

THE EFFECT OF NEUTRAL SALTS ON THE HYDROLYSIS OF
BARIUM CHLORIDE

A THESIS

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INTRODUCTION

If a salt of a strong acid and a weak base is dissolved in water, it will hydrolyze to give an acid solution. Such a salt is barium chloride. We find that it has a pH of 5.536 in a 0.1 molar solution. This corresponds to a degree of hydrolysis of 1.455×10^{-5} .

Thomas and Whitehead¹ in their investigation of the effect of neutral salts on aluminum salts found that the pH of the solution increased slightly with KCl, Na₂SO₄, K₂SO₄, and decreased slightly with NaCl. These results show that neutral salts have some effect on the degree of hydrolysis.

In 1933, Friedman and Stokes² became interested in the effect that neutral salts have on the hydrolysis of CuSO₄. This was the first time that such a work had been carried out; all previous investigations of hydrolysis having been made mostly upon organic substances, mainly esters. They found that NaCl and KCl both increased the degree of hydrolysis and that Na₂SO₄ and K₂SO₄ decreased the degree of hydrolysis. Also they tried NaNO₃ and KNO₃ and were able to show only qualitatively that these both increased the extent of hydrolysis of copper sulfate.

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

(2) J. A. Stokes, Jr., Thesis, 1933, Georgia School of Technology Library.

Friedman and Whitley³ continuing the work of Friedman and Stokes, decided to investigate another type of salt other than the 2-2 type which was originally used. For this they chose $\text{Al}_2(\text{SO}_4)_3$, which is a 3-2 type salt and which was used by Thomas and Whitehead in some of their measurements. However, the measurements of Thomas and Whitehead were far from complete and could not be used in this work. Whitley reports that the following salts decreased the degree of hydrolysis, in the order listed, KNO_3 , KCl , Na_2SO_4 , and K_2SO_4 . Also, NaNO_3 was reported as having practically no effect upon the hydrolysis and NaCl decreased the hydrolysis at low concentrations, but increased it at higher concentrations.

The data obtained showed (1) that the degree of hydrolysis increases greatly with increasing dilution, and (2) that the effect that the neutral salt has on the extent of hydrolysis is almost a linear function of its concentration.

Since these studies have produced such interesting results, it was decided to continue the work, and find what effect neutral salts would have on other valence type salts. For this particular study, a 2-1 type salt, BaCl_2 was chosen.

It is a simple matter to calculate our degree of hydrolysis, if we can measure the hydrogen ion concentration of our solutions. Stokes² lists several methods for measuring hydrogen ion concentrations, none of which are satisfactory for use in this work because they do not give accurate results

(3) W. C. Whitley, Thesis, 1934, Georgia School of Technology Library

with low hydrogen ion concentrations. The use of any of the electrometric methods furnishes a sensitive and reproducible means of obtaining our hydrogen ion concentrations. The most commonly used of these are the hydrogen, the glass, and the quinhydrone half cells.

Horvorka and Dearing⁴ have measured the salt error that the hydrogen electrode exhibits with the addition of neutral salts.

Clark⁵ states that since only the concentration of the hydrogen ion appears in the equation for the electromotive force of the quinhydrone half cell, there should be no salt error involved in measurements made with it. He also lists the salt error for particular salts when measuring the pH of solutions colorimetrically. However, this method does not give sufficient accuracy (rarely better than ± 0.1 pH) to be of any use in these determinations.

Therefore, the quinhydrone electrode seems to be the best means of measuring the effects that added neutral salts may have on the degree of hydrolysis.

(4) Horvorka and Dearing, J.A.C.S., 57, (1935), 446

(5) W. M. Clark, Determination of Hydrogen Ions, 3rd Ed.,
Chap. 19.

PREPARATION AND PURIFICATION OF MATERIALS

The salts used in this investigation were C. P. grade and were further purified by recrystallization from distilled water, when a sufficient change of solubility with temperature made this possible. After two recrystallizations, the salts were dried in an oven at 105° for a period of 24 hours, after which they were removed, ground in an agate mortar and redried for at least 24 more hours. After this, they were kept in bottles with ground glass stoppers and used as soon as possible.

Barium Chloride--After two recrystallizations of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$, this salt was dried for a period of 72 hours in order to insure that no water of crystallization should be present.

All the stock solutions were made up by weighing the anhydrous salt. Similarly to calcium chloride, barium chloride tends to pick up water on standing, but much slower. By using a glass stoppered weighing bottle no difficulty was encountered in the direct weighing of the samples. In order to be sure that there was no water of crystallization present, the chloride present was titrated with a silver nitrate solution, which had previously been standardized against sodium chloride. The results are given with the data.

Sodium Chloride--Since the difference in solubility of this salt in hot and cold water amounts to only four grams in 100 cc. of water, it was necessary to find some other method for the purification. Previously the sodium chloride had been

twice recrystallized by passing HCl gas into a saturated solution of the salt. This method was used and the product dried at 110° and heated to 300°; but without fusion, the removal of the occluded HCl was incomplete.

To get around this difficulty, and at the same time obtain the salt in a very high state of purity, it was decided to throw it out of solution by the addition of ethyl alcohol. Upon adding 95% alcohol about one-third of the salt in the solution was thrown out. In this manner, the salt was twice recrystallized and then dried, using the procedure which has been previously described. Colorimetric tests, using bromthymol blue with a Hellige color disk, showed that sodium chloride solutions made up in this way had a pH of 7.0 ± 0.1 .

Potassium Chloride, Sodium Nitrate, and Potassium Nitrate--These salts were recrystallized twice from distilled water and then dried. Colorimetric tests, the same as described above, gave a pH of 7.0 ± 0.1 .

Quinhydrone--This was the standard Eastman product and no attempt was made at further purification. Whitley³ gives the melting point as 169.3° C., corrected.

Mercurous Chloride--C. P. calomel was used in the preparation of the saturated calomel half cell. It was not purified further.

Mercury--A sample of redistilled mercury was used.

Potassium Acid Phthalate--This material was obtained from the Bureau of Standards (for use as a primary standard in acidimetry). Without further treatment, it can be weighed

out directly to an accuracy of one part in two thousand, which is well inside the limit of experimental error. A 0.05 molar solution of KHPthalate was made up, and according to Clark⁵ has an EMF of 0.2187 volts at 25° C. This solution was kept in a Pyrex, glass stoppered, bottle which had previously been thoroughly cleaned and steamed out, and was used as the standard buffer solution. Very reproducible results were obtained with this solution, and it would keep for over three months.

APPARATUS

The thermostat held about 160 liters of water and was regulated by a metastatic thermoregulator. The temperature was maintained at $25^{\circ}\text{C} \pm 0.01^{\circ}$. Heating was provided for by means of two Cenco knife blade heaters, one of 250 watt and the other of 125 watt capacity. When the thermostat was being heated up to 25° both were used, but as soon as the temperature had been reached, the 250 watt heater was disconnected in order to prevent overheating, and only the smaller heater was used. The water in the thermostat was kept in constant circulation by means of a motor-driven stirrer. No difference in temperature was detectable upon moving the thermometer from one end of the thermostat to the other.

A Beckman thermometer, equipped with a reading glass, and calibrated against a Bureau of Standards thermometer, was used for measuring the temperature of the thermostat.

The saturated calomel half cells were prepared as described in Getman and Daniels⁶ by covering the bottom of the electrode vessel with a layer of mercury, upon which was poured a paste, prepared by rubbing together in a mortar, mercury and calomel moistened with saturated KCl. The vessel was then filled with saturated KCl solution, which was also saturated with calomel, and a small crystal of KCl was added to insure that the solution would remain saturated. Originally two half cells were prepared and checked against one another. There was no detectable

(6) Getman and Daniels, Outlines of Theoretical Chemistry, 5th Ed., 246.

difference in EMF. Thereafter only one was made up at a time, and it was checked by using the phthalate buffer solution. At the same time this checked the whole set-up, platinum electrodes, salt bridges, and calomel half cell.

