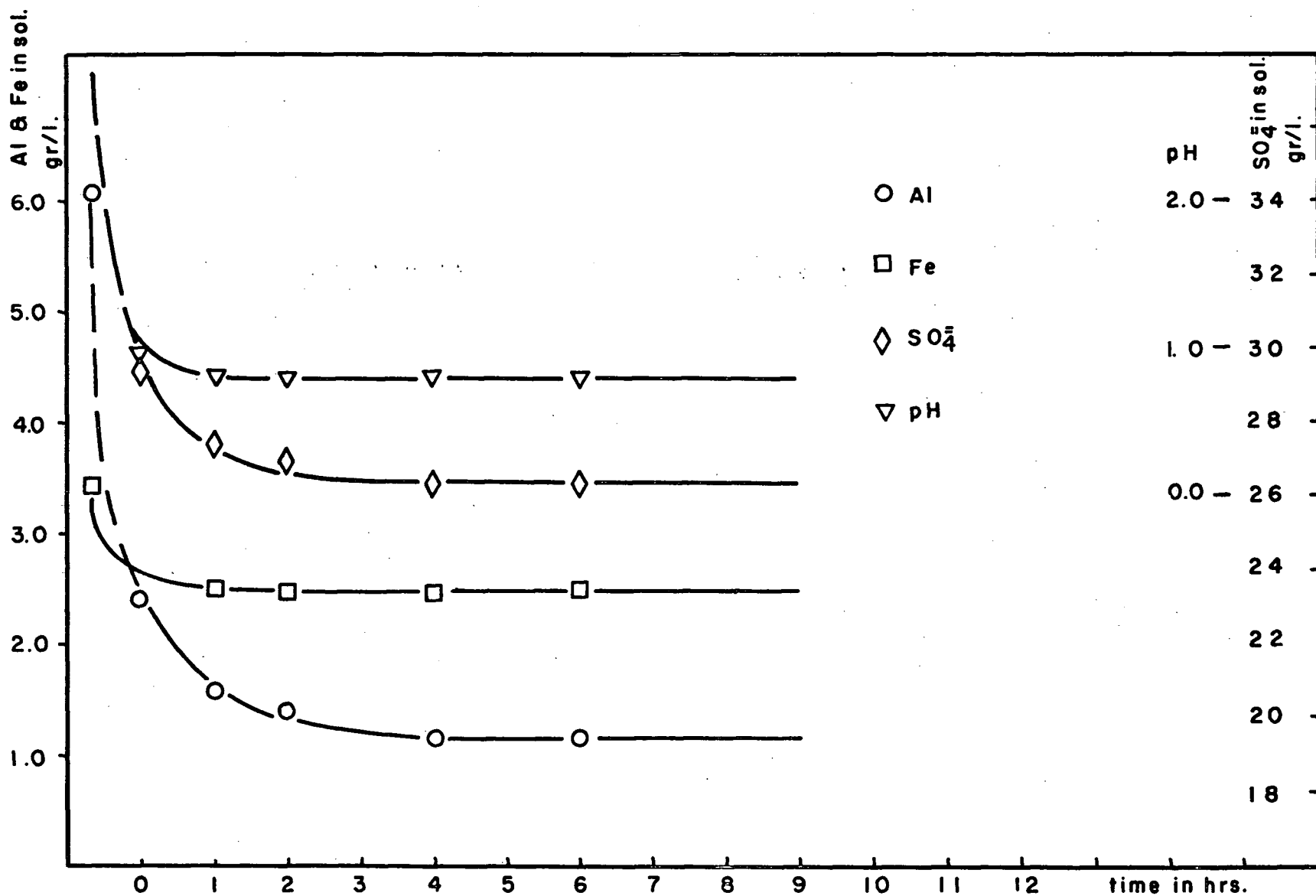
Fig. 27. HYDROLYSIS OF IRON—ALUMINIUM SULPHATE
SOLUTION AT 225 C°

4.8 Application of the Hydrolysis Process

Basic aluminum sulphate of the form $3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O$ is the product of high temperature hydrolysis of aluminum sulphate solutions with a wide range of initial $SO_3:Al_2O_3$ ratios. A basic salt of the form $M_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$ is a high temperature hydrolysis product of aluminum sulphate solutions containing alkali metals (Li, Na or K). Thermal decomposition of such basic salts yields alumina as a final product which can be used for aluminum production. Thermal decomposition of a few samples of basic aluminum sulphate was followed by D.T.A. A typical D.T.A. curve is shown in Fig. 28. The first endothermic peak in the temperature range 200-400°C corresponds to the loss of interstitial lattice water.[9] The peak at about 450°C corresponds to the dehydroxylation process. This process is completed at temperatures around 600°C where anhydrous basic aluminum sulphate exists.