THESIS

BY

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THE DISTRIBUTION OF PICRIC ACID BETWEEN WATER AND BENZENE AND THE EFFECT ON THE EQUILIBRIUM OF ADDED SODIUM AND HYDROGEN CHLORIDES.

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INTRODUCTION :

This investigation was undertaken in order to study the distribution of picric acid between the immiscible solvents water and benzene at different concentrations, and to determine the effect upon this equilibrium of the addition of successive amounts to sodium chloride and hydrogen chloride to the aqueous phase.

Data of this character is very similar to that relating to the effect of added electrolytes upon the solubility of slightly soluble salts and the theoretical conclusions which may be drawn are of a similar nature. The distribution results have, however, advantages over the solubility data: (1) in the former the activity may be varied over a considerable range, while in the latter it is fixed at an arbitrary value by the solubility of the salt; (2) the degree of ionization of the electrolyte used in the distribution experiments may be more accurately determined, for in the case of slightly soluble salts the range over which their concentration may be measured is very limited.

Picric acid was chosen for these experiments because its degree of ionization is that of a typical electrolyte and because it is one of the very few highly ionized substances which distribute themselves in a convenient ratio between water and the more miscible solvent.

The distribution of picric acid between water and benzene in the absence of added electrolytes has been studied by Walden (1) Kuriloff (2), and by Rothmund and Druker (3). The work of the latter investigators only is of sufficient accuracy to warrant careful study. Recently Eherenfeld (4) obtained some preliminary data regarding the effect of added salts upon the distribution ratio. The results of these investigations will be compared with the data obtained in this, after that data has been presented.

EXPERIMENTAL PROCEDURES.

Purification of Materials.

Water: The ordinary distilled water of the laboratory was found to be slightly acidic, probably due to the presence of carbon dioxide. As this would affect the volumetric determination of the picric acid, the water was made slightly alkaline and again distilled by means of a special conductivity water still and this redistilled water, which was neutral, was used in the analytical work.

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(1) Zeitscrift der Physikalische Chemie, 46, 827.

(2) " " " " 46, 827.

(3) " " " " 46, 827.

(4) Masters thesis, California Institute of Technology, 1919.

Benzene: Ordinary commercial benzene was the source of that used in the distribution experiments. Portions of about 300cc. each were shaken with successive portions of C.P. concentrated sulfuric acid until the acid no longer turned straw colored. The benzene was then shaken with water to remove the excess acid and finally washed with a dilute solution of sodium carbonate and again washed with water until the washings were no longer alkaline to phenolphthalein. If the isatin test (Technical Methods and Chemical Analysis, Lunge, Vol. II, Part II, pg. 797.) showed the benzene to be now free of thiophene, it was allowed to stand so that the remainder of the water could settle out and was then shaken with powdered quick lime in a large distilling flask to remove the remainder of the water. The benzene was next distilled off and the first distillate redistilled. The resulting distillate was finally frozen twice in small glass stoppered conical flasks placed in a salt-ice mixture. When most of the liquid had solidified, the remaining unfrozen benzene, which contained any impurities, was poured off and the solid benzene allowed to melt.

The benzene that had been used in the various experiments was saved and both the picric acid and the benzene recovered. This benzene had been purified and was therefore free from thiophene, the only impurities were picric acid and its salts. It was first shaken with water to remove most of the picrate present and then washed with a dilute solution of sodium carbonate to remove the remainder of the acid. The benzene was next washed thoroughly with water to remove all traces of the sodium and barium picrates.

The washed benzene was allowed to stand some hours in order to allow the water to settle out and then distilled from calcium oxide and the distillate added to the purified stock benzene. The first aqueous washings of the benzene containing the larger amounts of barium and sodium picrates were saved for the picric acid recovery.

Picric Acid: The general outline of the process employed to purify the picric acid was to partially neutralize a known amount of the acid by means of an aqueous solution of sodium carbonate, separate the sodium picrate, wash and then partially neutralize the picrate with hydrochloric acid, separate the solution from the remaining salt and collect the picric acid by crystallization and purify by recrystallization. 100 grams of the acid are neutralized by 46.4 grams of sodium carbonate and the carbonate neutralized by 262 cc. of 6. N.hydrochloric acid. Slightly smaller amounts of both the carbonate and the hydrochloric acid were used. About 50 grams of picric acid was dissolved in 600 cc. of boiling water and the carbonate added slowly in the form of a hot concentrated aqueous solution. The sodium salt of the picric acid is precipitated immediately in the presence of the carbonate. (1) The salt forms a very bulky precipitate in even a large volume of solution. On standing a short time the precipitate becomes hard and a thick pasty mass which is somewhat difficult to filter, forms in the solution. The solution was therefore

(1) Dictionary of Applied Chemistry, Thorpe, IV,265.
Also Jour. Chem. Soc., 1904, II, 517.

filtered, while still hot, thru a Beuchner funnel and the solid washed with hot water. The sodium salt is fairly soluble in pure water. (1) Therefore the washings were saved and when a sufficient amount was collected they were concentrated, acidified and the picric acid crystallized out, washed and saved to be run thru the recovery process.