Several platinum electrodes were made up. At first considerable difficulty was encountered in obtaining electrodes that would give no difference in EMF when they were checked against one another. However, by following the instructions for making up platinum electrodes given by Morgan, Lammert, and Campbell⁷ these were prepared and checked to see that they did not have an original difference of EMF of more than 0.0002 volt. Thereafter they were kept in a dilute solution of BaCl_2 when not in use, and shorted. It was found that this method of keeping the electrodes prevented them from gradually developing a small difference in EMF which showed up at the beginning of the measurements in any particular series.

The salt bridges consisted of U-tubes filled with a hot solution of agar-agar and KCl, which upon cooling formed a gel and prevented diffusion of the KCl. It was found that the best salt bridges were prepared when two grams of agar-agar were dissolved in 100 cc. of distilled water on a water bath. When all the agar dissolved, 38 grams of KCl (C.P.) were added and the solution stirred until the KCl dissolved. This solution was then used to fill about fifteen salt bridges. Care was taken in filling the U-tubes to prevent bubbles from getting in the tube, since they greatly increased the

(7) Morgan, Lammert, and Campbell, J.A.C.S., 53, (1931), 454.

resistance of the set-up. The bridges were then placed with the ends dipping in a shallow dish, which had about an inch of a saturated KCl solution in it. Bridges made up in this manner were checked from time to time against one another and in the set-up, and no appreciable difference in EMF was detected. After about three hours use, however, it was found that a difference of about 0.0005 volt would develop, and the bridge had to be discarded.

A Leeds and Northrup Student's Potentiometer was used in measuring the EMF of the cells, and a Leeds and Northrup Galvanometer No. 2320, with a current sensitivity of 0.5 μ a/div. and a coil resistance of 1000 ohms was used in finding the null point. A reproducibility of 0.0002 volt was obtainable with this arrangement. Due to the short period of the galvanometer, readings could be taken in a minimum of time.

METHOD AND PROCEDURE

For determining the degree of hydrolysis of the barium chloride, the hydrogen ion concentration of the solutions was measured by an electrometric method, using the quinhydrone electrode and the saturated calomel electrode. Liquid junction potentials were reduced to a minimum by the use of saturated KCl salt bridges.

In the actual measurements, a stock solution of BaCl_2 was made up by accurately weighing out enough of the material to make a solution of the desired concentration. Several of these solutions were checked by titration of the chloride with a standard silver nitrate solution, and it was found that this method of making up the stock solutions was both accurate and reproducible.

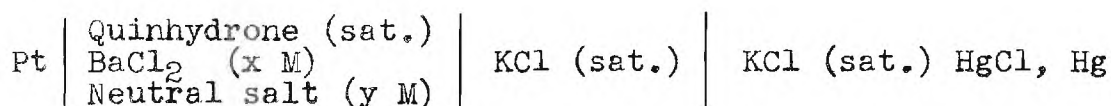
The neutral salt was weighed out and sufficient BaCl_2 solution was added to make the volume up to the desired concentration of the added salt. This method was found to be better than making up solutions of the neutral salts, since they are apt to change on standing in contact with soft glass bottles for any considerable length of time.

A small amount of quinhydrone (in most cases approximately 0.1 gram) was added and the solution stirred. The solubility of quinhydrone is very slight, and there was always some left at the bottom of the electrode vessel at the end of the run.

Then two platinum electrodes, shorted, were placed in the electrode vessel, and the whole was placed in the

thermostat. Two electrodes were used in the place of one because they gave a much better reproducibility. E. Biilmann⁸ states that it is always advisable to use more than one electrode in making measurements of EMF as the metal may easily be poisoned in many ways. He states that they frequently used two or three electrodes in making measurements in his laboratory. By using two electrodes shorted, it was found that very reproducible results were obtained. The most frequent cause of error in the electrodes was cracks in the electrode at the place where the platinum was sealed in.

The cell set-up was



Measurements were taken at intervals of from two to seven minutes over periods ranging from 5 to 20 minutes. It was found that the cell usually reached a constant value within a few minutes, and thereafter the drift would be slight for some period of time. Therefore it was not necessary to take the readings for long periods.

During the period when the EMF was being measured, the solution was occasionally stirred and in some instances a little more quinhydrone was added. If the cell was very far from equilibrium, it was found that this would speed up the attainment of that state.

Instead of drying the electrodes between the runs, they were rinsed off with a little of the solution in which they

(8) E. Biilmann, Trans. Far. Soc., 19, (1923-24), 820.

were being used.

Using one saturated calomel electrode, two cells were run at the same time. They were connected to the saturated KCl solution in the center of the set-up by means of the salt bridges. Since the KCl in this center portion was in danger of being contaminated, it was changed frequently. The calomel half-cell was checked by means of the standard buffer solution frequently and a new one was made up twice during the entire series of runs to insure its being uncontaminated and reproducible.

CALCULATIONS

For the calculation of the pH of the solution, the following formula from Leeds and Northrup, Notes on Hydrogen Ion Measurements⁹ was used.

$$\text{pH} = \frac{0.7177 - 0.00074t - V - v}{0.0001983 T}$$

where t is the temperature of the solutions and the electrodes, V is the measured voltage due to the difference in potential of the two electrodes, v is the reference potential of the calomel electrode, and T is the absolute temperature.

When we use a saturated calomel electrode at 25°C., the reference potential is 0.2458, and our equation simplifies to

$$\text{pH} = \frac{0.4534 - V}{0.05912}$$

where V in this case is our measured EMF.

The hydrogen ion concentration was then calculated by our definition of pH.

$$-\log (\text{H}^+) = \text{pH}$$

Since we might postulate according to the classical theory that BaCl_2 would hydrolyze in the following manner



we can obtain the degree of hydrolysis by simply dividing our hydrogen ion concentration by twice the molality of the original barium chloride solution, since one mol of BaCl_2 would give two mols of HCl .

A sample calculation showing the general principle

(9) Leeds and Northrup, Notes on Hydrogen Ion Measurements, Note Book 3, (1931), 41.

involved is given.

$$\text{pH} = \frac{0.4534 - V}{0.05912} = \frac{0.4534 - 0.1260}{0.05912} = \frac{0.3274}{0.05912} = 5.5379$$

$$\text{pH} = -\log (\text{H}^+) = 5.5379$$

$$\log (\text{H}^+) = 4.4621 - 10 = \overline{6}.4621$$

$$(\text{H}^+) = 2.898 \times 10^{-6}$$

Now since our solution was 0.1 M BaCl_2 to begin with, we obtain our degree of hydrolysis

$$x = \frac{(\text{H}^+)}{2 \text{ M}}$$

$$x = \frac{2.898 \times 10^{-6}}{2 \times 0.1} = 1.499 \times 10^{-5}$$

EXPERIMENTAL RESULTS

Each of the following results represents an independent measurement of a cell and is an average of not less than three readings. Each cell was made up individually, giving two checks on each value.

Table No. 1
No neutral salt present

Molarity of BaCl_2	EMF	pH	$(\text{H}^+) \times 10^6$	$x \cdot 10^5$
0.1000	0.1260	5.536	2.911	1.455
	0.1263			
	0.1259			
	<u>0.1261</u>			
0.0750	0.1245	5.560	2.755	1.337
	0.1248			
	0.1247			
	<u>0.1247</u>			
0.0500	0.1229	5.589	2.579	2.579
	0.1231			
	0.1230			
	<u>0.1230</u>			
0.0375	0.1220	5.604	2.480	3.306
	0.1220			
	0.1222			
	<u>0.1221</u>			
0.0250	0.1200	5.638	2.303	4.606
	0.1202			
	0.1201			
	<u>0.1201</u>			

Table No. 2
Neutral salt--1.0 M NaCl

Molarity of BaCl_2	EMF	pH	$(\text{H}^+) \times 10^6$	$x \cdot 10^5$
0.1000	0.1307	5.458	3.484	1.742
	0.1306			
	0.1305			
	<u>0.1306</u>			

Table No. 2 (cont.)
Neutral salt--1.0 M NaCl

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x · 10 ⁵
0.0750	0.1303	5.467	3.413	2.275
	0.1303			
	0.1300			
	<u>0.1302</u>			
0.0500	0.1283	5.497	3.183	3.183
	0.1285			
	0.1283			
	<u>0.1284</u>			
0.0375	0.1276	5.508	3.108	4.144
	0.1279			
	0.1280			
	<u>0.1278</u>			
0.0250	0.1249	5.555	2.787	5.574
	0.1251			
	0.1249			
	<u>0.1250</u>			