[9] At temperatures above 600°C, SO_3, SO_2 and O_2 are evolved yielding amorphous alumina which subsequently crystallizes to γ-alumina at higher temperatures. γ-Alumina is transformed to α-alumina at temperatures of 1000°C and higher. A few samples of $K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$ were calcined at about 1000°C for 2 hrs. The decomposition of these samples was followed by the weight loss. Results of one of the decomposition experiments is shown below.

$$1.0811 \text{ gr } K_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O \xrightarrow[1000°C]{\text{calc.}} 0.5857 \text{ gr } K_2SO_4 + Al_2O_3 + \uparrow \begin{array}{l}\text{sulphurous}\\\text{gases}\end{array}$$

$$0.5857 \text{ gr } K_2SO_4 + Al_2O_3 \xrightarrow[25°C, H_2O]{\text{leach}} 0.365 \text{ gr } Al_2O_3$$
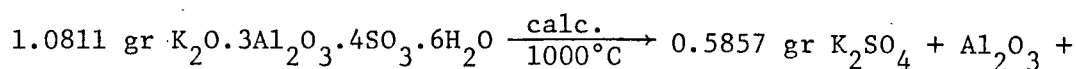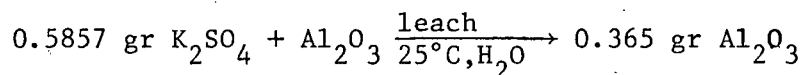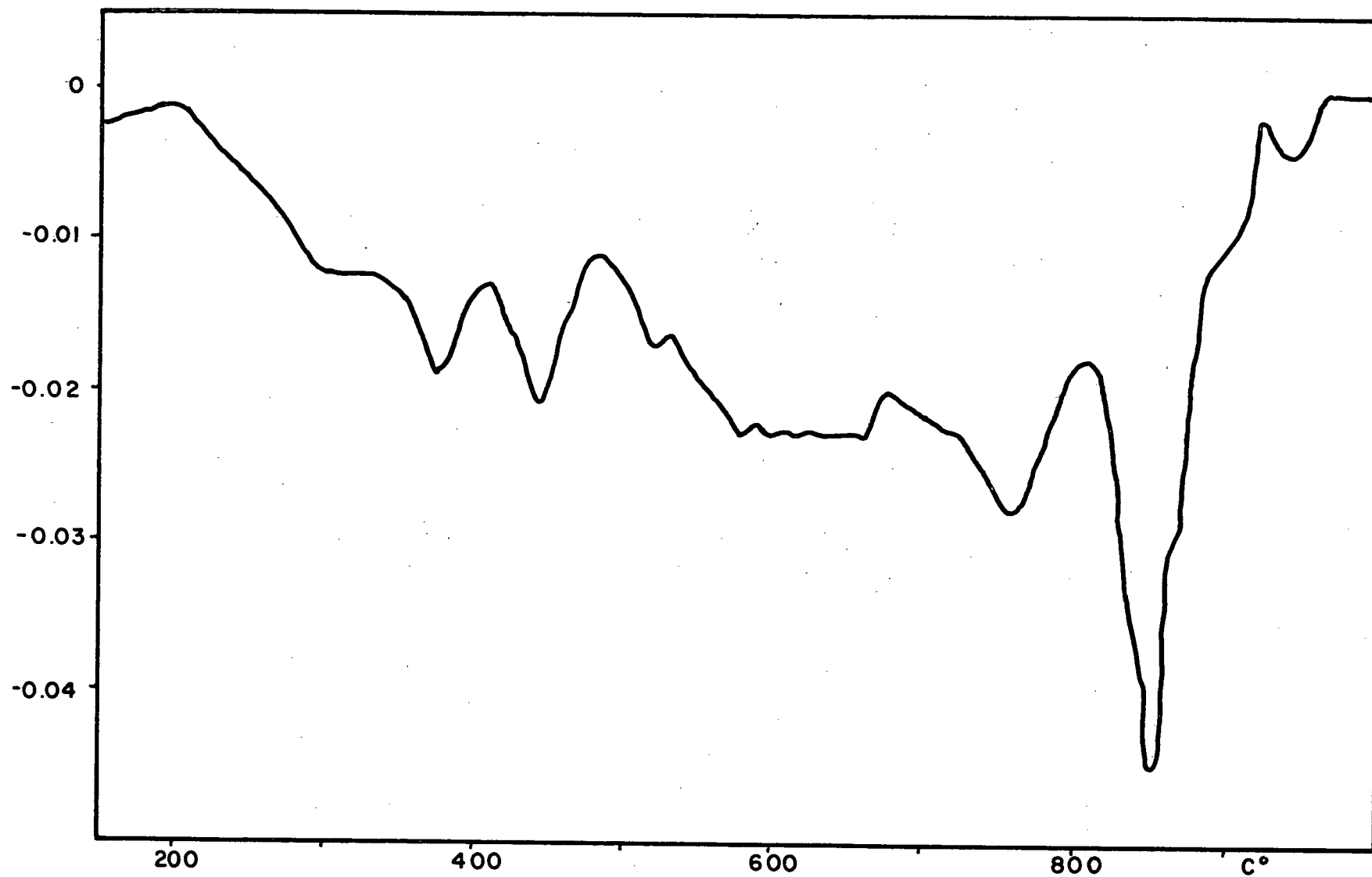
Fig. 28. D.T.A. OF $3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O$