Knowing the amount of sodium carbonate used in the precipitation and the volume of the solution at the time of the precipitation, the amount dissolved was calculated. The amount lost in the washings was also taken into account. The washed picrate was removed from the funnel with a large spatula and dissolved in boiling water and slightly less than the calculated amount of hydrochloric acid added to the solution and the solution allowed to cool. The remaining picrate which crystallizes out is filtered off, an excess of hydrochloric acid added to the filtrate and the solution concentrated down until the acid begins to crystallize out of the hot solution and the solution allowed to cool. The solid acid from the cold solution was filtered thru a small Beuchner funnel. In case the purification was made from the original stock and not from the recovered product, this precipitate was then dissolved, reconcentrated, and recrystallized. The final picric acid crystals were then washed with cold water and dried by placing it in a small suction flask immersed in a hot water bath and allowing a slow current of dry air to pass over the solid. The final dried acid was then crystallized from purified benzene, dried, powdered and mixed. This material was employed in the preparation of the solutions in the distribution experiments.

(1)

Solubility per liter at 25°C.	Solution
42.5 gms.	0.0 N Na_2CO_3
6.0	0.01
3.2	0.1
4.1	1.0

Solubility of Chemical Compounds, Siedell, p.664.

It is evident that in these various steps of purification quite a large amount of acid was lost, the yield was about 33%. However, all washings were saved for recovery. If this purification process had been repeated from time to time, using the same recovered acid and salts from the soluble portions, the impurities would tend to collect and concentrate to such an extent that the recovery process would be a detriment. A sufficiently large amount of acid was prepared in the beginning so that the recovered salt was only used once in the entire series of experiments. It would not be possible in one or two recoveries, where only a small amount of recovered salt was added to a large amount of the original stock purified acid, to introduce any impurities which might have been collected by this practice.

Preparation of Solutions

The barium hydroxide solution was prepared by the usual methods (1) from Bakers C.P. product and was standardized against Kahlbaum's "Zur Analysis" Oxalic Acid. It was also standardized against hydrochloric acid and the two methods were found to check very well. (0.09863 with HCl and 0.09867 with $(COOH)_2$).

The hydrochloric acid solution was prepared from Bakers C.P. Acid, (1.187 Sp. Gr.) and carbon dioxide free distilled water. It was standardized by precipitation as silver chloride.

The sodium chloride solutions were made from Bakers C.P. chemical. Solutions of this salt were made up by weight.

(1) Analytical Chemistry, Treadwell and Hall, Vol. II, pg 557.

Analytical Methods.

Rothmund and Druker found that the alklimetris volumetric method, using barium hydroxide solution with phenolphthalein as an indicator, was satisfactory. "In the benzene phase the hydroxide can be used if one is careful to agitate the mixture during the titration." (1) Kunster states that he used barium hydroxide as an alkali and lakmoid as an indicator. (2) Best also reports the use of lakmoid and barium hydroxide. (3)

In the preliminary tests of the present investigation, the color change was found to be satisfactory when phenolphthalein and barium hydroxide were employed. The end-point was quite delicate. The change from the light yellow color of the acqueous picric acid to the pinkish yellow color of the neutral solution could, under ordinary conditions, be checked with an accuracy of one tenth of one per cent. In the determination of the acidity of the benzene phase, a small portion of distilled, carbon dioxide free water was introduced and then the base added with constant agitation until the mixture was distinctly basic, thereby removing all of the acid from the benzene. The excess base was then neutralized with standard acid and the end point determined in the usual manner.

The solutions to which the sodium chloride had been added were analyzed for picric acid in the same manner as the pure water solutions. However, the analysis of the picric acid solutions which contained added hydrogen chloride was carried out by two methods. First, the picric acid

(1) Zeitscrift der Phylikalische Chemie, 46, 827.
(2) Berichte der Deutsche Chemischen Gesselschaft, 27, 1102, 1894. also Chem. Zeitg., 1888, Rep. 210. and Analyse und Konstitutionsermittelung Organische Verbindindinger, II auflage, 575.
(3) H. Meyer Chemie, 950.

content was determined by subtracting from the total acid concentration, that of the original solution of hydrogen chloride to which the picric acid had been added. This method was evidently unreliable in those cases where the picric acid concentration was small compared with the total acidity. Hence a gravimetric method which consisted essentially in evaporating a known volume of the acid mixture to dryness, and weighing the residual solid picric acid, was also used. As picric acid is slightly volatile under certain conditions of evaporation, experiments were conducted for the purpose of studying this effect. It was found that a distinct loss due to sublimation occurred when the nearly dried acid was heated about 60°C. in an electrically heated vacuum dessicator. When the dessicators were placed under a strong vacuum, the evaporation of water was very rapid at first, but the moisture collected on the top of the apparatus and fell back into the evaporating dishes, thus introducing a possibility of contamination. To overcome this difficulty, the top of the dessicator was left slightly open and just sufficient vacuum to cause a slow current of air thru the apparatus, was employed. In further tests it was found that the most satisfactory results were secured when the solutions were kept at a temperature of about 45°C. The water was removed until the acid appeared to be dry and then the top was closed completely and a strong vacuum applied for a few moments to insure complete dehydration. The temperature was not raised during this final evacuation. All of the determinations on the stronger acid solutions were carried out in this manner. Any error due to the change from the volumetric method of the analysis to the gravimetric method was assumed to be less than the general limit of error involved in the other manipulations.

