THE EFFECT OF NEUTRAL SALTS ON THE HYDROLYSIS OF ALUMINUM SULFATE

A THESIS

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CONTENTS

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1. INTRODUCTION

This work is a continuation of the work started by Dr. Harold B. Friedman and J. A. Stokes, Jr.(1) in 1933. They studied the effect of neutral salts on the hydrolysis of $CuSO_4$ in aqueous solution and found that the following salts increased the hydrolysis in the order listed: KNO_3, $NaNO_3$, KCl, NaCl. Those that showed a decrease in the hydrolysis are, in the order listed: Na_2SO_4, K_2SO_4. The data obtained show an increase in hydrolysis, (1) with dilution of the $CuSO_4$, (2) with increase in the concentration of the neutral salt, which is almost proportional to the concentration of the neutral salt.

Since this study produced such interesting results in the case of a 2-2 valence type of salt the authors were curious to know what would be the effect of the same neutral salts on the hydrolysis of a 3-2 valence type of salt. Aluminum sulfate was chosen as the salt to be studied.

Thomas and Whitehead[2] have made a study of the effect of the chloride and sulfate ions on solutions of aluminum salts. They found that the pH values of the solutions increased for the following neutral salts, in the order listed, and increased slightly with increasing concentration: KCl, Na_2SO_4, K_2SO_4. When solid NaCl was added to the solution of aluminum sulfate the pH value decreased slightly with increasing concentration of NaCl. The explanation offered for this effect is that given by Harned[3] and Lewis and Randall[4] and has to do with the removal of water molecules from the solvent by hydration of the sodium and chloride ions. The work they did was carried out in such a way that the results wanted in this case could not be obtained from their data.

1. J. A. Stokes, Jr., Thesis, Ga. Tech. Library

2. A. W. Thomas and T. H. Whitehead, J. Am. Leather Chem. Assoc., 25, 127 (1930).

3. H. S. Harned, J. Am. Chem. Soc., 47, 930 (1925).

4. G. N. Lewis and M. Randall, J. Am. Chem. Soc., 43, 1112(1921)

PREPARATION AND PURIFICATION OF MATERIALS

All salts used in this investigation were of C.P. grade and in each case were carefully purified further by recrystallization from distilled water. The purified salts were then dried in an oven at 120°C. for a period of 12 to 15 hours, and were either used immediately or kept in a desiccator over concentrated H_2SO_4 until used.

Aluminum Sulfate. The aluminum sulfate used was Baker's C.P. grade. The analysis indicated a high degree of purity, but it was recrystallized once by making a rather concentrated solution, filtering while hot and then allowing to cool. After cooling, as much of the liquor as possible was pulled out by suction. The rest, including practically all the water of hydration, was driven off by heat. It was then pulverized in an agate mortar and completely dehydrated in an oven at 120°C.

The standard solution of 0.1000 molar aluminum sulfate was prepared by weighing out enough of the purified salt to make a solution slightly more than 0.1 molar. The exact concentration of this solution was then determined by precipitating the sulfate radical as $BaSO_4$. It was then diluted to the proper concentration and checked. The different concentrations studied were prepared by diluting the stock solution.

Sodium and Potassium Chlorides. Purification of these salts consisted of saturating distilled water at 100°C. with the salts, filtering while hot, and then precipitating the salts by passing in HCl gas. In the case of

NaCl this operation was repeated and the precipitated salt was dried in an oven from 10 to 12 hours at 120°C. The dried salt was then pulverized in an agate mortar and put back in the oven for 6 hours to insure complete removal of the occluded HCl. The potassium chloride was recrystallized from distilled water and then dried.

Sodium Nitrate, Potassium Nitrate, Sodium Sulfate, and Potassium Sulfate. These salts were recrystallized twice from distilled water and dried in an oven.

Stock solutions of the neutral salts were prepared by carefully weighing out enough of each purified salt to make two liters of two molar concentration. The concentrations studied were made by diluting the stock solutions.

Quinhydrone. The quinhydrone was the standard Eastman product and was not further purified. The melting point, corrected, was 169.3°C. The literature gives 171°C.

Mercurous Chloride. The best grade of C. P. Mercurous chloride was used. It was not further purified.

Mercury. Redistilled mercury was used. It had a clean surface.

Standard Buffer solution. This solution was prepared by mixing 100 cc of a normal solution of sodium hydroxide, 200 cc of a normal solution of acetic acid, and 700 cc of distilled water. The hydrogen ion concentration of this solution at 25°C is 2.35×10^{-5} molar, and the corresponding pH value is 4.63 ($\pm$ 0.005). The voltage developed by this solution using the quinhydrone electrode is 0.1797 volt. Before making a series of readings the apparatus was checked by this standard solution and was required to read within 0.5 of a millivolt of the correct reading.

APPARATUS

The constant temperature bath consisted of a large container filled with water and maintained at a temperature of 25°C (± 0.01°C). The different sections of the bath gave a constant temperature reading when checked with a Beckman thermometer. The bath was heated electrically by a Cenco knife blade heater and the temperature was controlled by a mestatic thermo-regulator. The water was circulated by means of a motor driven stirrer.

The saturated calomel half cells were prepared in the usual manner and checked against each other. There was no detectable difference in the E. M. F. produced by the two cells used.

Several platinum electrodes were made and the two that gave the most accurate checks were used. These checked within 0.0002 volt.

Salt bridges were prepared by filling glass tubes in the shape of an inverted U with hot agar agar that contained enough KCl to make it saturated when the gel cooled to 25°C. If very much of the KCl crystallized out upon cooling it caused the gel to crumble and shortened the life of the bridge. Each bridge used was carefully checked with the standard buffer solution, and while readings were being made, a check was made about every two hours. It was found that after being used for some time the salt bridges caused an inaccurate E. M. F. to be produced. This was probably caused by the gradual diffusing of the KCl from the gel.

A Leeds and Northrup Student's Potentiometer was used for measuring the E. M. F. of the cells. A Leeds and Northrup Wall Type Galvanometer was used as the null instrument. A 10,000 ohm variable resistance was placed across the terminals of the galvanometer, and after the critical damping resistance was determined, that much resistance was used, which enabled readings to be taken in the minimum of time.

The standard of electromotive force was the Weston cell which gives an E.M.F. of 1.0183 volts at 20°C. The cell used was checked by two other standard cells. A lead storage cell was the source of opposing E.M.F. This was checked against the standard cell about every three hours while readings were being made to correct for changes in the E.M.F. of the storage cell.

METHOD AND PROCEDURE

An electrometric method using the quinhydrone electrode was employed for measuring the hydrogen ion concentration, from which the degree of hydrolysis was calculated. The saturated calomel half cell was used as the reference electrode. The liquid junction potentials were practically eliminated by salt bridges of saturated KCl in agar agar gel solution. The gel retarded the diffusion of KCl.

Two complete cells were employed so as to obtain duplicate readings and furnish a means of checking the reproducibility of the cells. This also saved time in making the readings. Enough of the solution to be measured was made up and divided between the two cells. At least three readings were taken of each cell. Then as a check, new cell contents were made up of the same concentration from the stock solutions and readings taken.

The cell arrangement was as follows:

Pt	Quinhydrone (sat.) $Al_2(SO_4)_3$ (x M) Neutral salt (y M)	KCl (sat.)	KCl (sat.), HgCl, Hg

The salt solution upon which measurements were to be made was placed in the quinhydrone electrode vessel and a sufficient amount of the quinhydrone added to saturate the solution at 25°C. The quinhydrone is almost insoluble, so only a small amount is needed for a measurement. The cell and its contents were then placed in the bath and sufficient time allowed for it to reach the temperature of the thermostat before measurements were taken.

The solutions were kept at a temperature near the temperature of the bath, so an equilibrium was usually reached within a period of 10 minutes. Measurements were then taken at intervals of 2 to 4 minutes over a period of 6 to 30 minutes, depending upon the constancy of the readings.

The electrode vessels were carefully washed and dried each time and then rinsed with some of the solution upon which measurements were to be made. The platinum electrodes were occasionally activated by placing them as electrodes in a dilute solution of H_2SO_4 and passing an alternating current through for a period of about 10 minutes. At the conclusion of each measurement the electrodes were washed and kept in distilled water until used again. They were carefully dried before placing them in the cell.

The KCl solution in the half cells and in the center unit of the set-up was changed about every 10 days. A few crystals of KCl were added to insure complete saturation when the cells reached the temperature of the bath.

The salt bridges were the greatest source of trouble and error in the whole apparatus. Each day new salt bridges were prepared and checked with the buffer solution before use. After each experiment they were washed on the outside and dried before use again. At intervals of about two hours they were checked and new ones prepared if they gave readings more than 0.5 of a millivolt off the standard.

CALCULATIONS

The following formula was used in calculating the pH value of the solutions, where V refers to the potentiometer reading,

$$pH = \frac{0.4534 - V}{0.0591} \quad (1)$$

The hydrogen ion concentration was calculated by means of the following relationship:

$$- \log C_H = pH$$

The degree of hydrolysis, x, was calculated by substituting in the following formula, where M refers to the molality of the aluminum sulfate,

$$x = \frac{C_H}{6M}$$

1. Victor K La Mer and T. R. Parsons, J. Biol. Chem., 57, 613 (1923)

EXPERIMENTAL RESULTS

Each of the following results represents an independent measurement of a cell and is an average of not less than three readings. In each case the first two readings were taken from cells where the contents had been made up and divided. They served as checks. In the second two readings new cell contents were made from the stock solutions and divided.