Table No. 3
Neutral salt--0.75 M NaCl

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x · 10 ⁵
0.1000	0.1297	5.476	3.339	1.669
	0.1294			
	0.1297			
	<u>0.1296</u>			
0.0750	0.1290	5.490	3.234	2.156
	0.1288			
	0.1287			
	<u>0.1288</u>			
0.0500	0.1265	5.529	2.958	2.958
	0.1266			
	0.1265			
	<u>0.1265</u>			
0.0375	0.1264	5.529	2.958	3.940
	0.1265			
	0.1265			
	<u>0.1265</u>			

Table No. 3 (cont.)
Neutral salt--0.75 M NaCl

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x . 10 ⁵
0.0250	0.1239			
	0.1241			
	0.1240			
	<u>0.1240</u>	5.572	2.681	5.362

Table No. 4
Neutral salt--0.50 M NaCl

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x . 10 ⁵
0.1000	0.1285			
	0.1282			
	0.1283			
	<u>0.1283</u>	5.499	3.170	1.585
0.0750	0.1277			
	0.1275			
	0.1275			
	<u>0.1276</u>	5.511	3.085	2.056
0.0500	0.1253			
	0.1253			
	0.1255			
	<u>0.1254</u>	5.548	2.831	2.831
0.0375	0.1250			
	0.1255			
	0.1255			
	<u>0.1253</u>	5.549	2.820	3.760
0.0250	0.1230			
	0.1229			
	0.1228			
	<u>0.1229</u>	5.590	2.569	5.138

Table No. 5
Neutral salt--0.375 M NaCl

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x . 10 ⁵
0.1000	0.1273			
	0.1275			
	0.1274			
	<u>0.1274</u>	5.514	3.061	1.531

Table No. 5 (cont.)
Neutral salt--0.375 M NaCl

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x . 10 ⁵
0.0750	0.1259			
	0.1262			
	<u>0.1263</u>			
	0.1261	5.536	2.909	1.940
0.0500	0.1242			
	0.1241			
	<u>0.1243</u>			
	0.1242	5.568	2.702	2.702
0.0375	0.1243			
	0.1245			
	<u>0.1244</u>			
	0.1244	5.565	2.723	3.631
0.0250	0.1216			
	0.1216			
	<u>0.1220</u>			
	0.1217	5.611	2.452	4.904

Table No. 6
Neutral salt--1.0 M KCl

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x . 10 ⁵
0.1000	0.1193			
	0.1187			
	<u>0.1188</u>			
	0.1189	5.658	2.198	1.099
0.0750	0.1150			
	0.1149			
	<u>0.1153</u>			
	0.1151	5.722	1.895	1.263
0.0500	0.1111			
	0.1109			
	<u>0.1110</u>			
	0.1110	5.792	1.615	1.615
0.0375	0.1103			
	0.1101			
	<u>0.1103</u>			
	0.1102	5.805	1.566	2.088

Table No. 6 (cont.)
Neutral salt--1.0 M KCl

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x . 10 ⁵
0.0250	0.1073 0.1074 <u>0.1074</u> 0.1074	5.853	1.404	2.808

Table No. 7
Neutral salt--0.75 M KCl

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x . 10 ⁵
0.1000	0.1200 0.1203 <u>0.1206</u> 0.1203	5.634	2.322	1.161
0.0750	0.1179 0.1174 <u>0.1177</u> 0.1176	5.680	2.089	1.393
0.0500	0.1143 0.1143 <u>0.1141</u> 0.1142	5.738	1.830	1.830
0.0375	0.1131 0.1136 <u>0.1134</u> 0.1134	5.738	1.774	2.365
0.0250	0.1112 0.1111 <u>0.1111</u> 0.1111	5.790	1.622	3.244

Table No. 8
Neutral salt--0.50 M KCl

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x . 10 ⁵
0.1000	0.1228 0.1230 <u>0.1230</u> 0.1229	5.590	2.569	1.285

Table No. 8 (cont.)
Neutral salt--0.50 M KCl

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x . 10 ⁵
0.0750	0.1193	5.650	2.242	1.495
	0.1192			
	0.1198			
	<u>0.1194</u>			
0.0500	0.1170	5.686	2.057	2.057
	0.1173			
	0.1173			
	<u>0.1172</u>			
0.0375	0.1167	5.694	2.025	2.700
	0.1170			
	0.1167			
	<u>0.1168</u>			
0.0250	0.1147	5.729	1.866	3.732
	0.1147			
	0.1148			
	<u>0.1147</u>			

Table No. 9
Neutral salt--0.375 M KCl

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x . 10 ⁵
0.1000	0.1232	5.589	2.579	1.289
	0.1230			
	0.1228			
	<u>0.1230</u>			
0.0750	0.1221	5.604	2.480	1.653
	0.1220			
	0.1223			
	<u>0.1221</u>			
0.0500	0.1187	5.661	2.181	2.181
	0.1187			
	0.1186			
	<u>0.1187</u>			
0.0375	0.1181	5.672	2.130	2.840
	0.1180			
	0.1182			
	<u>0.1181</u>			

Table No. 9 (cont.)
Neutral salt--0.375 M KCl

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x . 10 ⁵
0.0250	0.1152	5.714	1.933	3.866
	0.1158			
	0.1158			
	<u>0.1156</u>			

Table No. 10
Neutral salt--1.0 M NaNO₃

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x . 10 ⁵
0.1000	0.1205	5.631	2.339	1.169
	0.1207			
	0.1203			
	<u>0.1205</u>			
0.0750	0.1183	5.665	2.164	1.443
	0.1187			
	0.1185			
	<u>0.1185</u>			
0.0500	0.1187	5.665	2.164	2.164
	0.1183			
	0.1185			
	<u>0.1185</u>			
0.0375	0.1168	5.692	2.033	2.711
	0.1170			
	0.1169			
	<u>0.1169</u>			
0.0250	0.1166	5.697	2.001	4.002
	0.1166			
	0.1163			
	<u>0.1165</u>			

Table No. 11
Neutral salt--0.75 M NaNO₃

Molarity of BaCl ₂	EMF	pH	(H ⁺) x 10 ⁶	x . 10 ⁵
0.1000	0.1216	5.611	2.452	1.226
	0.1217			
	0.1218			
	<u>0.1217</u>			

Table No. 11 (cont.)
Neutral salt--0.75 M NaNO_3

Molarity of BaCl_2	EMF	pH	$(\text{H}^+) \times 10^6$	$x \cdot 10^5$
0.0750	0.1200			
	0.1200			
	<u>0.1203</u>			
	0.1201	5.638	2.303	1.535
0.0500	0.1193			
	0.1191			
	<u>0.1190</u>			
	0.1192	5.563	2.224	2.224
0.0375	0.1179			
	0.1178			
	<u>0.1179</u>			
	0.1179	5.675	2.114	2.819
0.0250	0.1175			
	0.1175			
	<u>0.1175</u>			
	0.1175	5.682	2.081	4.162

Table No. 12
Neutral salt--0.50 M NaNO_3

Molarity of BaCl_2	EMF	pH	$(\text{H}^+) \times 10^6$	$x \cdot 10^5$
0.1000	0.1234			
	0.1233			
	<u>0.1230</u>			
	0.1232	5.585	2.599	1.299
0.0750	0.1218			
	0.1218			
	<u>0.1218</u>			
	0.1218	5.609	2.461	1.641
0.0500	0.1197			
	0.1198			
	<u>0.1197</u>			
	0.1197	5.644	2.268	2.268
0.0375	0.1185			
	0.1183			
	<u>0.1185</u>			
	0.1184	5.666	2.156	2.875

Table No. 12 (cont.)
Neutral salt--0.50 M NaNO_3

Molarity of BaCl_2	EMF	pH	$(\text{H}^+) \times 10^6$	$x \cdot 10^5$
0.0250	0.1180			
	0.1183			
	<u>0.1177</u>			
	0.1180	5.673	2.122	4.244