Apparatus.

All of the volumetric apparatus employed had been carefully standardized. On account of the difference in density and surface tension between benzene and water, the pipettes used to measure the benzene were re-standardized, using this liquid. The benzene was warmed in a thermostat to the temperature at which the distribution determinations were to be made and then pipetted out in tared weighing bottles. The drop in temperature during the pipetting was noted and from the weight of the delivery and the specific gravity of the liquid at that temperature, the volume delivery was calculated. The variation in the results between the water and benzene delivery is shown in the following table.

Pipette used	Time of delivery	Volume of Benzene delivered
10.00 cc.	61. sec.	9.97 cc.
25.00 cc.	65. sec.	24.91 cc.
50.00 cc.	36. sec.	49.82 cc.
Specific gravity of benzene at 25°C.		0.8765

The presence of picric acid in the benzene does not affect the pipette delivery. Care had to be taken to remove all moisture from the benzene pipettes, and therefore separate sets of pipettes were used for benzene and water solutions respectively.

The benzene was separated from the water layer by means of an automatic pipetting apparatus. The sample bottle was removed from the thermostat and placed in a small bath containing water at the same temperature as that of the thermostat. The pipette, held by a burette clamp mounted on a large ringstand, was carefully lowered into the benzene layer until the opening of the pipette was slightly above the surface of the water layer. The top of the pipette was connected to the suction thru a wash bottle, which had an outlet stopcock to adjust the vacuum. With the pipette clamped in this position, a gentle suction was applied and the benzene drawn slightly above the graduation mark. The liquid level was then lowered to the mark by means of the thumb. By using a stationary pipette, in this manner, the level can be watched very carefully and the suction controlled with very little trouble. After some practice the pipetting could be run faster than by ordinary method and with a very small waste of benzene. The following figures, for the benzene phase, illustrate the efficiency of the apparatus. The solutions were drawn from an ordinary narrow mouthed, glass stoppered, 750 cc. bottle.

Volume of sample	Number of sample	Volume drawn off	Volume in flask	Waste
10.00 cc.	2	20.00 cc.	35. cc.	15. cc.
25.00	2	50.00	70.0	20.
50.00	2	100.00	115.	15.
150.00	2	300.00	350.	50. (1)

In drawing off the accqueous solution, not as much care had to be taken and the special apparatus was not employed. The benzene layer was drawn off first leaving only a thin layer of the upper phase. As the pipette was lowered thru this phase, a gentle current of air was blown thru it in order to prevent any benzene from entering the pipette. After removing the pipette all of the benzene was wiped from the outside of it before placing it over the titration flask.

(1) Used a liter bottle having a greater diameter than the 750 cc. bottle.

Preliminary Experiments.

Preliminary experiments were conducted in order to determine the time necessary for equilibrium conditions to be reached and the effect of the change in temperature upon the distribution. The length of the time required for the system to come to equilibrium was first determined. In order to run the sample under as nearly the same conditions as possible, one large amount of the liquid sample was made up. This was divided into two portions to be used in the four tests, and the acid was added to each at the same time. All of the solid was dissolved by agitation before the bottle was placed in the bath. At the time of this test it was not known whether continuous shaking in the thermostat would be necessary or not, but the first trials were run without this. The samples were taken and well agitated every half hour for about four hours, the first short period samples were then pipetted out and the remainder replaced for the longer period treatment. The second samples were taken from each bottle after it had remained in the bath about twenty four hours. The average results of these tests are given in the following table:

Time in Thermostat	C	Z/C
3 hours	0.02343 M./L.	3.69
27	0.02324	3.67

These experiments indicate that, with several preliminary agitations, equilibrium conditions could be reached within twenty four hours with a solution of moderate concentration (0.03 M/L. in Z. and 0.1 M/L. in C.)

and with special precautions, a time slightly greater than that for the concentrated solutions. These conditions were observed in all subsequent experiments. With the concentrated solutions the solid acid was added to the bottle containing the two phases and the solution placed in a special bath at about 45°C. and the solution shaken at frequent intervals until as complete a saturation as possible could be obtained at that temperature. The warm bottles were placed in the thermostat and allowed to cool down to the required temperature. In this way it was thought that the equilibrium conditions would be reached easier than by trying to get saturation at the same temperature as the equilibrium was attained. To prevent supersaturation in the saturated solutions, an excess of solid was kept in the bottle even at the higher bath temperatures.