Table No 1
No neutral salt present

Molality of $Al_2(SO_4)_3$	E. M. F.	pH	Log C_H	$x.10^3$
0.1000	0.2665			
	0.2669			
	0.2667			
	0.2669			
	0.2668	3.1556	$\bar{4}.8444$	1.164
0.0500	0.2602			
	0.2601			
	0.2602			
	0.2600			
	0.2602	3.2691	$\bar{4}.7309$	1.794
0.0375	0.2566			
	0.2566			
	0.2564			
	0.2563			
	0.2565	3.3333	$\bar{4}.6667$	2.063
0.0250	0.2505			
	0.2510			
	0.2510			
	0.2510			
	0.2509	3.4264	$\bar{4}.5736$	2.497
0.0188	0.2469			
	0.2467			
	0.2471			
	0.2469			
	0.2469	3.4941	$\bar{4}.5059$	2.849
0.0125	0.2430			
	0.2431			
	0.2435			
	0.2431			
	0.2432	3.5567	$\bar{4}.4433$	3.700

Table No 2
Neutral salt: 1.0 molar NaCl

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2636			
	0.2636			
	0.2642			
	0.2641			
	0.2639	3.2064	$\bar{4}.7936$	2.073
0.0375	0.2576			
	0.2586			
	0.2587			
	0.2585			
	0.2586	3.3165	$\bar{4}.6835$	2.248
0.0250	0.2534			
	0.2538			
	0.2541			
	0.2540			
	0.2537	3.722	$\bar{4}.6278$	2.830
0.0188	0.2490			
	0.2495			
	0.2489			
	0.2495			
	0.2492	3.4552	$\bar{4}.5448$	3.116
0.0125	0.2463			
	0.2455			
	0.2459			
	0.2458			
	0.2459	3.5110	$\bar{4}.4890$	4.111

Table No 3
Neutral salt: 0.75 molar NaCl

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2603			
	0.2596			
	0.2603			
	0.2601			
	0.2600	3.2724	$\bar{4}.7276$	1.780
0.0375	0.2565			
	0.2565			
	0.2570			
	0.2565			
	0.2566	3.3333	$\bar{4}.6667$	2.063
0.0250	0.2519			

0.0250	0.2519			
	0.2522			
	0.2521			
	0.2520			
	0.2520	3.4078	$\bar{4}.5922$	2.607
0.0188	0.2482			
	0.2476			
	0.2475			
	0.2480			
	0.2478	3.4788	$\bar{4}.5212$	2.952
0.0125	0.2434			
	0.2427			
	- 0.2432			
	0.2432			
	0.2432	3.5567	$\bar{4}.4433$	3.700

Table No 3
Neutral salt: 0.50 molar NaCl

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2585			
	0.2581			
	0.2587			
	0.2585			
	0.2585	3.2978	$\bar{4}.7022$	1.679
0.0375	0.2552			
	0.2545			
	0.2549			
	0.2551			
	0.2549	3.3587	$\bar{4}.6413$	1.946
0.0250	0.2504			
	0.2499			
	0.2506			
	0.2498			
	0.2502	3.4382	$\bar{4}.5618$	2.485
0.0188	0.2473			
	0.2464			
	0.2474			
	0.2465			
	0.2469	3.4941	$\bar{4}.5059$	2.849
0.0125	0.2427			
	0.2417			
	0.2422			
	0.2425			
	0.2424	3.5702	$\bar{4}.4298$	3.587

Table No 5
Neutral salt: 0.25 molar NaCl

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2582			
	0.2576			
	0.2579			
	0.2575			
	0.2578	3.3096	$\bar{4}.6906$	1.634
0.0375	0.2543			
	0.2542			
	0.2543			
	0.2545			
	0.2543	3.3688	$\bar{4}.6312$	1.901
0.0250	0.2500			
	0.2495			
	0.2502			
	0.2496			
	0.2498	3.4450	$\bar{4}.5550$	2.393
0.0188	0.2464			
	0.2462			
	0.2468			
	0.2465			
	0.2465	3.5008	$\bar{4}.4992$	2.806
0.0125	0.2418			
	0.2416			
	0.2418			
	0.2418			
	0.2418	3.5804	$\bar{4}.4196$	3.504

Table No 6

Neutral salt: 1.0 molar KCl

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2554			
	0.2554			
	0.2557			
	0.2555			
	0.2555	3.3485	$\bar{4}.6515$	1.494
0.0375	0.2515			
	0.2515			
	0.2516			
	0.2515			
	0.2515	3.4163	$\bar{4}.5837$	1.704

0.0250	0.2460 0.2457 0.2458 0.2457 0.2457	3.6887	$\bar{4}$.4856	2.039
0.0188	0.2415 0.2414 0.2416 0.2415 0.2415	3.5854	$\bar{4}$.4146	2.309
0.0125	0.2354 0.2353 0.2356 0.2355 0.2354	3.6887	$\bar{4}$.3113	2.731

Table No 7
Neutral salt: 0.75 molar KCl

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2559 0.2557 0.2557 0.2556 0.2557	3.3452	$\bar{4}$.6548	1.505
0.0375	0.2517 0.2516 0.2516 0.2516 0.2516	3.4145	$\bar{4}$.5855	1.711
0.0250	0.2460 0.2460 0.2461 0.2460 0.2460	3.5093	$\bar{4}$.4907	2.063
0.0188	0.2419 0.2417 0.2418 0.2417 0.2417	3.5820	$\bar{4}$.4180	2.327
0.0125	0.2360 0.2358 0.2360 0.2360 0.2360	3.6785	$\bar{4}$.3215	2.795

Table No 8

Neutral salt: 0.50 molar KCl

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2556			
	0.2556			
	0.2561			
	0.2560			
	0.2558 (mean)	3.3435	$\bar{4}$.6565	1.511
0.0375	0.2524			
	0.2523			
	0.2523			
	0.2524			
	0.2523 (mean)	3.4027	$\bar{4}$.5973	1.758
0.0250	0.2470			
	0.2467			
	0.2468			
	0.2466			
	0.2468 (mean)	3.4958	$\bar{4}$.5042	2.129
0.0188	0.2425			
	0.2426			
	0.2427			
	0.2425			
	0.2426 (mean)	3.5668	$\bar{4}$.4332	2.410
0.0125	0.2370			
	0.2370			
	0.2368			
	0.2369			
	0.2369 (mean)	3.6633	$\bar{4}$.3367	2.895

Table No 9

Neutral salt: 0.25 molar KCl

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2565			
	0.2565			
	0.2566			
	0.2567			1.558
	0.2566 (mean)	3.3300	$\bar{4}$.6700	~~xx10~~
0.0375	0.2534			
	0.2531			
	0.2530			
	0.2532			
	0.2532 (mean)	3.3892	4.6108	1.814

0.0250	0.2482			
	0.2480			
	0.2480			
	0.2480			
	0.2480	3.4755	$\bar{4}.5245$	2.231
0.0188	0.2445			
	0.2443			
	0.2443			
	0.2443			
	0.2443	3.5380	$\bar{4}.4620$	2.575
0.0125	0.2388			
	0.2389			
	0.2388			
	0.2388			
	0.2388	3.6311	$\bar{4}.3689$	3.118

Table No 10
Neutral salt: 1.0 molar $NaNO_3$

Molality of $Al_2SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2604			
	0.2605			
	0.2605			
	0.2606			
	0.2605	3.2639	$\bar{4}.7361$	1.815
0.0375	0.2565			
	0.2566			
	0.2567			
	0.2566			
	0.2566	3.3300	$\bar{4}.6700$	2.079
0.0250	0.2513			
	0.2511			
	0.2512			
	0.2509			
	0.2511	3.4230	$\bar{4}.5770$	2.517
0.0188	0.2465			
	0.2468			
	0.2470			
	0.2466			
	0.2467	3.4974	$\bar{4}.5026$	2.828
0.0125	0.2408			
	0.2410			
	0.2411			
	0.2410			
	0.2410	35938	$\bar{4}.4062$	3.397

Table No 11

Neutral salt: 0.75 molar $NaNO_3$

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2598			
	0.2599			
	0.2599			
	0.2599			
	0.2599	3.2741	$\bar{4}$.7259	1.773
0.0375	0.2560			
	0.2560			
	0.2559			
	0.2559			
	0.2559	3.3418	$\bar{4}$.6582	2.023
0.0250	0.2505			
	0.2503			
	0.2505			
	0.2504			
	0.2504	3.4348	$\bar{4}$.5652	2.450
0.0188	0.2464			
	0.2463			
	0.2465			
	0.2464			
	0.2464	3.5025	$\bar{4}$.4975	2.795
0.0125	0.2405			
	0.2405			
	0.2407			
	0.2406			
	0.2406	3.6007	$\bar{4}$.3997	3.344

Table No 12

Neutral salt: 0.50 molar $NaNO_3$

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2592			
	0.2590			
	0.2591			
	0.2591			
	0.2591	3.2873	$\bar{4}$.7127	1.720
0.0375	0.2555			
	0.2556			
	0.2555			
	0.2556			
	0.2555	3.3485	$\bar{4}$.6515	1.995

0.0250	0.2504			
	0.2501			
	0.2502			
	0.2504			
	0.2503	3.4365	$\bar{4}$.5635	2.440
0.0188	0.2464			
	0.2463			
	0.2461			
	0.2464			
	0.2463	3.5042	$\bar{4}$.4958	2.784
0.0125	0.2504			
	0.2407			
	0.2408			
	0.2407		[illegible]	4
	0.2406	3.6007	$\bar{4}$.3993	3.3[illegible]4

Table No 13

Neutral salt: 0.25 molar $NaNO_3$

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2587			
	0.2585			
	0.2590			
	0.2587			
	0.2587	3.2944	$\bar{4}$.7056	1.692
0.0375	0.2555			
	0.2554			
	0.2555			
	0.2554			
	0.2555	3.3485	$\bar{4}$.6515	1.992
0.0250	0.2505			
	0.2504			
	0.2505			
	0.2504			
	0.2505	3.4339	$\bar{4}$.5661	2.455
0.0188	0.2466			
	0.2466			
	0.2471			
	0.2467			
	0.2467	3.5854	$\bar{4}$.5026	2.828
0.0125	0.2415			
	0.2415			
	0.2415			
	0.2415			
	0.2415	3.5854	$\bar{4}$.4146	3.463

Table No 14

Neutral salt: 1.0 molar KNO_3

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2562			
	0.2554			
	0.2557			
	0.2553			
	0.2557	3.3453	$\bar{4}.6547$	1.505
0.0375	0.2516			
	0.2510			
	0.2516			
	0.2519			
	0.2515	3.4163	$\bar{4}.5837$	1.704
0.0250	0.2467			
	0.2455			
	0.2458			
	0.2462			
	0.2461	3.5076	$\bar{4}.4924$	2.072
0.0188	0.2414			
	0.2419			
	02415			
	0.2418			
	0.2417	3.5920	$\bar{4}.4180$	2.327
0.0125	0.2362			
	0.2355			
	0.2355			
	0.2359			
	0.2358	3.6819	$\bar{4}.3181$	~~3.491~~ 2.773