Table No. 13
Neutral salt--0.375 M NaNO_3

Molarity of BaCl_2	EMF	pH	$(\text{H}^+) \times 10^6$	$x \cdot 10^5$
0.1000	0.1248			
	0.1247			
	<u>0.1246</u>			
	0.1247	5.560	2.755	1.378
0.0750	0.1231			
	0.1232			
	<u>0.1235</u>			
	0.1233	5.584	2.609	1.739
0.0500	0.1210			
	0.1210			
	<u>0.1211</u>			
	0.1210	5.622	2.386	2.386
0.0375	0.1203			
	0.1201			
	<u>0.1202</u>			
	0.1202	5.636	2.312	3.082
0.0250	0.1183			
	0.1185			
	<u>0.1189</u>			
	0.1186	5.663	2.172	4.344

Table No. 14
Neutral salt--1.0 M KNO_3

Molarity of BaCl_2	EMF	pH	$(\text{H}^+) \times 10^6$	$x \cdot 10^5$
0.1000	0.1191			
	0.1185			
	<u>0.1183</u>			
	0.1186	5.663	2.172	1.086

Table No. 14 (cont.)
Neutral salt--1.0 M KNO_3

Molarity of BaCl_2	EMF	pH	$(\text{H}^+) \times 10^6$	$x \cdot 10^5$
0.0750	0.1172	5.690	2.041	1.361
	0.1171			
	0.1168			
	<u>0.1170</u>			
0.0500	0.1165	5.702	1.986	1.986
	0.1165			
	0.1160			
	<u>0.1163</u>			
0.0375	0.1152	5.722	1.895	2.526
	0.1150			
	0.1152			
	<u>0.1151</u>			
0.0250	0.1128	5.766	1.713	3.426
	0.1123			
	0.1124			
	<u>0.1125</u>			

Table No. 15
Neutral salt--0.75 M KNO_3

Molarity of BaCl_2	EMF	pH	$(\text{H}^+) \times 10^6$	$x \cdot 10^5$
0.1000	0.1212	5.622	2.386	1.193
	0.1209			
	0.1208			
	<u>0.1210</u>			
0.0750	0.1193	5.656	2.206	1.471
	0.1188			
	0.1190			
	<u>0.1190</u>			
0.0500	0.1177	5.680	2.089	2.089
	0.1176			
	0.1174			
	<u>0.1176</u>			
0.0375	0.1163	5.702	1.986	2.648
	0.1163			
	0.1164			
	<u>0.1163</u>			

Table No. 15 (cont.)
Neutral salt--0.75 M KNO_3

Molarity of BaCl_2	EMF	pH	$(\text{H}^+) \times 10^6$	$\times . 10^5$
0.0250	0.1132			
	0.1135			
	<u>0.1134</u>			
	0.1134	5.751	1.774	3.548

Table No. 16
Neutral salt--0.50 M KNO_3

Molarity of BaCl_2	EMF	pH	$(\text{H}^+) \times 10^6$	$\times . 10^5$
0.1000	0.1232			
	0.1228			
	<u>0.1229</u>			
	0.1230	5.589	2.579	1.289
0.0750	0.1212			
	0.1215			
	<u>0.1210</u>			
	0.1212	5.619	2.404	1.603
0.0500	0.1187			
	0.1190			
	<u>0.1192</u>			
	0.1189	5.658	2.198	2.198
0.0375	0.1187			
	0.1188			
	<u>0.1188</u>			
	0.1188	5.659	2.189	2.919
0.0250	0.1171			
	0.1168			
	<u>0.1167</u>			
	0.1168	5.694	2.025	4.050

Table No. 17
Neutral salt--0.375 M KNO_3

Molarity of BaCl_2	EMF	pH	$(\text{H}^+) \times 10^6$	$\times . 10^5$
0.1000	0.1236			
	0.1238			
	<u>0.1230</u>			
	0.1234	5.582	2.619	1.309

Table No. 17 (cont.)
Neutral salt--0.375 M KNO_3

Molarity of BaCl_2	EMF	pH	$(\text{H}^+) \times 10^6$	$x \cdot 10^5$
0.0750	0.1228	5.590	2.569	1.713
	0.1231			
	0.1227			
	<u>0.1229</u>			
0.0500	0.1202	5.633	2.331	2.331
	0.1203			
	0.1207			
	<u>0.1204</u>			
0.0375	0.1200	5.641	2.285	3.046
	0.1201			
	0.1198			
	<u>0.1199</u>			
0.0250	0.1180	5.677	2.106	4.212
	0.1178			
	0.1177			
	<u>0.1178</u>			

Standardization of BaCl_2

Grams of NaCl	Milli-eq. of NaCl	cc. AgNO_3	Norm. AgNO_3
0.1468	2.507	50.70	0.04945
0.1485	2.540	51.03	0.04977
0.1400	2.395	48.30	<u>0.04960</u>
Avg.			0.04960

50 cc. of 0.1 M BaCl_2 were diluted to 250 cc. and this used for analysis.

cc. BaCl_2	cc. AgNO_3	Molarity of Orig. Soln.
50.00	40.20	0.09969
50.00	40.44	0.10029
50.00	40.35	<u>0.10006</u>
Avg.		0.10001

100 cc. of 0.0375 M BaCl_2 were diluted to 200 cc. and this was used for analysis.

cc. BaCl_2	cc. AgNO_3	Molarity of Orig. Soln.
50.00	37.62	0.03732
50.00	37.80	<u>0.03750</u>
Avg.		0.03742