In order to determine the effect of temperature on the distribution, a series of four tests were run at 20° and 25°, but difficulty was encountered with the relay on the thermostat and the results were not sufficiently accurate to form any definite conclusions. They did show, however, that the distribution ratio is effected by a change in temperature. Upon repeating these experiments, distribution ratios of 3.69 and 3.59 were obtained for the temperature 20° and 25° respectively. As it was easily possible to control the bath within a half of a degree without special precautions, and within a tenth of a degree rather readily, it was concluded that for dependable results the temperature would be held as near one value as possible. The standard temperature of 25°C. ± 0.2° was employed thruout the subsequent experiments.

Experimental Results.

The results of the distribution experiments are given in some detail in Table 1. This is divided into sections, which refer to the amounts of added sodium chloride or hydrogen chloride in the acqueous layer. The first column gives the volume in cc.'s of the sample used for analysis. The following three columns give data regarding the analysis of the acqueous layer; the second and third, the results in moles of picric acid per liter (c.) of duplicate analysis, and the fourth, the mean value of these. The remaining four columns give data for the benzene phase. As it has been explained in the preceding section, the picric acid concentration of many of the solutions containing hydrochloric acid was determined both volumetrically and gravimetrically. In such cases both sets of data are given, that determined gravimetrically being indicated by placing the letter G after the numerical result.

The detailed data presented in Table I are summarized and compared in Table II. The first column gives the concentrations of solutions used; the second, the mean value of the concentration of the picric acid in the acqueous layer (C); the third, the mean value of the benzene phase (Z.); the fourth, the distribution ratio Z/C calculated from the analytical results. Values of the distribution ratio were, for each series of experiments, plotted against those of the concentration in the water layer, and the most representative curves drawn. Values interpolated from the curves are given in the fifth column and the percentage differences between the observed and interpolated values in the last column. From the same curves, values of the distribution ratios were, in the case of each series, read off for round values of the concentration of the picric acid in the water layer. The results of these interpolations are given in Table III.

TABLE I

Data Sheet # 1

ORIGINAL DATA:

Distribution and Analytical Data Concerning :

The Water (C) and Benzene (Z) Phases.

Vol. C. Sample used for Analysis	Analysis 1st C Sample	Analysis 2nd C sample	Mean of 1st and 2nd samples	Vol. Z. sample used for analysis	Analysis 1st Z sample	Analysis 2nd Z sample	Mean of 1st and 2nd samples	Distribution Ratio Z / C
cc's	In moles of picric acid /L.			cc's	In moles of picric acid /L.			Z / C
200.	0.004992	0.005006	0.004999	150.	0.004900	0.004935	0.004917	0.985
100.	0.0110	0.01106	0.01103	50.	0.02030	0.02178	0.02190	1.98
100.	0.01074	0.01079	0.01076	50.	0.02168	0.02180	0.02174	2.02
150.	0.01945	0.01939	0.01942	25.	0.06256	0.06205	0.06230	3.12
150.	0.01937	0.02009	0.01973	50.	0.06220	0.06210	0.06215	3.15
100.	0.02850	0.02848	0.02849	25.	0.1253	0.1251	0.1252	4.40
100.	0.0297	0.02828	0.02878	25.	0.1303	0.1308	0.1305	4.54
50.	0.0470	0.04055	0.04062	10	0.2356	0.2357	0.2356	5.81
50.	0.05037	0.05014	0.05027	10	0.3539	0.3472	0.3505	6.91
100.	0.05364	0.05374	0.05369	25.	0.3935	0.3931	0.3933	7.34
The 0.005 N. Sodium Chloride Solution and Benzene Phases.								
200.	0.005250	0.005215	0.005210	150.	0.005154	--	0.005154	0.991
100.	0.01550	0.01570	0.01560	50.	0.04009	0.03987	0.03999	2.56
100.	0.01998	0.01983	0.01990	25.	0.06327	0.06327	0.06327	3.18
100.	0.02852	--	0.02852	25.	0.1219	0.1226	0.1222	4.30
50.	0.04851	0.04851	0.04851	10.	0.3244	0.3242	0.3243	6.69

TABLE I - continued.

Data Sheet # 2.

The 0.01 N. Sodium Chloride and Benzene Phases.

200.	0.006996	0.007023	0.007009	150.	0.008236	0.008290	0.008263	1.18
100.	0.01422	0.01426	0.01424	50.	0.03145	0.03149	0.03147	2.21
100.	0.01126	0.01130	0.01128	25.	0.02785	0.02789	0.02787	2.48
150.	0.01925	0.01937	0.01931	50.	0.06087	0.06087	0.06087	3.15
50.	0.03789	0.03774	0.03781	25.	0.1913	0.1914	0.1914	5.09
150.	0.01517	0.01518	0.01517	25.	0.08214	0.08228	0.08221	5.41
50.	0.05220	0.05221	0.05220	10.	0.3581	0.3582	0.3582	6.85

The 0.05 N. Sodium Chloride Solution and Benzene Phases.