Table No 15

Neutral salt: 0.75 molar KNO_3

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2552			
	0.2549			
	0.2553			
	0.2553			
	0.2552	3.3537	$\bar{4}.6463$	1.476
0.0375	0.2514			
	0.2514			
	0.2512			
	0.2514			
	0.2514	3.4179	$\bar{4}.5821$	1.698

0.0250	0.2458			
	0.2459			
	0.2459			
	0.2459			
	0.2459	3.5110	$\bar{4}$.4890	2.055
0.0188	0.2416			
	0.2416			
	0.2416			
	0.2416			
	0.2416	3.5837	$\bar{4}$.4163	2.318
0.0125	0.2358			
	0.2359			
	0.2357			
	0.2358			
	0.2358	3.6819	$\bar{4}$.3181	~~3.492~~ 2.773

Table No 16

Neutral Salt: 0.50 molar KNO_3

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2546			
	0.2546			
	0.2547			
	0.2547			
	0.2546	3.3638	$\bar{4}$.6362	1.442
0.0375	0.2517			
	0.2514			
	0.2514			
	0.2517			
	0.2516	3.4145	$\bar{4}$.5855	1.711
0.0250	0.2467			
	0.2460			
	0.2466			
	0.2461			
	0.2463	3.5042	$\bar{4}$.4958	2.088
0.0188	0.2425			
	0.2421			
	0.2423			
	0.2420			
	0.2422	3.5736	$\bar{4}$.4864	2.373
0.0125	0.2365			
	0.2370			
	0.2372			
	0.2365			
	0.2367	3.6667	$\bar{4}$.3333	~~3.516~~ 2.872

Table No 17

Neutral salt: 0.25 molar KNO_3

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2563			
	0.2562			
	0.2564			
	0.2563			
	0.2563	3.3350	$\bar{4}.6650$	1.541
0.0375	0.2528			
	0.2530			
	0.2530			
	0.2530			
	0.2530	3.3909	$\bar{4}.6091$	1.807
0.0250	0.2481			
	0.2481			
	0.2480			
	0.2480			
	0.2480	3.4712	$\bar{4}.5288$	2.253
0.0188	0.2445			
	0.2446			
	0.2447			
	0.2446			
	0.2446	3.5330	$\bar{4}.4670$	2.605
0.0125	0.2392			
	0.2392			
	0.2391			
	0.2391			
	0.2391	3.6260	$\bar{4}.3748$	~~3.971~~ 3.161

Tablm No 18

Neubral salt: 1.0 molar Na_2SO_4

Molality of $Al_2SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2434			
	0.2435			
	0.2436			
	0.2435			
	0.2435	3.5516	$\bar{4}.4484$	0.936
0.0375	0.2392			
	0.2386			
	0.2390			
	0.2389			
	0.2389	3.6294	$\bar{4}.3706$	1.043

0.0250	0.2319			
	0.2318			
	0.2319			
	0.2319			
	0.2319	3.7478	$\bar{4}$.2522	1.192
0.0188	0.2267			
	0.2267			
	0.2265			
	0.2264			
	0.2266	3.8375	$\bar{4}$.1625	1.292
0.0125	0.2240			
	0.2241			
	0.2239			
	0.2240			
	0.2240	3.9255	$\bar{4}$.0745	1.583

Table No 19

Neutral salt: 0.75 molar Na_2SO_4

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2436			
	0.2440			
	0.2442			
	0.2442			
	0.2440	3.5432	$\bar{4}$.4568	0.954
0.0375	0.2396			
	0.2388			
	0.2395			
	0.2392			
	0.2393	3.6227	$\bar{4}$.3773	1.060
0.0250	0.2333			
	0.2334			
	0.2334			
	0.2330			
	0.2333	3.7242	$\bar{4}$.2758	1.258
0.0188	0.2295			
	0.2294			
	0.2296			
	0.2297			
	0.2296	3.7868	$\bar{4}$.2132	1.486 1.448
0.0125	0.2235			
	0.2239			
	0.2230			
	0.2224			
	0.2227	3.9035	$\bar{4}$.0935	1.665

Table No 20

Neutral salt: 0.50 molar Na_2SO_4

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2454			
	0.2457			
	0.2455			
	0.2456			
	0.2456	3.5161	$\bar{4}.4839$	1.016
0.0375	0.2406			
	0.2408			
	0.2406			
	0.2405			
	0.2406	3.6008	$\bar{4}.3992$	1.114
0.0250	0.2340			
	0.2340			
	0.2338			
	0.2340			
	0.2340	3.7055	$\bar{4}.2945$	1.313
0.0188	0.2292			
	0.2295			
	0.2290			
	0.2293			
	0.2292	3.7936	$\bar{4}.2064$	1.430
0.0125	0.2229			
	0.2232			
	0.2229			
	0.2229			
	0.2230	3.8985	$\bar{4}.1015$	1.684

Table No 21

Neutral salt: 0.25 molar Na_2SO_4

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2471			
	0.2472			
	0.2476			
	0.2476			
	0.2475	3.4849	$\bar{4}.5151$	1.091
0.0375	0.2436			
	0.2434			
	0.2433			
	0.2433			
	0.2434	3.5533	$\bar{4}.4467$	1.283

0.0250	0.2367			
	0.2365			
	0.2368			
	0.2368			
	0.2367	3.6667	$\bar{4}$.3333	1.436
0.0188	0.2324			
	0.2323			
	0.2322			
	0.2320			
	0.2322	3.7429	$\bar{4}$.2571	1.606
0.0125	0.2261			
	0.2258			
	0.2260			
	0.2257			
	0.2259	3.8494	$\bar{4}$.1506	1.886

Table No 22

Neutral salt: 0.50 molar K_2SO_4

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	2 0.2395			
	0.2400			
	0.2401			
	0.2397			
	0.2398	3.6142	$\bar{4}$.3868	0.810
0.0375	0.2355			
	0.2358			
	0.2360			
	0.2358			
	0.2358	3.6918	$\bar{4}$.3181	0.925
0.0250	0.2299			
	0.2296			
	0.2300			
	0.2297			
	0.2298	3.7834	$\bar{4}$.2166	9 1.008
0.0188	0.2254			
	0.2255			
	0.2256			
	0.2253			
	0.2255	3.8561	$\bar{4}$.1439	1.238
0.0125	x 0.2192			
	0.2194			
	0.2194			
	0.2191	3.9611	$\bar{4}$.0389	1.459

Table No 23

Neutral salt: 0.25 molar K_2SO_4

Molality of $Al_2(SO_4)_3$	EMF	pH	Log C_H	$x.10^3$
0.0500	0.2424			
	0.2428			
	0.2432			
	0.2426			
	0.2428	3.5634	$\bar{4}.4366$	0.911
0.0375	0.2389			
	0.2393			
	0.2387			
	0.2388			
	0.2389	3.6294	$\bar{4}.3706$	1.043
0.0250	0.2361			
	0.2365			
	0.2364			
	0.2360			
	0.2362	3.6751	$\bar{4}.3249$	1.409
0.0188	0.2317			
	0.2318			
	0.2318			
	0.2318			
	0.2318	3.7495	$\bar{4}.2505$	1.583
0.0125	0.2254			
	0.2256			
	0.2255			
	0.2256			
	0.2255	3.8561	$\bar{4}.1439$	1.857

SUMMARY OF EXPERIMENTAL DATA

Table No 24

Degree of Hydrolysis of $Al_2(SO_4)_3$ x 10^3

Neutral salt: None

Molality of $Al_2(SO_4)_3$

Molality of neutral salt	0.0500	0.0375	0.0250	0.0188	0.0125
0.00	1.794	2.063	0.2497	2.849	3.700

Table 25

Degree of Hydrolysis of $Al_2(SO_4)_3$
$(x.10^3)$

Neutral salt: NaCl

Molality of NaCl	Molality of $Al_2SO_4)_3$ 0.0500	0.0375	0.0250	0.0188	0.0125
1.00	2.073	2.248	2.830	3.116	4.111
0.75	1.780	2.063	2. 607	2.952	3.700
0.50	1.679	1.946	2.485	2.849	3.587
0.25	1.634	1.901	2.393	2.806	3.504

Table No 26

Degree of Hydrolysis of $Al_2(SO_4)_3$
$(x.10^3)$

Neutral salt: KCl

Molality of KCl	Molality of $Al_2(SO_4)_3$ 0.0500	0.0375	0.0250	0.0188	0.0125
1.00	1.494	1.704	2.039	2.309	2.731
0.75	1.505	1.711	2.063	2.327	2.795
0.50	1.511	1.758	2.129	2.410	2.895
0.25	1.558	1.814	2.231	2.575	3.118

Table No 27

Degree of hydrolysis of $Al_2(SO_4)_3$
$(x.10^3)$
Neutral Salt: $NaNO_3$

Molality of $NaNO_3$	Molality of $Al_2(SO_4)_3$ 0.0500	0.0375	0.0250	0.0188	0.0125
1.00	1.815	2.079	2.517	2.828	3.397
0.75	1.773	2.023	2.450	2.795	3.344
0.50	1.720	1.995	2.440	2.784	3.344
0.25	1.692	1.992	2.455	2.828	3.463

Table No 28

Degree of Hydrolysis of $Al_2(SO_4)_3$ $(x.10^3)$
Neutral salt: KNO_3

Molality of KNO_3	Molality of $Al_2(SO_4)_3$ 0.0500	0.0375	0.0250	0.0188	0.0125
1.00	1.505	1.704	2.072	2.327	~~3.491~~ 2.773
0.75	1.476	1.698	2.055	2.318	~~3.492~~ 2.773
0.50	1.442	1.711	2.088	2.373	~~3.616~~ 2.872
0.25	1.541	1.807	2.253	2.605	~~3.971~~ 3.162

Table No 29

Degree of Hydrolysis of $Al_2(SO_4)_3$ $(x.10^3)$
Neutral salt: Na_2SO_4

Molality of Na_2SO_4	Molality of $Al_2(SO_4)_3$ 0.0500	0.0375	0.0250	0.0188	0.0125
1.00	0.936	1.043	1.192	1.292	1.583
0.75	0.954	1.060	1.258	1.486	1.665
0.50	1.016	1.114	1.313	1.430	1.684
0.25	1.091	1.243	1.436	1.606	1.886

Table No 30

Degree of Hydrolysis of $Al_2(SO_4)_3$ $(x.10^3)$
Neutral salt: K_2SO_4

Molality of K_2SO_4	Molality of $Al_2(SO_4)_3$ 0.0500	0.0375	0.0250	0.0188	0.0125
0.50	0.810	0.925	1.098	1.238	1.458
0.25	0.911	1.043	1.409	1.583	1.857