In leaching processes at high temperatures where aluminum is present in solution it precipitates as a basic salt in autoclaves and pipelines[11] which necessitates "forced" shutdowns of the process in order to clean autoclaves and/or pipelines. With increasing sulphuric acid concentration and decreasing temperature the solubility of basic aluminum sulphate was found to increase. Therefore running concentrated solutions of sulphuric acid through the system at low temperatures should dissolve the precipitate.

In dump leaching solutions aluminum is present as aluminum sulphate. If aluminum is not recovered the viscosity of the solution will increase. To remove the aluminum from solution, a part of the liquor after cementation can be treated in an autoclave to precipitate basic aluminum sulphate. Liberated acid from the hydrolysis can be recycled to the heap.

5. CONCLUSIONS

1.   Dilute solutions of normal and acid aluminum sulphate hydrolyze when heated above 125°C to yield a basic salt of the nominal composition $3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O$.

2.   Hydrolysis yield is a function of the temperature and initial concentration of sulphuric acid in solution.

3.   Only one solid phase was found to be in equilibrium with the liquid phase in the temperature region 125-250°C, but there are some indications that a less basic salt may exist in the system.

4.   When Li, Na or K ions are present in solutions of aluminum sulphate a basic salt of the form $M_2O \cdot 3Al_2O_3 \cdot 4SO_3 \cdot 6H_2O$ is precipitated.

5.   The hydrolysis yields are increased in the presence of alkali metal sulphates in the following series: K > Na > Li.

6.   Aluminum can be selectively precipitated in the presence of Cu^{++} and Fe^{++} as $3Al_2O_3 \cdot 4SO_3 \cdot 9H_2O$.

7.   Both basic aluminum sulphate and alunites can be calcined at temperatures above 1000°C to yield alumina.

APPENDIX I

SOLUBILITY OF ALUMINUM SULPHATE

I-A   Solubility of $Al_2(SO_4)_3$ in water

Temp. °C	20	30	40	50	60	70	80	90	100
$\frac{gr\ Al_2(SO_4)_3}{100\ gr\ sat.\ sol.}$	26.7	28.8	31.4	34.3	37.2	39.8	42.2	44.7	47.1

I-B   Solubility of aluminum sulphate in aqueous solutions of

sulpuric acid at 25°C.