200.	0.005141	--	0.005141	150.	0.003589	0.004139	0.003864	0.752
100.	0.01033	0.01034	0.01033	50.	0.01703	0.01689	0.01694	1.64
150.	0.01408	0.01408	0.01408	50.	0.03134	0.03122	0.03128	2.22
150.	0.02147	0.02151	0.02149	25.	0.06770	0.06752	0.06761	3.15
100.	0.02833	0.02835	0.02834	25.	0.1081	0.1092	0.1086	3.82
50.	0.03954	0.03970	0.03962	10.	0.2082	0.2084	0.2083	5.26
50.	0.05143	0.05133	0.05137	10.	0.3400	0.3405	0.3402	6.62
50.	0.05151	0.05153	0.05142	10.	0.3471	--	0.3471	6.76

TABLE I - continued

Data Sheet #3.

The 0.1 N. Sodium Chloride Solution and Benzene Phases.

200.	0.004892	0.004882	0.004887	150.	0.003518	0.002384	0.002951	0.603
100.	0.009313	0.009295	0.009304	50.	0.01287	--	0.01287	1.38
150.	0.01382	0.01382	0.01382	50.	0.02816	0.02803	0.02809	2.08
150.	0.01970	--	0.01970	25.	0.05502	0.05505	0.05503	2.80
150.	0.02804	0.02804	0.02804	25.	0.1038	0.1039	0.1039	3.70
50.	0.03466	0.03473	0.03470	25.	0.1543	0.1553	0.1548	4.46
150.	0.03907	0.03907	0.03907	25.	0.1924	0.1926	0.1925	4.85
50.	0.04838	0.04824	0.04831	10.	0.2855	--	0.2855	5.97
50.	0.04964	0.04966	0.04965	10.	0.3021	0.3026	0.3023	6.09

The 0.2 N. Sodium Chloride Solution and Benzene Phases.

150.	0.005155	0.005159	0.005157	150.	0.003522	0.003498	0.003510	0.68
100.	0.01021	0.01020	0.01021	50.	0.01374	0.01415	0.01394	1.37
150.	0.01434	0.01436	0.01435	50.	0.02673	0.02667	0.02670	1.86
150.	0.01936	--	0.01936	25.	0.04668	0.04460	0.04668	2.41
150.	0.02558	0.02560	0.02559	25.	0.07768	0.07761	0.07765	3.03
50.	0.04180	0.04201	0.04190	25.	0.2005	0.2004	0.2002	4.78
50.	0.05895	0.05893	0.05894	10.	0.3775	0.3770	0.3772	6.40

TABLE I - continued

Data Sheet #4.

The 0.005032 N. Hydrochloric Acid Solutions and Benzene Phases.

100.	0.002277	--	0.002277	100.	0.002204	--	0.002204	0.967
100.	0.008877	--	0.008877	50.	0.02356	--	0.02356	2.68
150.	0.01405	0.01407	0.01406	50.	0.04952	0.04958	0.04948	3.52
150.	0.01817	--	0.01817	25.	0.07454	0.07432	0.07443	4.09
100.	0.02650	0.02649	0.02648	25.	0.1367	0.1371	0.1369	5.17
50.	0.03830	0.03831	0.03831	10.	0.2546	0.2568	0.2557	6.77
50.	0.04881	0.04883	0.04882	10.	0.3854	0.3859	0.3857	7.89

The 0.01509 N. Hydrochloric Acid Solutions and Benzene Phases.

150.	0.00570	0.00574	0.00572	50.	0.01474	0.01474	0.01474	2.58
50.	0.01320	0.01320	0.01320	50.	0.06712	0.06710	0.06711	5.08
50.	0.01776	--	0.01776	25.	0.09992	--	0.09992	5.64
50.	0.01941	--	0.01941	25.	0.1135	0.1135	0.1135	5.85
50.	0.02702	0.02718	0.02710	10.	0.1855	0.1853	0.1854	6.84

The 0.05032 N. Hydrochloric Acid Solution and Benzene Phases.

100.	0.00598	0.00603	0.00600	50.	0.02054	0.02034	0.02044	3.42
50.	0.01486	0.01480	0.01483				(0.02044)	7.39 G
25.	0.01479	--	0.01479	10.	0.1093	0.1097	0.1095	7.40
25.	0.01461	--	0.01461	10.	0.1080	0.1082	0.1081	7.40
50.	0.01451	0.01450	0.01451				(0.1081)	7.46 G
10.	0.02101	--	0.02101	10.	0.1969	0.2051	0.2009	9.52
50.	0.02098	0.02084	0.02091				(0.2009)	9.58 G
10.	0.03492	--	0.03492	10.	0.4827	0.4833	0.4830	13.8
25.	0.03477	0.03490	0.03486				(0.4830)	13.9 G

TABLE I - continued

Data Sheet #5.