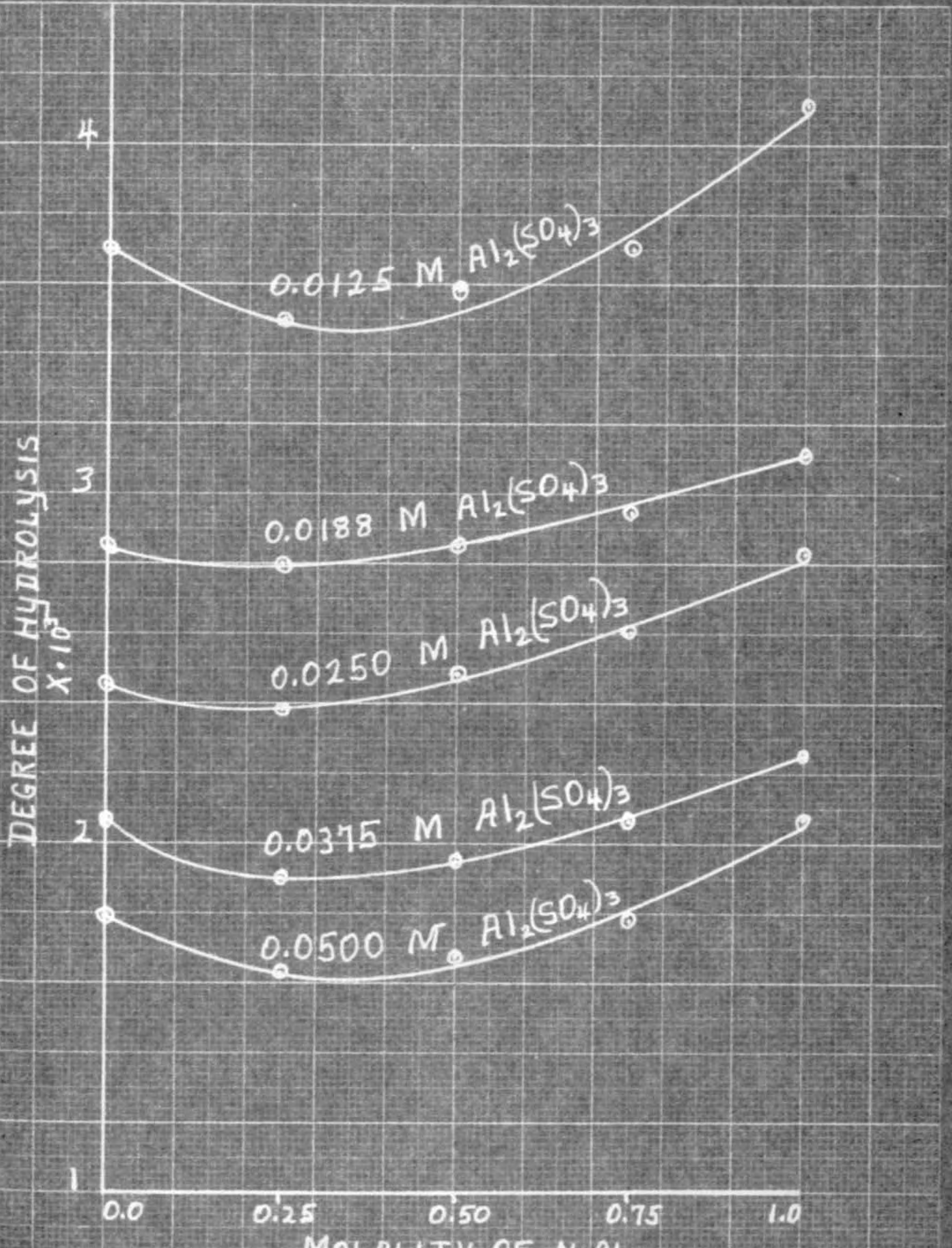

DEGREE OF HYDROLYSIS
X·10³
4
3
2
1
0.0125 M Al2(SO4)3
0.0188 M Al2(SO4)3
0.0250 M Al2(SO4)3
0.0375 M Al2(SO4)3
0.0500 M Al2(SO4)3