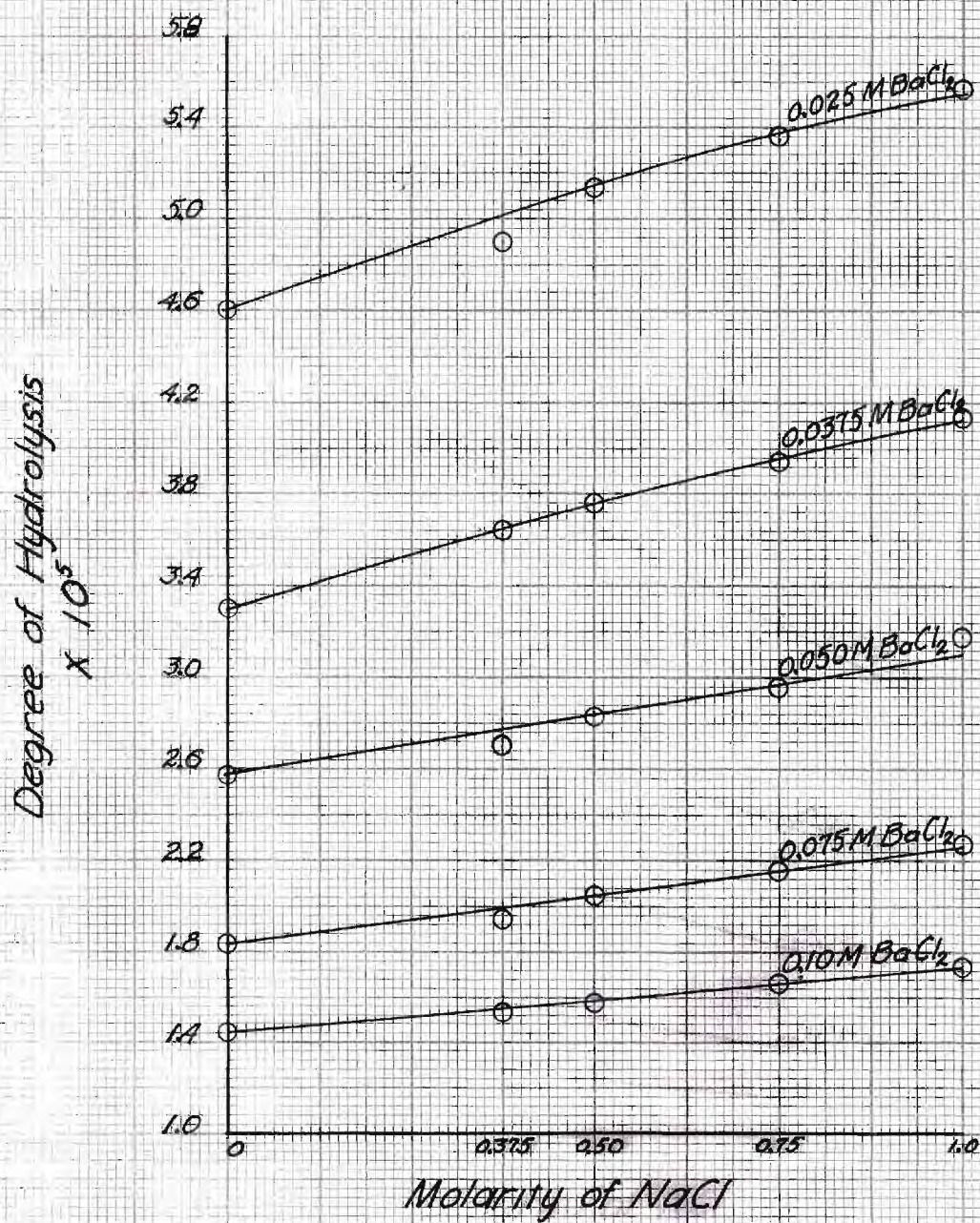


Fig. 1

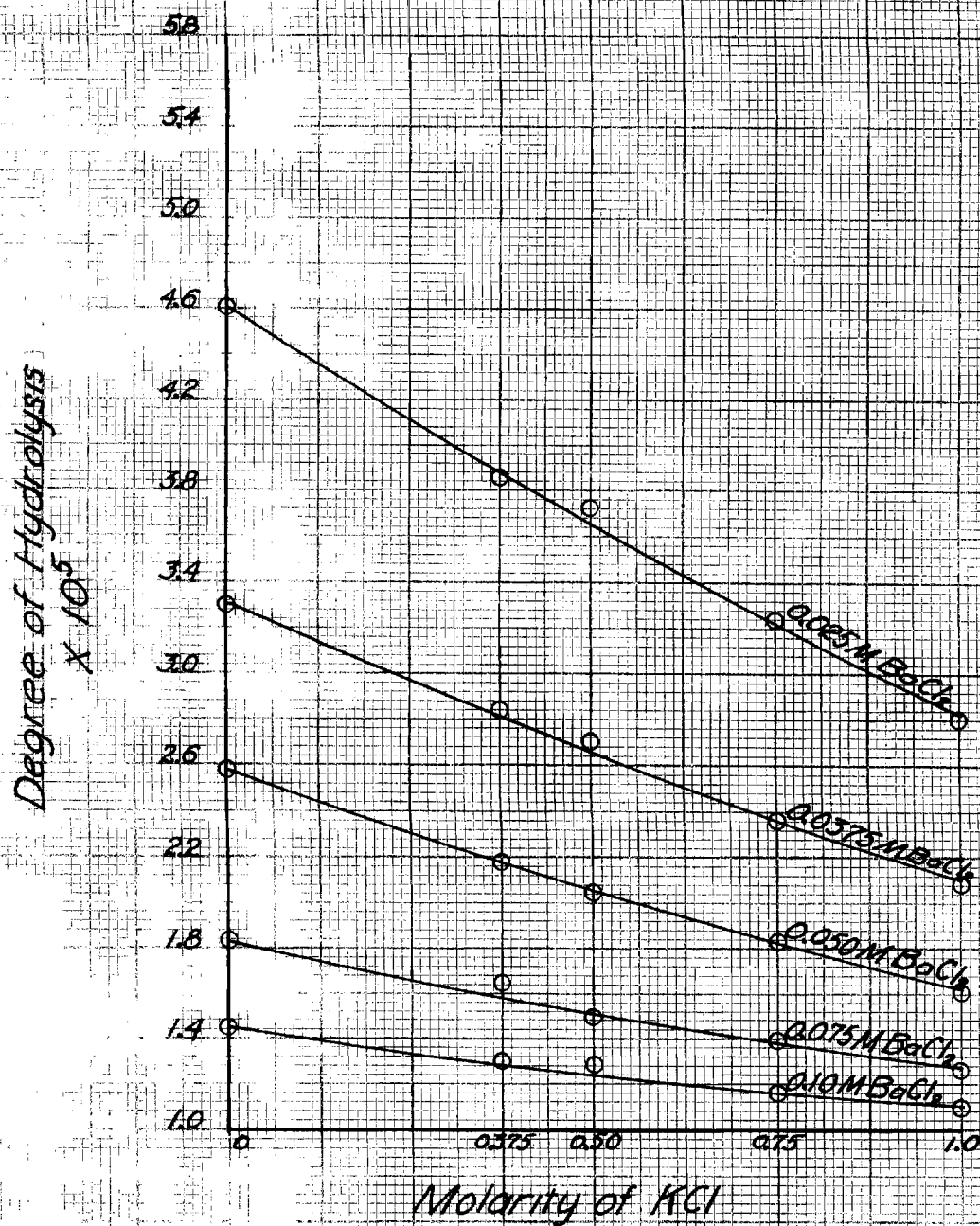


Fig. 2

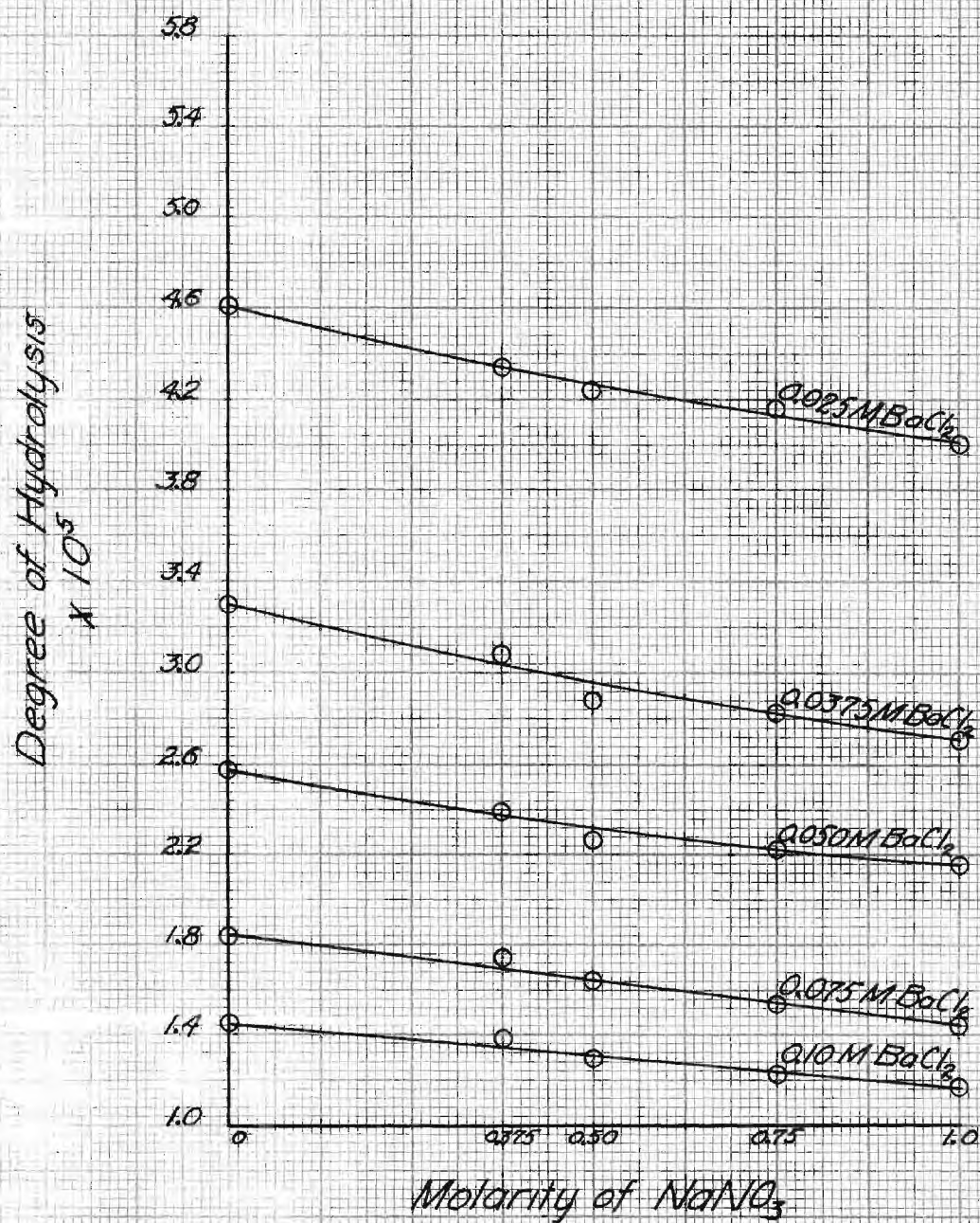


Fig. 3

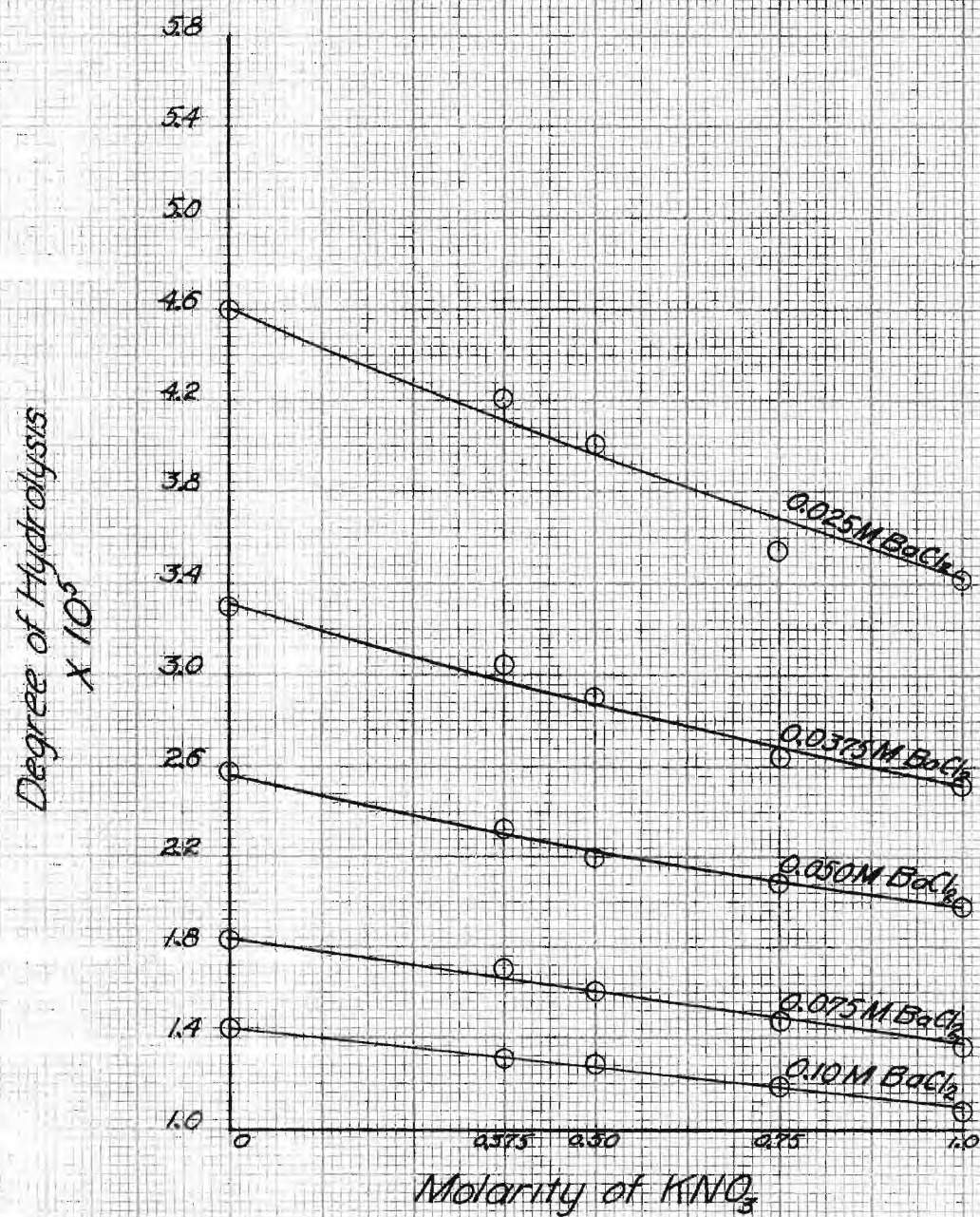


Fig. 4

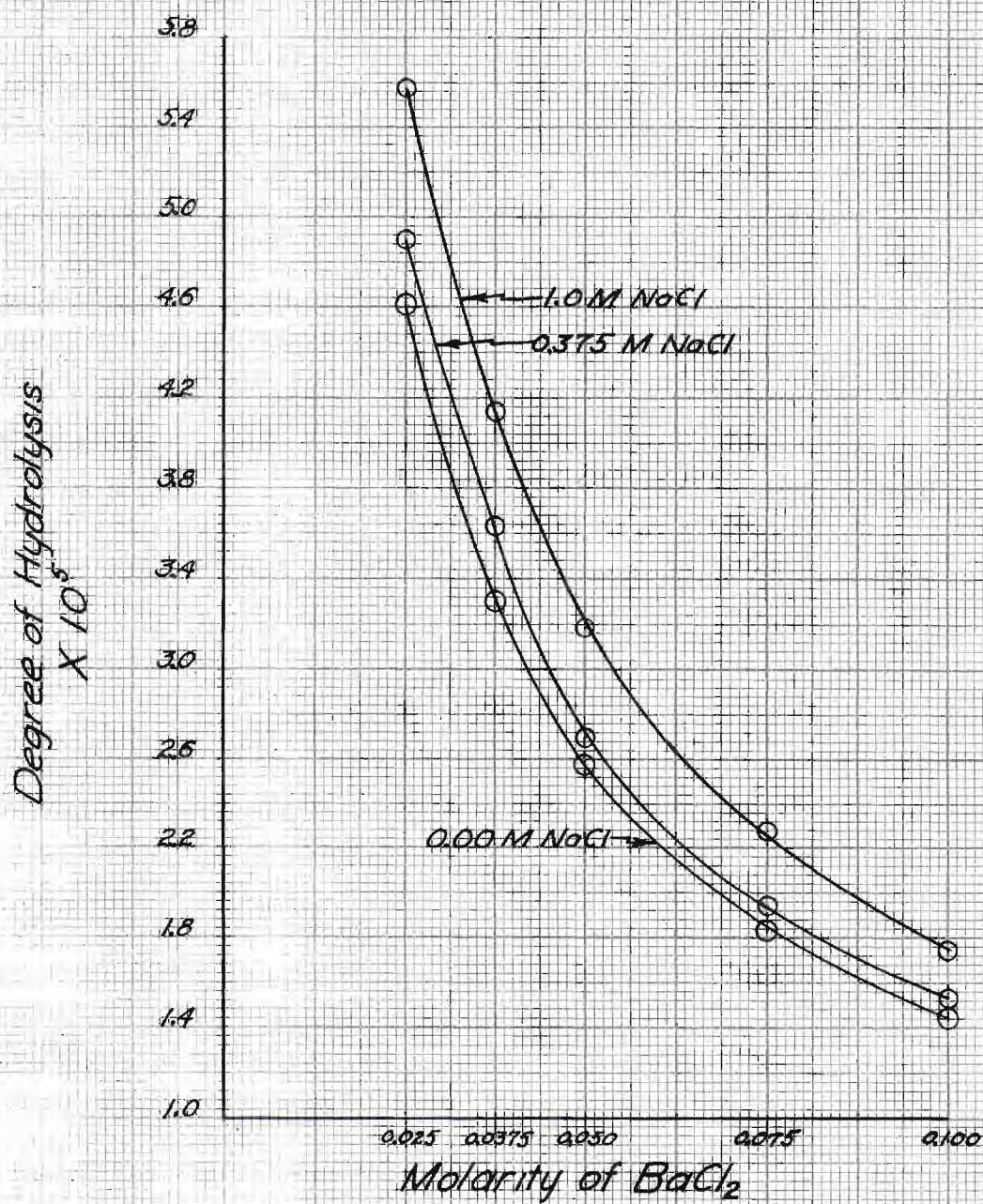


Fig. 5

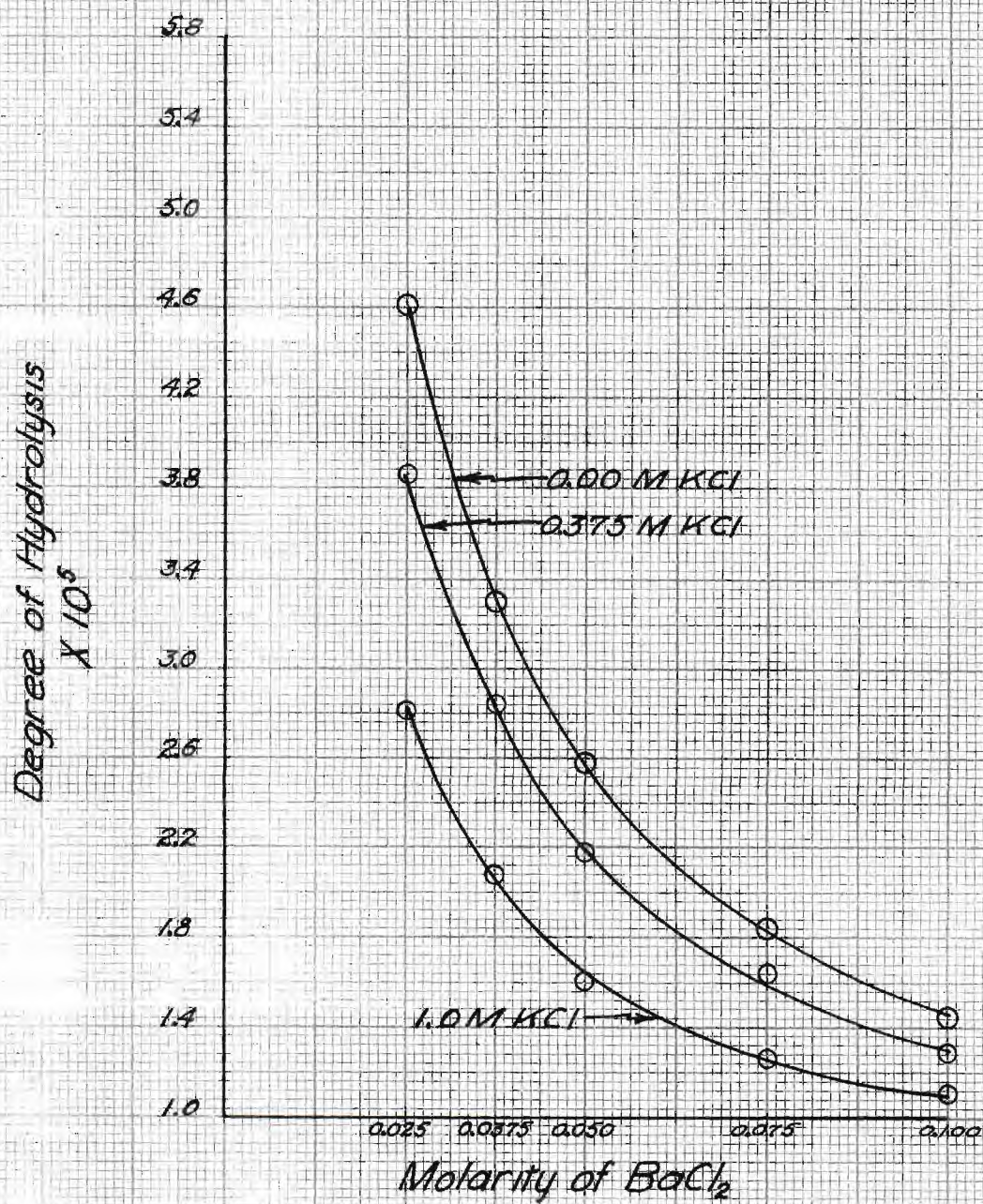


Fig. 6

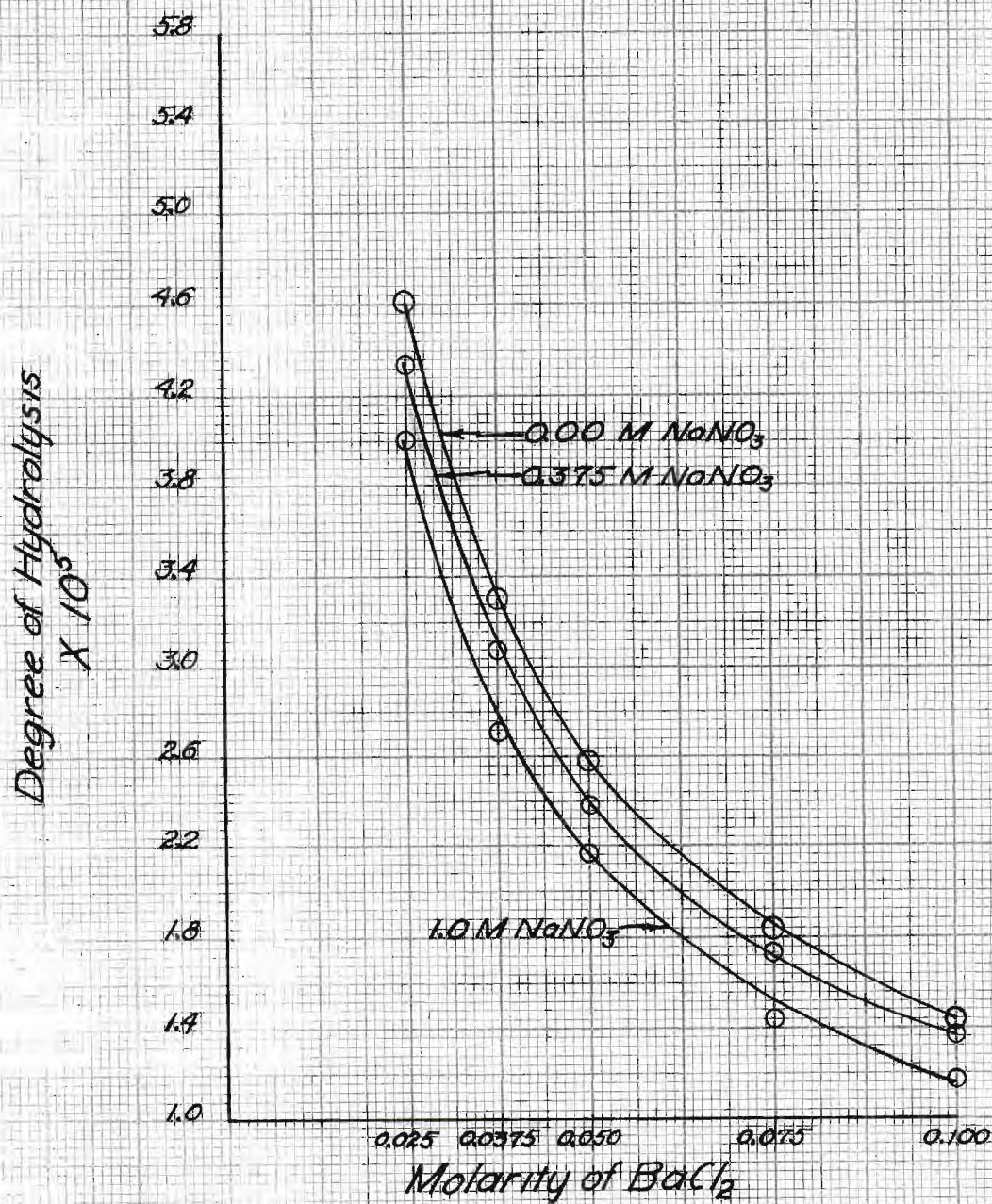


Fig. 7

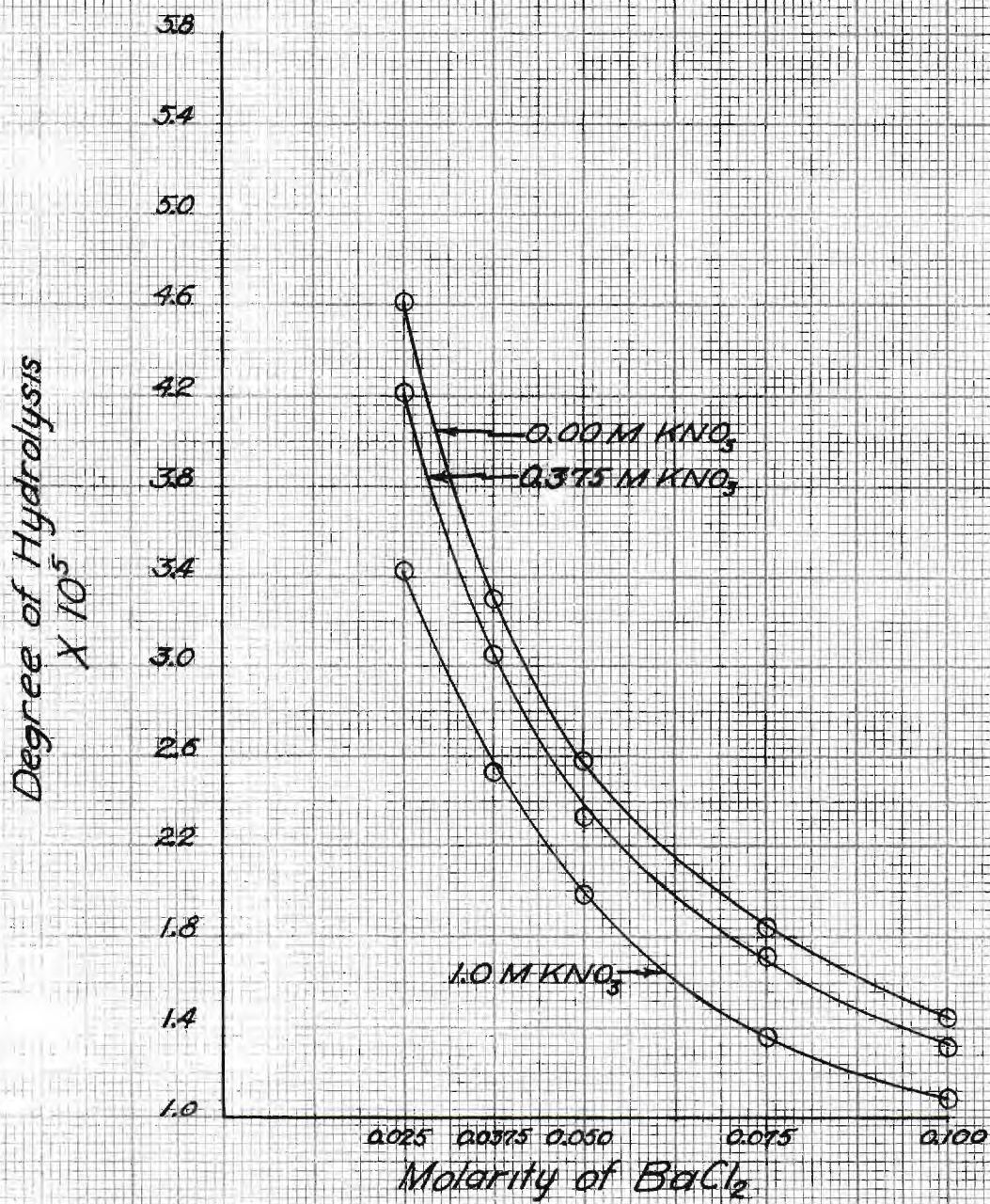


Fig. 8

DISCUSSION AND RESULTS

In this investigation we have found that the degree of hydrolysis increased when sodium chloride was added, and decreased when sodium nitrate, potassium nitrate, and potassium chloride were added. We have compared our results with those of Stokes and of Whitley in Table No. 18.

Table No. 18

Added Neutral salt	CuSO_4	Hydrolyzing salt $\text{Al}_2(\text{SO}_4)_3$	BaCl_2
NaCl	+	+	+
KCl	+	-	-
NaNO_3	+	=	-
KNO_3	+	-	-
Na_2SO_4	-	-	
K_2SO_4	-	-	
+ increased hydrolysis = no effect			
- decreased hydrolysis			

Figure 1 is a plot of the degree of hydrolysis of barium chloride solutions (each curve representing one concentration of barium chloride) as ordinates and the amount of added sodium chloride as abscissae. The deviation is approximately a linear one at all concentrations, and exactly so at the highest concentration of BaCl_2 . In Figure 5, we have again plotted the degree of hydrolysis of barium chloride as ordinates, but this time we have used the concentration of barium chloride as abscissae, with a particular concentration of added salt for each curve. The 0.5 M and 0.75M concentrations