The 0.05032 N. Hydrochloric Acid Solution and Benzene Phases. (Cont.)

10.	0.03544	--	0.03544	10.	0.4955	0.4956	0.4956	14.0
25.	0.03535	--	0.03535				(0.4956)	14.1 G

The 0.1006 N. Hydrochloric Acid Solution and Benzene Phases.

50.	0.0016	--	0.0016	50.	0.002823	--	0.002823	1.77
50.	0.0013	0.0017	0.0016				(0.002823)	1.77 G
50.	0.0067	--	0.0067	50.	0.05699	0.05507	0.05603	8.36
50.	0.0058	0.0061	0.0060				(0.05603)	8.35 G
10.	0.0180	--	0.0180	10.	0.3519	--	0.3519	19.5
50.	0.0186	--	0.0186				(0.3519)	18.9 G
10.	0.03130	--	0.0313	10.	0.9257	--	0.9257	29.6
50.	0.03140	--	0.03140				(0.9257)	29.4 G

The 0.2012 N. Hydrochloric Acid Solution and Benzene Phases.

25.	0.00191	--	0.00191	50.	0.008385	0.007994	0.008189	4.31
50.	0.0021	0.0017	0.0019				(0.008189)	4.2 G
10.	0.0032	--	0.0032	25.	0.01820	--	0.01820	5.69
50.	0.0032	--	0.0032				(0.01820)	5.7 G
10.	0.0055	--	0.0055	25.	0.06654	--	0.06654	13.1
25.	0.0049	0.0060	0.0050				(0.06654)	13.0 G
10.	0.0074	--	0.0074	25.	0.1245	0.1245	0.1245	16.8
50.	0.0074	--	0.0074				(0.1245)	16.8 G
10.	0.0090	--	0.0090	10.	0.2292	0.2300	0.2296	25.5
50.	0.0091	--	0.0091				(0.2296)	25.2 G
10.	0.0083	--	0.0083	10.	0.3555	--	0.3555	42.5 (?)
50.	0.0090	0.0083	0.0087				(0.3555)	40.9 G (?)

TABLE II

Data Sheet #6

DISTRIBUTION RATIOS :

Solution	Concentration C M / L	Concentration Z M / L	Z / C Found	Z / C Interpolated	Percentage Difference
C and Z	0.004999	0.004917	0.983	0.995	1.0
	0.01103	0.02190	1.98	1.91	1.7
	0.01076	0.02174	2.02	1.88	6.2
	0.01942	0.06230	3.12	3.12	0.0
	0.01973	0.06215	3.15	3.14	0.1
	0.02849	0.1252	4.40	4.38	0.2
	0.02878	0.1303	4.54	4.35	2.1
	0.03242	0.1548	4.78	4.78	0.0
	0.04062	0.2356	5.81	5.81	0.0
	0.05027	0.3505	6.96	6.96	0.0
	0.05369	0.3933	7.34	7.34	0.0
0.005 N NaCl and Z	0.005210	0.005154	0.991	0.988	1.6
	0.01560	0.03999	2.56	2.56	0.0
	0.01990	0.06327	3.18	3.14	0.6
	0.02852	0.1219	4.30	4.24	0.7
	0.04851	0.3243	6.69	6.69	0.0

TABLE II - continued

Data Sheet #7

0.01 N.	0.007009	0.008263	1.18	1.16	0.9
NaCl	0.01424	0.03147	2.21	2.19	0.8
and	0.03781	0.1914	5.09	5.09	0.0
Z	0.05220	0.3562	6.85	6.89	0.0
0.05 N.	0.005141	0.003864	0.752	0.760	5.0
NaCl	0.01033	0.01694	1.64	1.60	1.8
and	0.01408	0.03128	2.22	2.14	1.8
Z	0.02149	0.06761	3.15	3.10	2.7
	0.02834	0.1086	3.82	3.87	0.6
	0.03962	0.2083	5.26	5.16	0.9
	0.05137	0.3402	6.62	6.71	0.6
	0.05142	0.3471	6.76	6.70	0.4
0.1 N.	0.004887	0.003518	0.60	0.72	8.4
NaCl	0.009304	0.01287	1.38	1.36	0.8
and	0.01382	0.02809	2.08	2.08	0.0
Z	0.01970	0.05503	2.80	2.71	1.9
	0.02804	0.1039	3.70	3.70	0.0
	0.03470	0.1548	4.46	4.46	0.0
	0.03907	0.1925	4.85	4.90	1.0
	0.04965	0.3025	6.09	6.09	0.0