0.0
0.25
0.50
0.75
1.0
MOLALITY OF NaCl

FIG 1

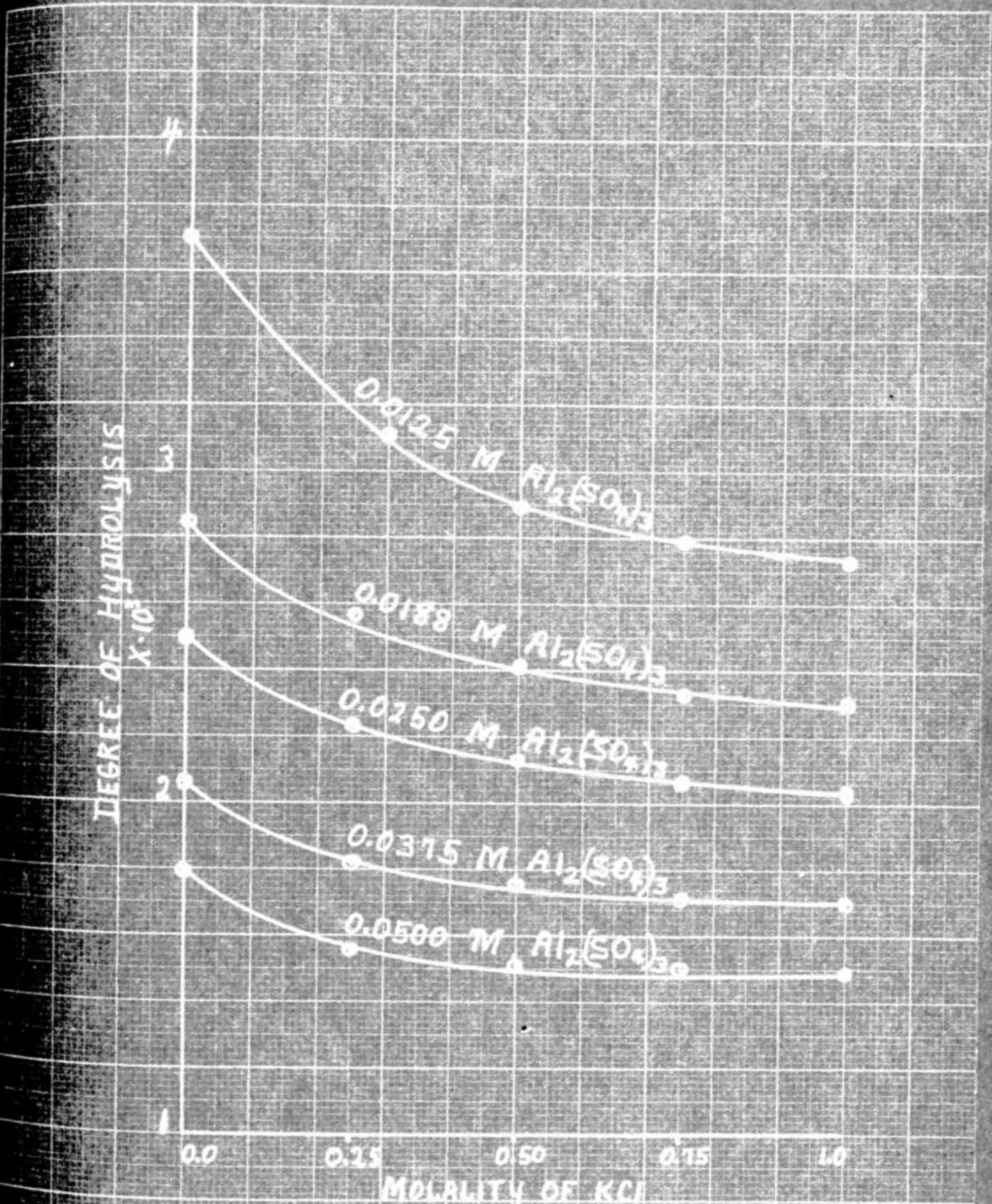
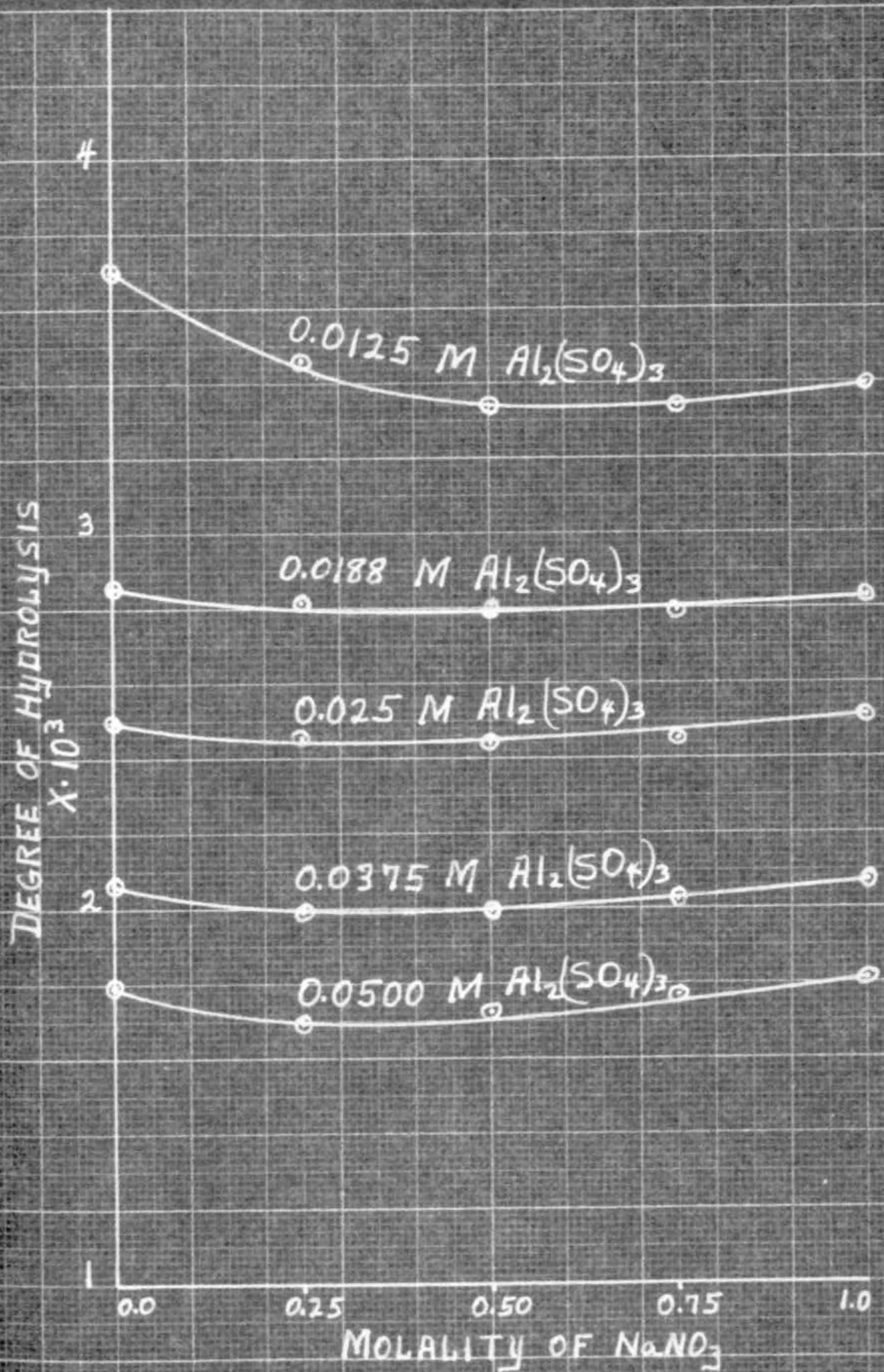
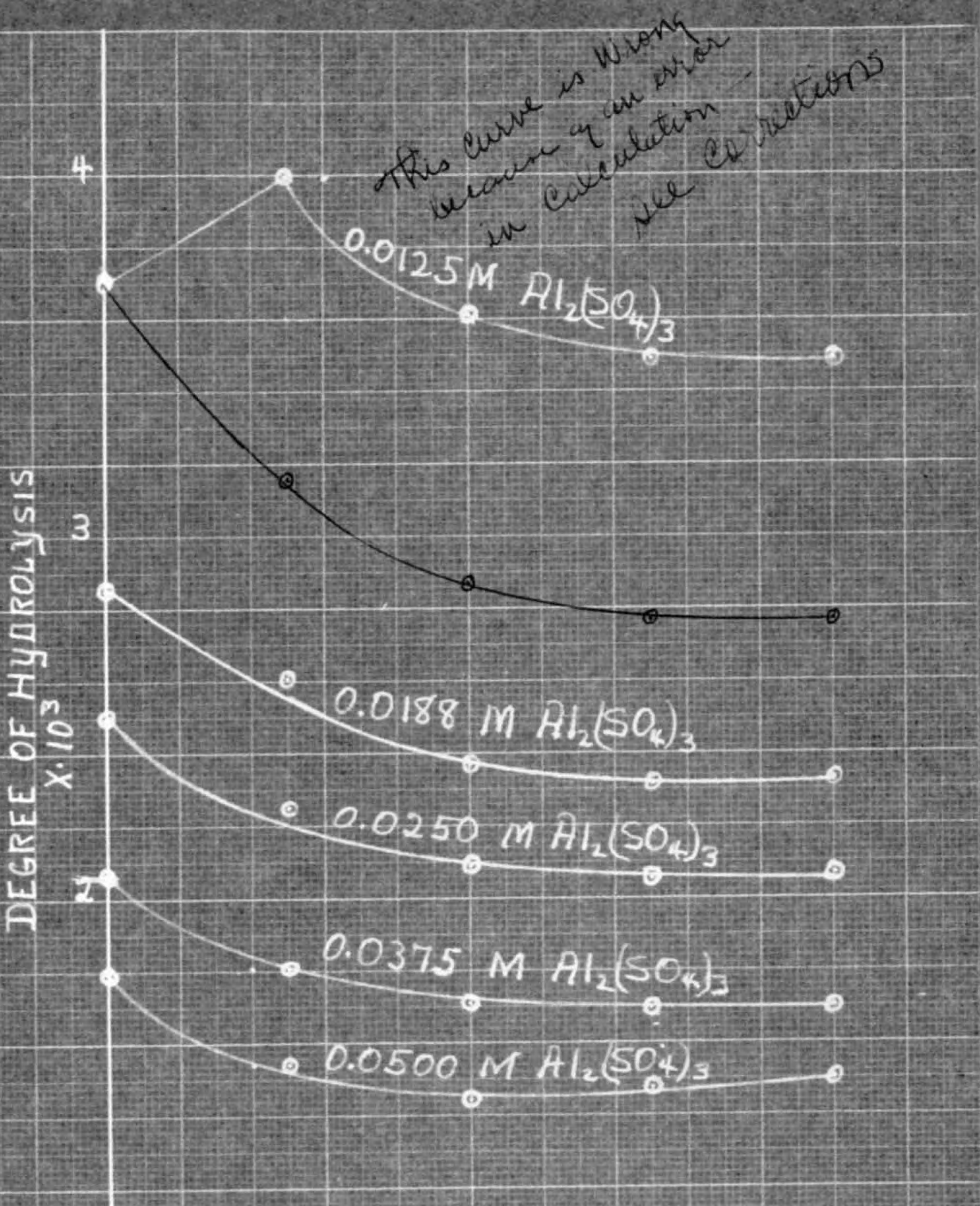