$\frac{gr\ Al_2(SO_4)_3}{100\ gr\ sat.\ sol.}$	27.82	29.21	26.2	19.5	11.6	4.8	1.5	1.0	2.3	4.0
$\frac{gr\ H_2SO_4}{100\ gr\ sat.\ sol.}$	0.0	5.73	10.0	20.0	30.0	40.0	50.0	60.0	70.0	75.0

I-C   Solubility of aluminum sulphate in aqueous 10% H_2SO_4

Temp. °C	30	42	50
$\frac{gr\ Al_2(SO_4)_3}{100\ gr\ sat.\ sol.}$	14.52	16.45	18.77

APPENDIX II

ANALYSIS OF THE SOLID PHASES

Time at hrs.	Temp. °C	% Al_2O_3	% SO_3	% M_2O	% H_2O	Starting pH
6.00	175	38.7	37.2	–	24.1	3.10
10.00	175	38.5	39.6	–	21.9	3.10
16.30	175	38.7	39.7	–	21.6	3.10
4.0	200	38.6	39.5	–	21.9	3.10
6.0	200	38.8	39.9	–	21.3	3.10
18.00	200	38.7	40.1	–	21.2	3.10
1.00	225	38.8	40.2	–	21.0	3.10
5.00	225	38.9	40.8	–	20.3	3.10
16.00	225	39.1	41.6	–	19.3	3.10
0.00	250	38.8	40.3	–	20.9	3.10
1.00	250	38.7	40.2	–	21.1	3.10
3.30	250	39.0	40.5	–	20.05	3.10
6.30	250	39.2	40.9	–	19.9	3.10
6.00	225	39.0	40.6	–	20.4	2.5
6.00	225	38.7	40.6	–	20.7	2.0
6.00	225	38.9	40.8	–	20.3	1.5
6.00	225	38.9	40.2	–	20.9	1.0
6.00	225	39.2	41.7	–	19.1	0.70
4.00	250	38.9	40.6	–	20.5	2.5
4.00	250	38.8	40.7	–	20.5	2.0
4.00	250	38.9	41.2	–	19.9	1.5
4.00	250	39.2	41.6	–	19.20	1.0
4.00	250	38.9	40.8	–	20.3	0.70
				Li_2O		
3.00	225	39.90	42.00	4.00	14.10	3.05
				Na_2O		
2.00	225	38.40	40.10	7.70	13.80	3.09
8.00	225	38.50	40.20	7.80	13.50	3.09
				K_2O		
0.00	225	37.05	38.39	11.36	13.20	3.09
0.00	225	36.91	38.91	11.38	12.80	3.09
1.00	225	37.12	38.48	11.30	13.10	3.09

APPENDIX III

X-RAY DIFFRACTION PATTERNS

III-A   Diffraction pattern of the precipitate obtained at 150°C

Prec. obtained in 10 hrs.		Prec. obtained in 16 hrs	
d A°	I/I_0	d A°	I/I_0
5.71	7	5.71	7
5.03	2	5.03	2
3.55	5	3.57	5
3.01	1	3.01	1
2.27	4	2.27	4
1.909	3	1.908	3
1.76	5	1.755	5
1.654	7	1.659	7
1.566	7	1.570	7
1.496	5	1.500	5
1.325	7	1.329	7
1.290	6	1.299	6
1.220	7	1.217	7
1.171	7	1.171	7
1.150	7	1.147	7

III-B   X-ray diffraction patterns of the precipitate obtained at 175°C

Prec. obtained in 2 hrs.		Prec. obtained in 16.5 hrs	
d A°	I/I_0	d A°	I/I_0
5.71	7	5.75	7
5.034	2	5.12	2
3.56	5	3.56	5
3.01	1	3.04	1
		2.87	7
		2.486	8
2.27	4	2.30	4
		2.22	8
1.908	3	1.920	3
1.757	5	1.770	5
1.654	7	1.654	7
1.566	7	1.570	7
1.495	5	1.500	5
		1.380	8
1.325	7	1.330	7
1.293	6	1.290	6
1.219	7	1.217	7
1.174	7	1.172	7
1.150	7	1.150	7

III-C   X-ray diffraction pattern of the precipitate obtained at 200°C.