TABLE II - continued

Data Sheet #8

0.2 N.	0.005157	0.005310	0.68	0.68	0.0
NaCl	0.01021	0.01394	1.37	1.27	3.8
and	0.1435	0.02670	1.86	1.84	0.5
Z	0.01936	0.04668	2.41	2.41	0.0
	0.02559	0.07765	3.03	3.10	1.1
	0.04190	0.2002	4.78	4.78	0.0
	0.05894	0.3772	6.40	6.45	0.4
0.005032 N.	0.002277	0.002204	0.967	0.990	2.8
HCl	0.008877	0.02356	2.68	2.60	3.0
and Z.	0.01406	0.04948	3.52	3.52	0.0
	0.01817	0.07443	4.09	4.14	1.2
	0.02648	0.1369	5.17	5.27	1.9
	0.03831	0.2557	6.77	6.77	0.0
	0.04882	0.3857	7.89	7.92	0.5
0.01509 N.	0.00572	0.01474	2.58	2.66	3.0
HCl	0.01320	0.06711	5.08	5.00	1.6
and Z.	0.01776	0.09992	5.64	5.71	1.2
	0.01941	0.1135	5.85	5.98	2.1
	0.02710	0.1854	6.84	6.91	1.0

TABLE II - continued

Data Sheet #9

0.05032 N.	0.00600	0.02044	3.42	3.41	0.3
HCl	0.01461	0.1081	7.40	7.32	1.0
and	0.01479	0.1095	7.40	7.40	0.0
Z.	0.02101	0.2009	9.52	9.52	0.0
	0.03492	0.4830	13.8	13.8	0.0
	0.03544	0.4956	14.0	14.0	0.0
0.1006 N.	0.0016	0.002823	1.77	2.0	10.0
HCl	0.0067	0.05603	8.36	8.12	3.0
and	0.0180	0.3519	19.5	19.5	0.0
Z	0.0313	0.9257	29.6	29.6	0.0
0.2012 N.	0.00191	0.008189	4.31	3.70	8.0
HCl	0.0032	0.01820	5.69	5.87	1.1
and	0.0055	0.06654	12.1	11.5	5.0
Z	0.0074	0.1245	16.8	16.8	0.0
	0.0090	0.2296	25.5	25.5	0.0
	0.0083	0.35555	42.5 (?)	42.5	0.0

TABLE III

Data Sheet #10

SUMMARY OF DISTRIBUTION RATIOS :

Concentration picric acid in C., M / L	Concentration of added salt in moles per liter					
	0.000	0.005	0.015	0.050	0.100	0.200
0.005	0.95	0.90	0.84	0.79	0.74	0.60
0.010	1.77	1.72	1.64	1.55	1.46	1.30
0.015	2.50	2.45	2.31	2.24	2.13	1.90
0.020	3.20	3.13	2.97	2.89	2.75	2.48
0.030	4.49	4.41	4.19	4.06	3.91	3.57
0.040	5.70	5.64	5.39	5.19	5.03	4.60
0.050	6.90	6.84	6.55	6.30	6.10	5.60
	Concentration of added acid. (HCl)					
	0.000	0.005032	0.01509	0.05032	0.1006	0.2012
0.005	0.95	1.70	2.33	2.85	6.05	9.91
0.010	1.77	2.83	4.21	5.35	11.75	--
0.015	2.50	3.70	5.31	7.44	16.80	--
0.020	3.20	4.42	6.06	9.29	21.14	--
0.030	4.49	5.75	7.30	12.36	28.65	--
0.040	5.70	6.97	--	15.26	--	--
0.050	6.90	8.10	--	--	--	--

The results of the experiments with picric acid may be readily compared with those relating to the effect of added salts upon the solubility of slightly soluble salts. In the latter case the activity of the salt is maintained constant at that determined by the solubility of the salt, while in the case of the picric acid solutions, the activity is varied and may be calculated from the concentration in the benzene phase. However by interpolation methods it is possible to compute for various concentrations of added salt, the concentration of picric acid in equilibrium with a definite concentration in the benzene phase, i.e. corresponding to a fixed activity value. Thallous chloride which has been extensively investigated, (1) was chosen as the salt with which to compare picric acid. At 25° C. the solubility of this salt in water is 0.0161 moles per liter. From the distribution curve for picric acid, it was determined that a 0.0428 molal solution of picric acid in benzene is in equilibrium with a 0.0161 molal aqueous solution. Hence from the various curves for different concentrations of added salt, there were found by interpolation the concentrations of picric acid in the water phase which are in equilibrium with a 0.0428 molal solution in benzene. The values thus obtained for solutions of constant activity for both picric acid and thallous chloride are given in Table IV, and are shown graphically in curve No. 1 . It will be readily seen from the latter that the effect of added salts, both those with and those without a common ion, is qualitatively the same for the two cases, tho the agreement is not quantitative. The results of this investigation are hence in

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(1) Noyes and Bray, J. Am. Chem. Soc. 33, 1639. (1910) +

substantial agreement with the conclusions drawn from the work on thallous chloride; the most important of these is that the activity-concentration ratio of a strong electrolyte is largely determined by the total salt or total ion concentration.