DEGREE OF HYDROLYSIS X·10³
4
3
2
1
0.0125 M Al₂(SO₄)₃
0.0188 M Al₂(SO₄)₃
0.0250 M Al₂(SO₄)₃
0.0375 M Al₂(SO₄)₃
0.0500 M Al₂(SO₄)₃
0.0
0.25
0.50
0.75
1.0
MOLALITY OF KCl

FIG. 2



DEGREE OF HYDROLYSIS X·10^3
4
3
2
1
0.0125 M Al2(SO4)3
0.0188 M Al2(SO4)3
0.025 M Al2(SO4)3
0.0375 M Al2(SO4)3
0.0500 M Al2(SO4)3
0.0
0.25
0.50
0.75
1.0
MOLALITY OF NaNO3

FIG. 3



This curve is wrong because of an error in calculation - see corrections
0.0125 M $Al_2(SO_4)_3$
0.0188 M $Al_2(SO_4)_3$
0.0250 M $Al_2(SO_4)_3$
0.0375 M $Al_2(SO_4)_3$
0.0500 M $Al_2(SO_4)_3$
DEGREE OF HYDROLYSIS
$X \cdot 10^3$
4
3
2
1
0.0
0.25
0.50
0.75
1.0
MOLALITY OF KNO_3

FIG. 4

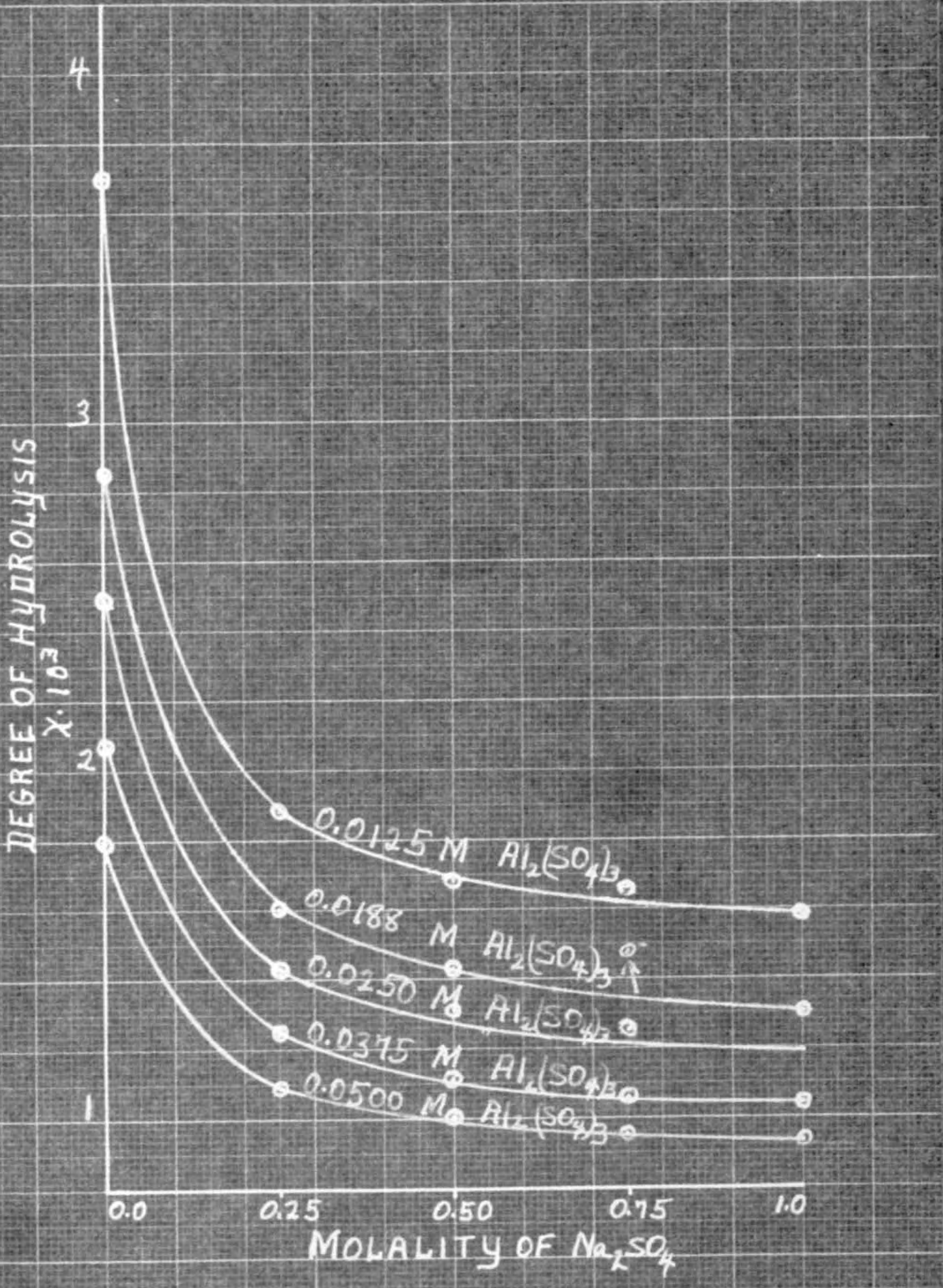
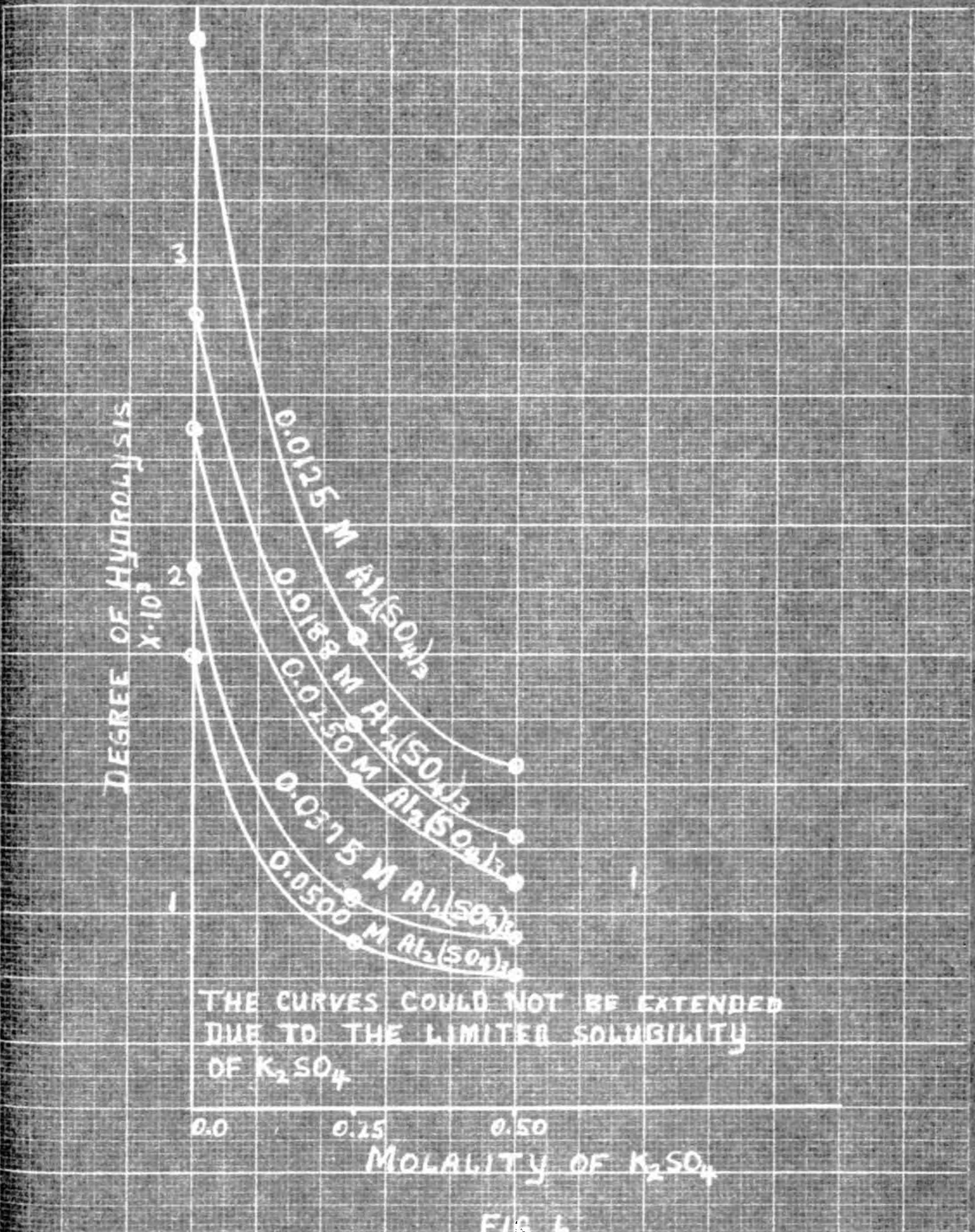

4
3
2
1
DEGREE OF HYDROLYSIS
$\chi \cdot 10^3$
0.0125 M $Al_2(SO_4)_3$
0.0188 M $Al_2(SO_4)_3$
0.0250 M $Al_2(SO_4)_3$
0.0375 M $Al_2(SO_4)_3$
0.0500 M $Al_2(SO_4)_3$
0.0
0.25
0.50
0.75
1.0
MOLALITY OF Na_2SO_4

FIG. 5



DEGREE OF HYDROLYSIS X·10³
3
2
1
0.0125 M Al₂(SO₄)₃
0.0188 M Al₂(SO₄)₃
0.0250 M Al₂(SO₄)₃
0.0375 M Al₂(SO₄)₃
0.0500 M Al₂(SO₄)₃
THE CURVES COULD NOT BE EXTENDED DUE TO THE LIMITED SOLUBILITY OF K₂SO₄
0.0
0.25
0.50
MOLALITY OF K₂SO₄