Prec. obtained in 18 hrs.	
d A°	I/I_0
5.72	7
5.03	2
3.56	5
3.04	1
2.87	7
2.27	4
2.22	8
1.910	3
1.756	5
1.654	7
1.565	7
1.490	5
1.387	8
1.290	6
1.217	7
1.171	7
1.151	7

III-D   X-ray diffraction pattern of the precipitate obtained at 225°C

Prec. obtained in 3 hrs at 225°C			
d A°	I/I_0	d A°	I/I_0
5.61	8	1.736	6
5.02	2	1.666	8
4.80	2	1.641	8
3.43	6	1.550	8
3.03	1	1.546	8
2.932	1	1.479	4
2.806	4	1.4227	8
2.440	8	1.362	8
2.304	4	1.316	8
2.241	3	1.281	4
2.191	8	1.205	8
1.925	8	1.195	8
1.880	3	1.161	8
1.767	8	1.132	8
1.758	6		

III-E X-ray diffraction pattern of the precipitate obtained at 250°C

Prec. obtained in 0.0 hrs.				Prec. obtained in 3.5 hrs.			
d A°	I/I_0	d A°	I/I_0	d A°	I/I_0	d A°	I/I_0
5.61	8	1.765	8	5.61	8		
4.02	2	1.736	6	5.01	2	1.742	6
4.80	2	1.665	8	4.85	2	1.646	8
4.27	8	1.557	8	-		1.555	
3.40	6	1.479	4	3.46	6	1.483	4
3.01	1	1.424	8	3.01	1	-	
2.91	1	1.367	8	2.95	1	1.369	8
2.79	4	1.317	8	2.81	4	1.317	8
2.45	8	1.286	4	2.46	8	1.286	4
2.296	4	1.208	8	-		1.208	8
2.24	3	1.200	8	2.24	3	-	
2.187	8	1.167	8	1.895	8	1.167	8
1.929	8	1.138	8	-		1.139	8
1.879	3						

III-F X-ray diffraction pattern of the precipitate obtained from

from $FeSO_4$-$Al_2(SO_4)_3$ solution at 225°C

Prec. obtained in 4.0 hrs at 250°C			
d A°	I/I_0	d A°	I/I_0
5.08	2	1.558	4
4.80	2	1.501	5
3.03	1	1.481	2
2.915	1	1.423	5
2.294	5	1.371	3
2.234	1	1.314	4
1.918	4	1.209	3
1.888	2	1.1969	5
1.768	5	1.1867	5
1.737	2	1.1364	5
1.637	4	1.1054	5

III-G   X-ray diffraction pattern of potassium alunite obtained at

225°C

Prec. obtained in 0.0 hrs. at 225°C			
d A°	I/I_0	d A°	I/I_0
5.71	5	1.560	8
5.01	2	1.546	8
3.49	3	1.489	3
3.01	1	1.422	8
2.90	8	1.380	8
2.47	8	1.316	8
2.29	3	1.281	5
2.20	5	1.205	5
1.888	2	1.161	6
1.736	2	1.132	6
1.641	8		

III-H   X-ray diffraction pattern of sodium alunite obtained at 225°C

Prec. obtained in 2.0 hrs. at 225°C			
d A°	I/I_0	d A°	I/I_0
5.70	5	1.746	2
5.01	2	1.644	8
3.496	3	1.554	8
3.01	1	1.538	8
2.91	8	1.505	3
2.45	8	1.281	5
2.212	3	1.205	5
1.896	2	1.161	6

III-K   X-ray diffraction pattern of lithium alunite obtained at 225°C

Prec. obtained in 3.0 hrs. at 225°C			
d A°	I/I_0	d A°	I/I_0
5.68	5	1.736	2
5.01	2	1.641	8
3.491	3	1.554	8
3.01	1	1.535	8
2.90	8	1.489	3
2.44	8	1.281	5
2.20	3	1.205	5
1.887	2	1.161	6

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