were omitted from the plots to prevent overcrowding, but in every case they would lie in between the 0.375 M and 1.0 M curves. The original curve, or the barium chloride with no neutral salt added lies below the curves representing added salt concentrations. These results agree qualitatively at least with those previously reported by Stokes and by Whitley. In this work, the sodium chloride had no trace of HCl (not having been recrystallized from it, as was done by previous workers). Therefore, it seems that the addition of sodium chloride will generally produce an increase in the extent of hydrolysis of salts whose aqueous solutions are acid. This increase might previously have been attributed to the fact that some HCl had remained with the NaCl and that in the stronger concentrations this HCl and not the increased extent of hydrolysis was producing the higher hydrogen ion concentrations.

We have plotted in Figure 2 the degree of hydrolysis of barium chloride against the concentration of added KCl. Here we find that there is a decrease in the degree of hydrolysis with addition of a neutral salt. At the higher concentrations of barium chloride, again the function is a linear one, while at lower concentrations, it curves very slightly. It would seem that if we continued the addition of these neutral salts (noting that the curves showing a decrease in hydrolysis are concave upward, and the one showing an increase is concave downward) that we are approaching as a limit of the degree of hydrolysis, some definite value. It might be well to continue

these curves on out to higher concentrations of added salt to see if this effect continues, or whether the curves themselves are going through a maximum or minimum. In Figure 6, we have plotted degree of hydrolysis against the molarity of barium chloride, and used potassium chloride as our added salt. Here the original curve lies above the two curves representing 0.375 M KCl and 1.0 M KCl.

The curves representing the addition of sodium and potassium nitrate have been plotted in Figures 3, 4, 7, and 8. These salts produce a decrease in the degree of hydrolysis.

In going from NaCl to KCl, and from NaNO_3 to KNO_3 , we find that there is a decrease in the degree of hydrolysis at corresponding concentrations. Thus it would appear that in changing from sodium ions to potassium ions, keeping the anion the same, that we have some specific effect. In other words, while there may be a general effect due only to primary salt action, there will be some specific effect when we pass from sodium ions to potassium ions.

We might therefore be led to believe that we should find some such effect when we changed from NaCl to NaNO_3 and from KCl to KNO_3 . Upon examination of the curves of Figure No. 1 and Figure No. 3, we find that the change from NaCl to NaNO_3 produced a further decrease in the degree of hydrolysis. But upon changing from KCl to KNO_3 we find that there is a slight increase in the degree of hydrolysis. Qualitatively, Whitley found the same thing, although the degree of hydrolysis of aluminum sulfate is about a hundred times greater than that of

barium chloride.

However, there are other influencing factors; i.e. the effect of a common chloride ion, and possible hydration of the ions as was suggested by Lewis and Randall.¹⁰

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

SUMMARY

1. A study has been made of the effects that four neutral salts have on the degree of hydrolysis of barium chloride. Four concentrations of the neutral salts have been used, and five concentrations of the barium chloride.
2. The degree of hydrolysis of barium chloride increases considerably with dilution.
3. The following salts decreased the hydrolysis: KCl , KNO_3 and NaNO_3 .
4. Sodium chloride produces an increase in the hydrolysis of barium chloride.
5. There is a decrease in extent of hydrolysis in changing from sodium to potassium ions at corresponding concentrations. No general conclusion can be drawn on changing from chloride to nitrate.