FIG. 6

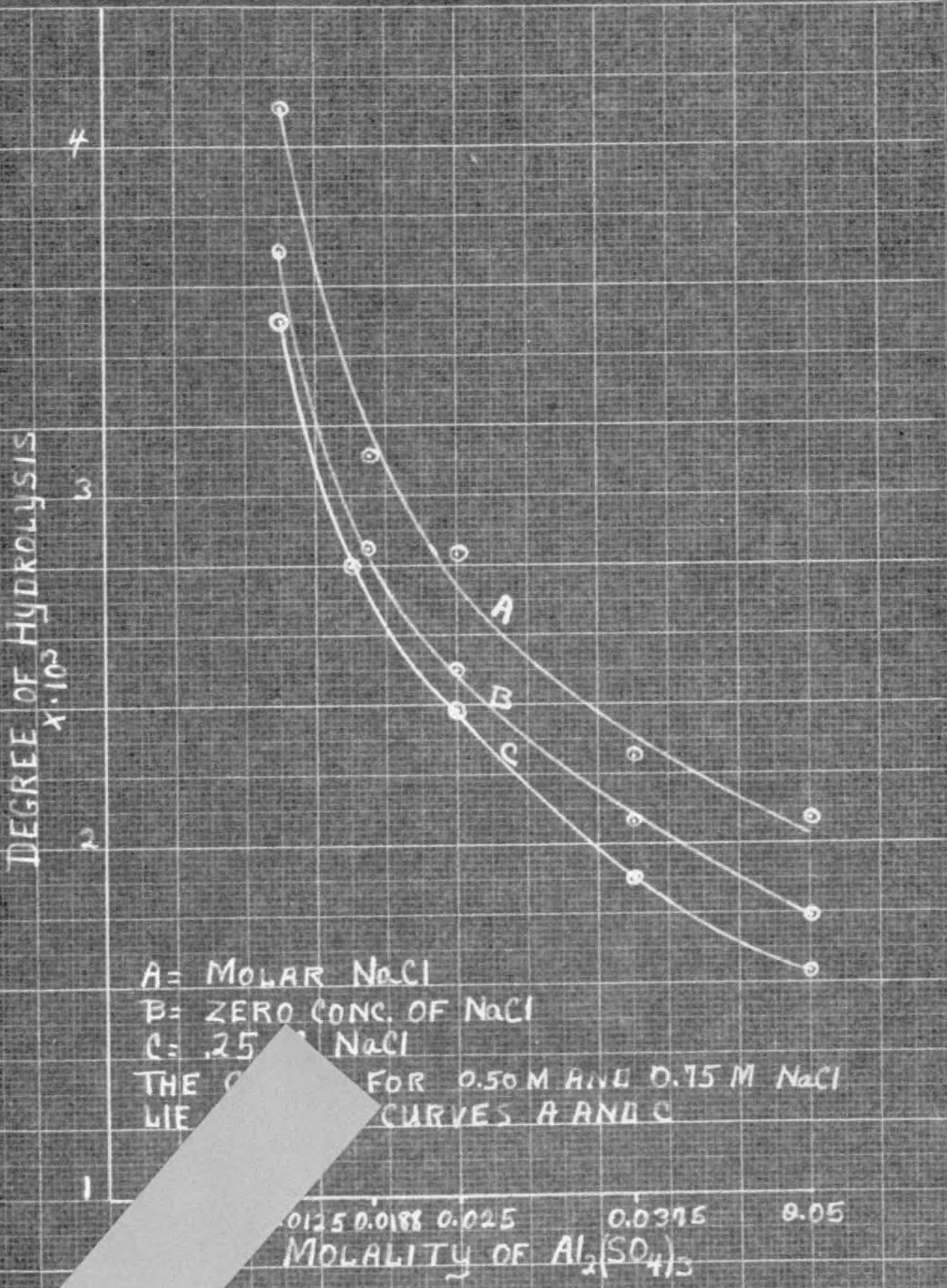
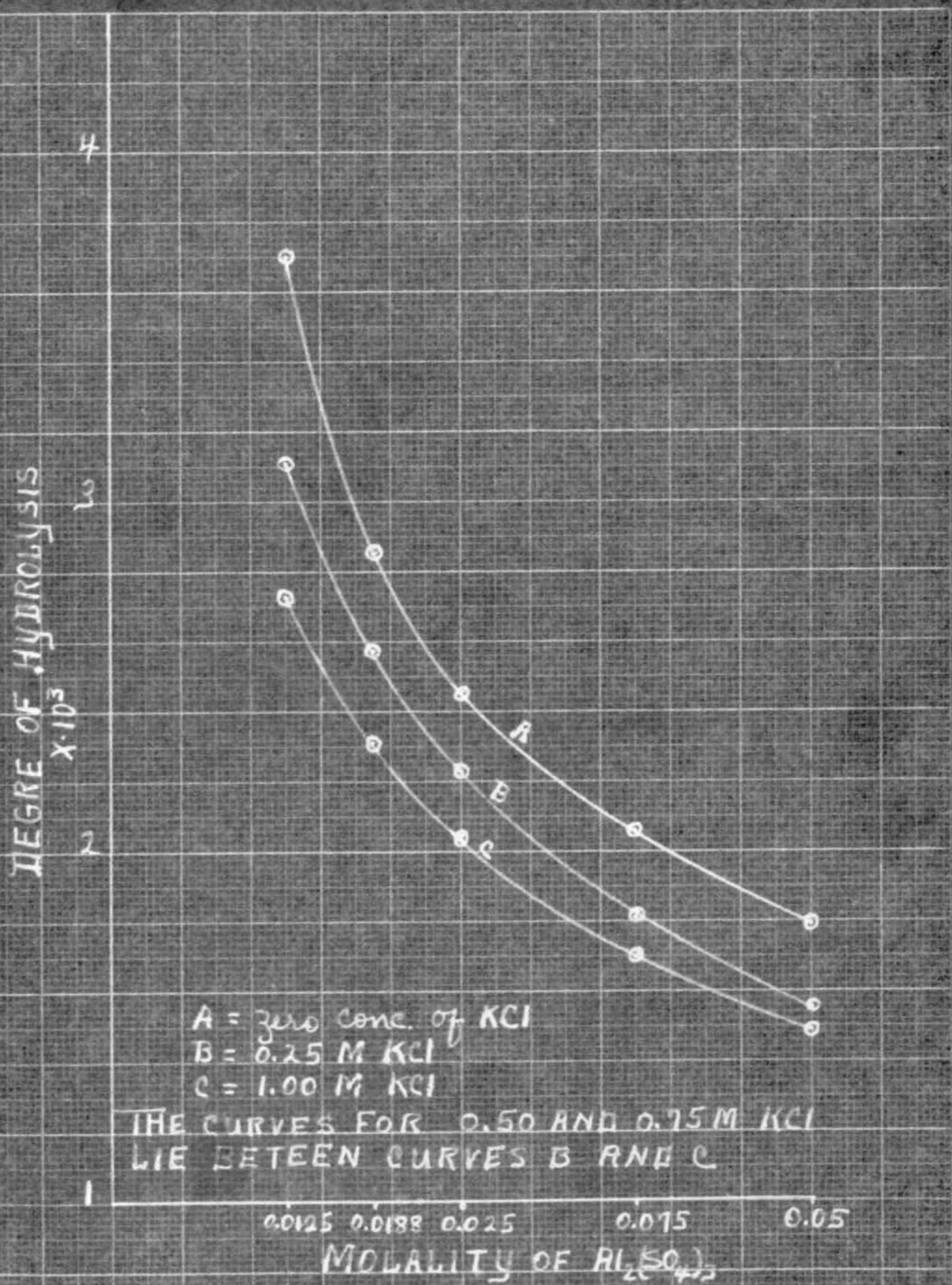
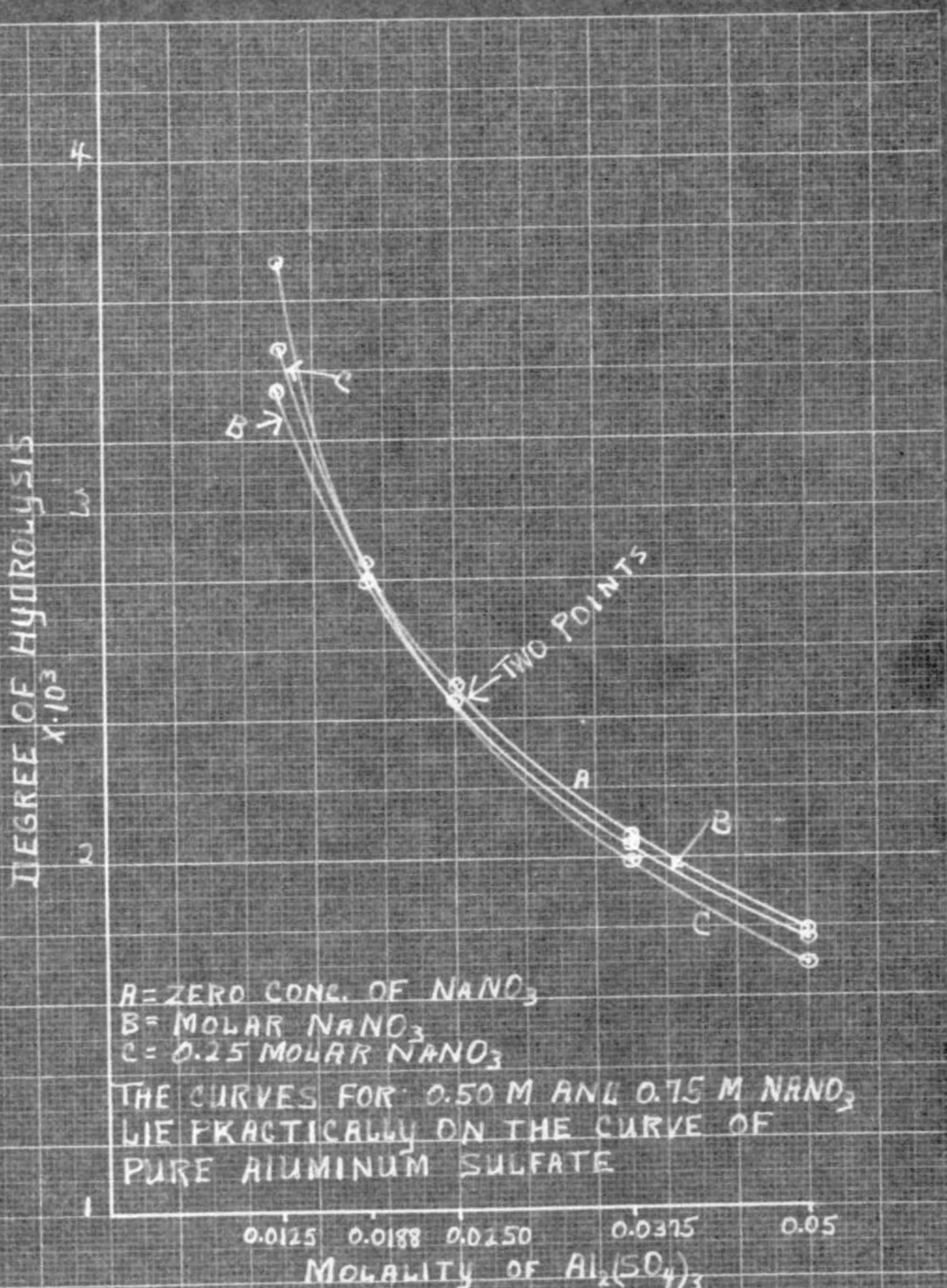

4
3
2
1
DEGREE OF HYDROLYSIS
X·10²
A
B
C
A= MOLAR NaCl
B= ZERO CONC. OF NaCl
C= .25
NaCl
THE
FOR 0.50 M AND 0.75 M NaCl
LIE
CURVES A AND C
0125 0.0188 0.025
0.0375
0.05
MOLALITY OF $Al_2(SO_4)_3$

FIG. 7



DEGRE OF HYDROLYSIS X·10³
4
3
2
1
A
B
C
A = zero conc. of KCl
B = 0.25 M KCl
C = 1.00 M KCl
THE CURVES FOR 0.50 AND 0.75 M KCl
LIE BETEEN CURVES B AND C
0.0125 0.0188 0.025 0.075 0.05
MOLALITY OF Al2(SO4)3

FIG. 8



DEGREE OF HYDROLYSIS
X·10³
4
3
2
1
B
C
TWO POINTS
A
B
C
A=ZERO CONC. OF NANO₃
B= MOLAR NaNO₃
C= 0.25 MOLAR NANO₃
THE CURVES FOR 0.50 M AND 0.75 M NANO₃
LIE PRACTICALLY ON THE CURVE OF
PURE ALUMINUM SULFATE
0.0125
0.0188
0.0250
0.0375
0.05
MOLALITY OF Al₂(SO₄)₃

FIG. 9

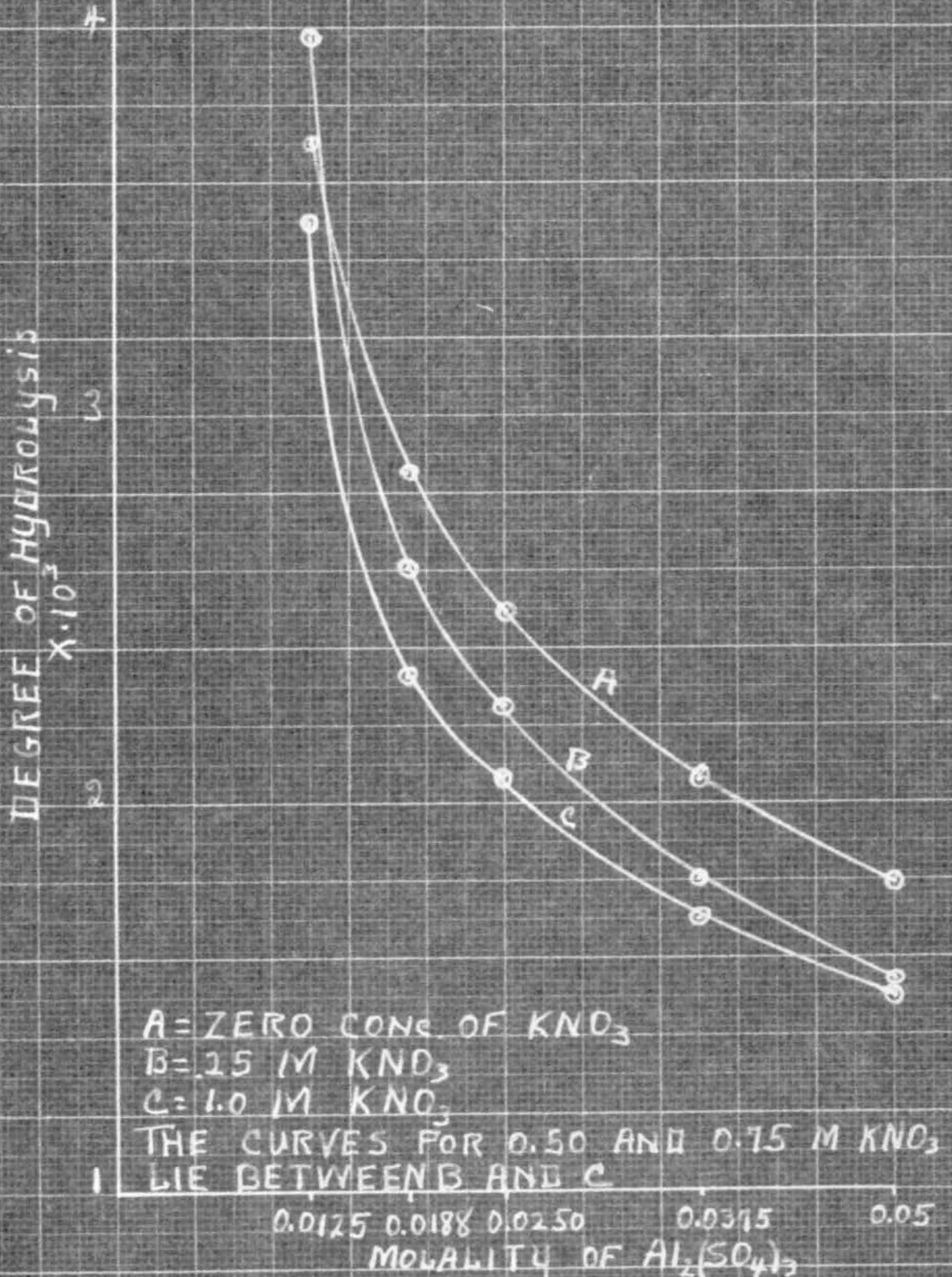
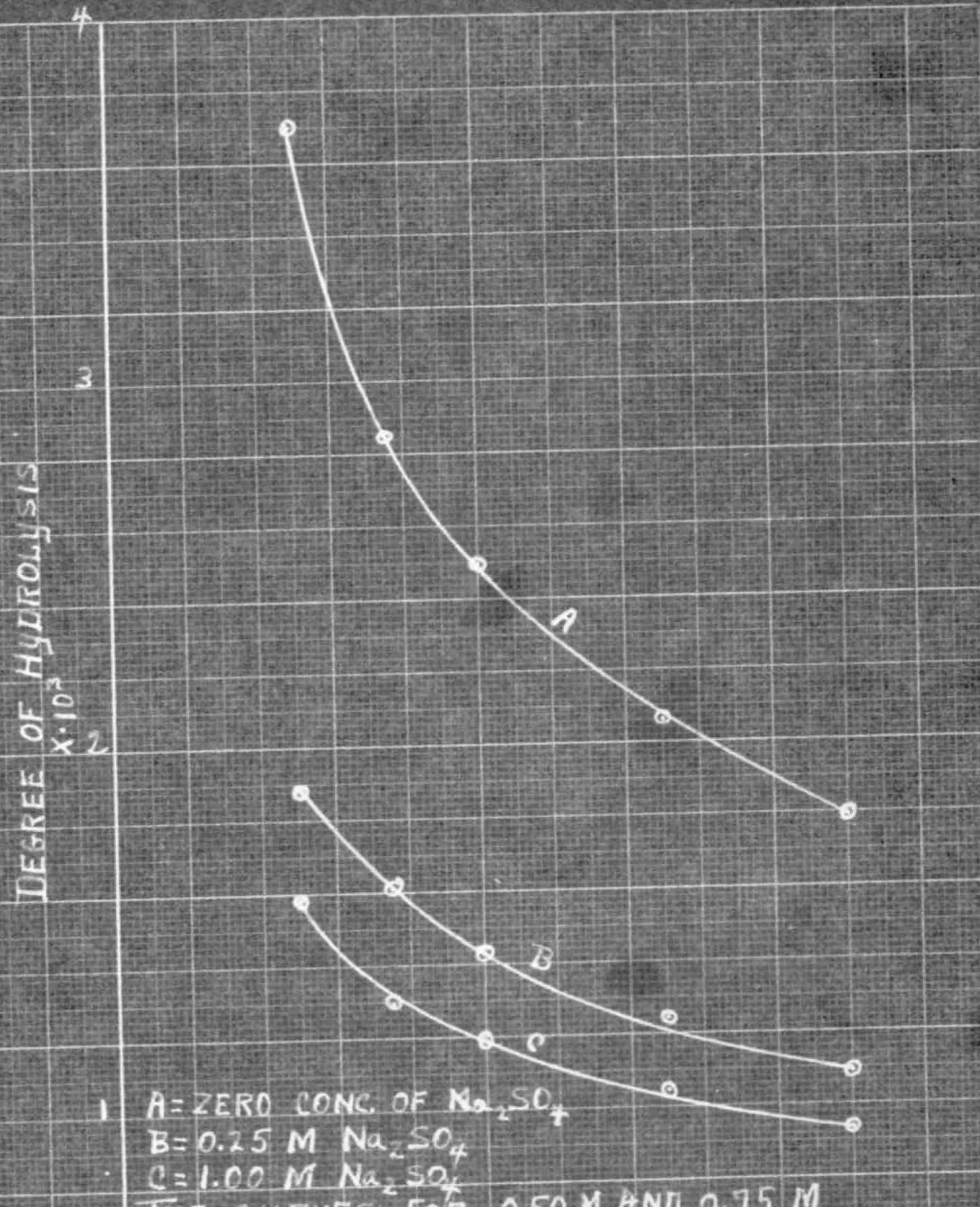

DEGREE OF HYDROLYSIS X·10^3
4
3
2
1
A
B
C
A = ZERO CONC OF KNO3
B = .25 M KNO3
C = 1.0 M KNO3
THE CURVES FOR 0.50 AND 0.75 M KNO3
LIE BETWEEN B AND C
0.0125 0.0188 0.0250 0.0375 0.05
MOLALITY OF Al2(SO4)3

FIG. 10



4
3
2
1
DEGREE OF HYDROLYSIS
X·10^3
A
B
C
A=ZERO CONC. OF Na2SO4
B=0.25 M Na2SO4
C=1.00 M Na2SO4
THE CURVES FOR 0.50 M AND 0.75 M
Na2SO4 LIE BETWEEN CURVES B AND C
0.0125 0.0188 0.025 0.0375 0.05
MOLALITY OF Al2(SO4)3

FIG. 11

DISCUSSION AND RESULTS

During this investigation the effect of several neutral salts upon the hydrolysis of aluminum sulfate has been studied. In all cases the degree of hydrolysis decreased when neutral salts were present, except in the cases of NaCl and $NaNO_3$.

In Fig. 1, the degree of hydrolysis of aluminum sulfate is plotted against the molality of NaCl. At low concentrations of the neutral salt there is a very small decrease in the degree of hydrolysis, but at concentrations greater than 0.35 molar the hydrolysis increases slowly with increasing concentration of the neutral salt. These results agree qualitatively with the data obtained by Thomas and Whitehead referred to earlier in this work. A better picture of the results is given in Fig. 7, where the degree of hydrolysis of aluminum sulfate is plotted against the concentration of aluminum sulfate. In the case of curve B there is no neutral salt present. It shows that the degree of hydrolysis of aluminum sulfate increases rapidly with dilution. Curve A refers to the hydrolysis when the concentration of NaCl is one molar. Curve C shows that when the concentration of NaCl is 0.25 molar there is a very small decrease in the degree of hydrolysis.

In Fig. 3, the degree of hydrolysis of aluminum sulfate is plotted against the concentration of $NaNO_3$. This figure shows that the hydrolysis for all concentrations of aluminum sulfate, except the most dilute solutions studied, is practically independent of the concentration of $NaNO_3$. For the 0.0125 molar solution of aluminum sulfate there is a small decrease in the hydrolysis for low concentrations of neutral salt, but at concentrations of $NaNO_3$ greater than 0.5 molar the degree of hydrolysis increases slightly. The effect in this case is very small and it may be due to the fact that at this concentration of aluminum sulfate the curve is exceedingly sensitive to small changes in the reading of the potentiometer. Credence is given to this explanation when figure 9 is studied. In this figure, curves B and C cross. Since the curves for all concentrations of the neutral salt lie practically on the curve for the hydrolysis of aluminum sulfate when no neutral salt is present, an error in the fourth place in the potentiometer reading could make two curves cross.

Similar curves have been plotted in Figs. 2, 4, 5, 6, 8, 10, 11, and 12, for all the other neutral salts studied. There is a small decrease in the hydrolysis for all concentrations of KCl and KNO_3. The most concentrated solutions produced the greatest effect, but the effect of the two salts was practically the same.

There is a rapid decrease in the hydrolysis of aluminum sulfate in the presence of Na_2SO_4 and K_2SO_4 as their concentrations are increased up to about 0.35 molar. Following that the effect becomes less noticeable with increasing concentration of the neutral salts. The K_2SO_4 has the greater effect.

In Fig. 4, there is one point on the curve for the 0.0125 molar solution of aluminum sulfate that is apparently out of place. In Fig. 5, on the curve for the 0.0188 molar solution there is another point apparently out of position. The readings that correspond to these points were carefully checked by making up new solutions from the stock solutions, and the apparatus was checked before and after the readings were made, using the standard buffer solutinn. The author has no explanation for these seeming anomalies, except the possibility of error. Lack of time prevented obtaining points on each side of these questionable points, but it is proposed that this be done.

The author did not have the same difficulty with the quinhydrone electrode in the presence of sodium and potassium nitrates that Mr. Stokes reported in his work. Lammert and Morgan[1] have made an exhaustive study of the quinhydrone electrode and the summary of their work includes this statement: "In unbuffered salt solutions in the neutral salt range, the quinhydrone electrode is likely to give erratic results, particularly if gold or graphite electrodes are used. The error, due to lack of reproducibility, may be greater than any constant error calculated by Sorensen and described as'salt error' ".

In this study it was found that data become less reproducible with the quinhydrone electrode as the pH value of the solution approaches 7. In this region the potentiometer reading becomes very sensitive to small changes in hydrogen ion concentration, and in an unbuffered solution one cannot obtain a constant potentiometer reading. Each case studied was characterized by a gradual increase in EMF. But with solutions well in the acid range satisfactorily constant readings were obtained, even with the most concentrated solutions of nitrates studied.

SUMMARY

1. A study has been made of the effect of several neutral salts upon the hydrolysis of aluminum sulfate. Six neutral salts were used and the effect of these at four concentrations was studied. Five concentrations of the aluminum sulfate were studied.

2. The degree of hydrolysis of aluminum sulfate increases rapidly with dilution.

3. The following salts decreased the hydrolysis in the order listed: KNO_3, KCl, Na_2SO_4, K_2SO_4. The greatest effect was at the highest concentration of the neutral salts.

4. $NaNO_3$ had practically no effect upon the hydrolysis at any concentration of the neutral salt or of the aluminum sulfate.

5. NaCl decreased the hydrolysis at low concentrations, but increased it at higher concentrations.

1. O.M. Lammert and J.L.R. Morgan, J. Am. Chem. Soc., 54, 910 (1932)

All solutions used in this investigation were molar instead of molal, as is indicated in some cases.