(Signed) [illegible] E. Hill.

California Institute of Technology,
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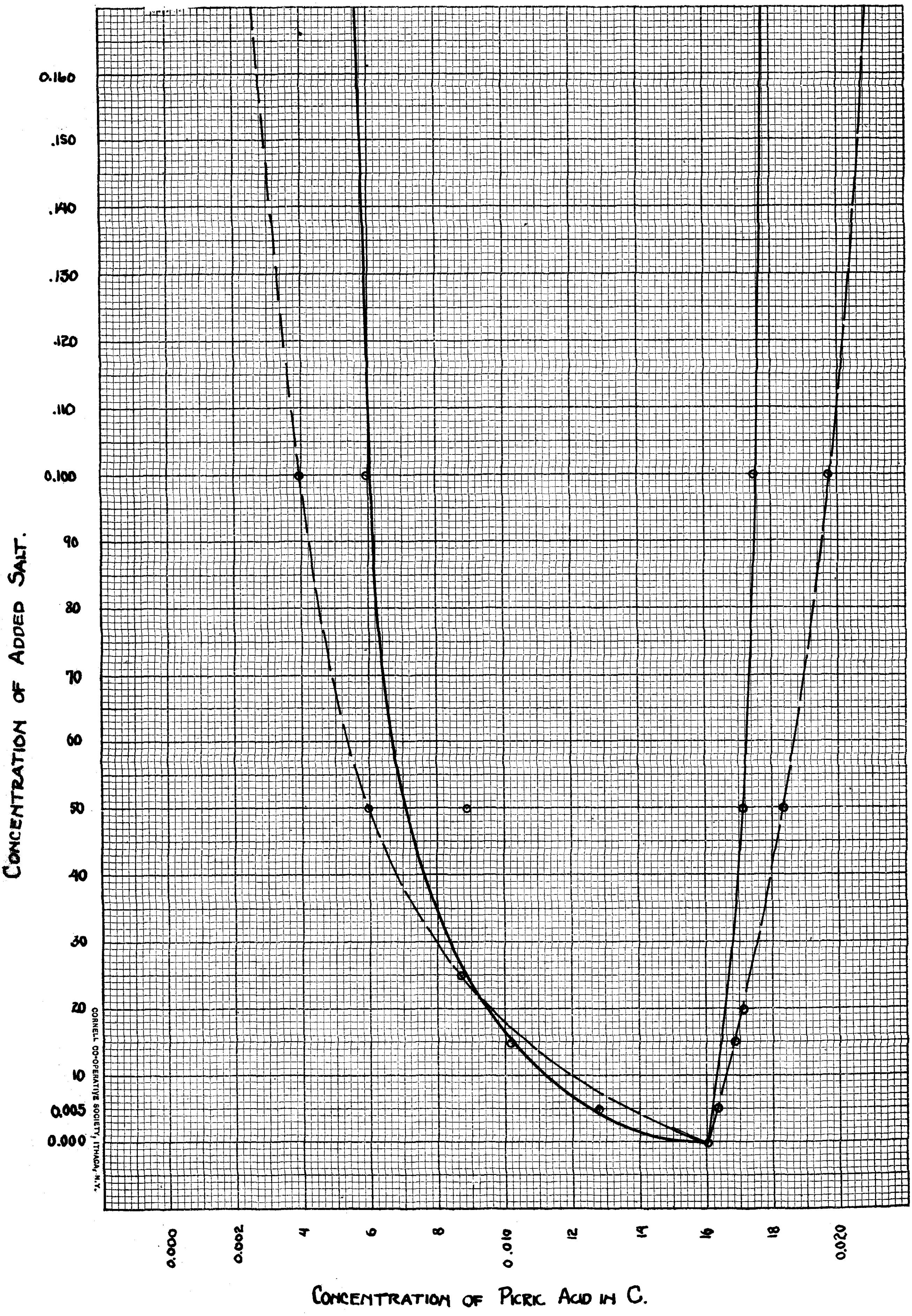
TABLE IV

Data Sheet #11

GENERAL DATA ACCOMPANYING DISCUSSION ON PAGES 24 and 25 :

Concentration of Solution	Z / C Found	Conc. of C. Calculated.
0.0 M / L NaCl	2.66	0.01610
0.005	2.62	0.01630
0.015	2.55	0.01680
0.050	2.51	0.01705
0.100	2.45	0.0175
0.200	2.31	0.0186
0.0 M / L HCl	2.66	0.01610
0.005	3.35	0.01275
0.015	4.25	0.01010
0.050	4.82	0.00886
0.100	7.16	0.00595
0.200	9.00	0.00495

Concentration of added salt	Conc. TlCl in KCl	Conc. TlCl in KNO_3
0.000 M / L	0.01607 M / L	0.01607 M / L
0.020	--	0.01716
0.025	0.00869	--
0.050	0.00590	0.01826
0.100	0.00396	0.01961
0.200	0.00268	--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.150
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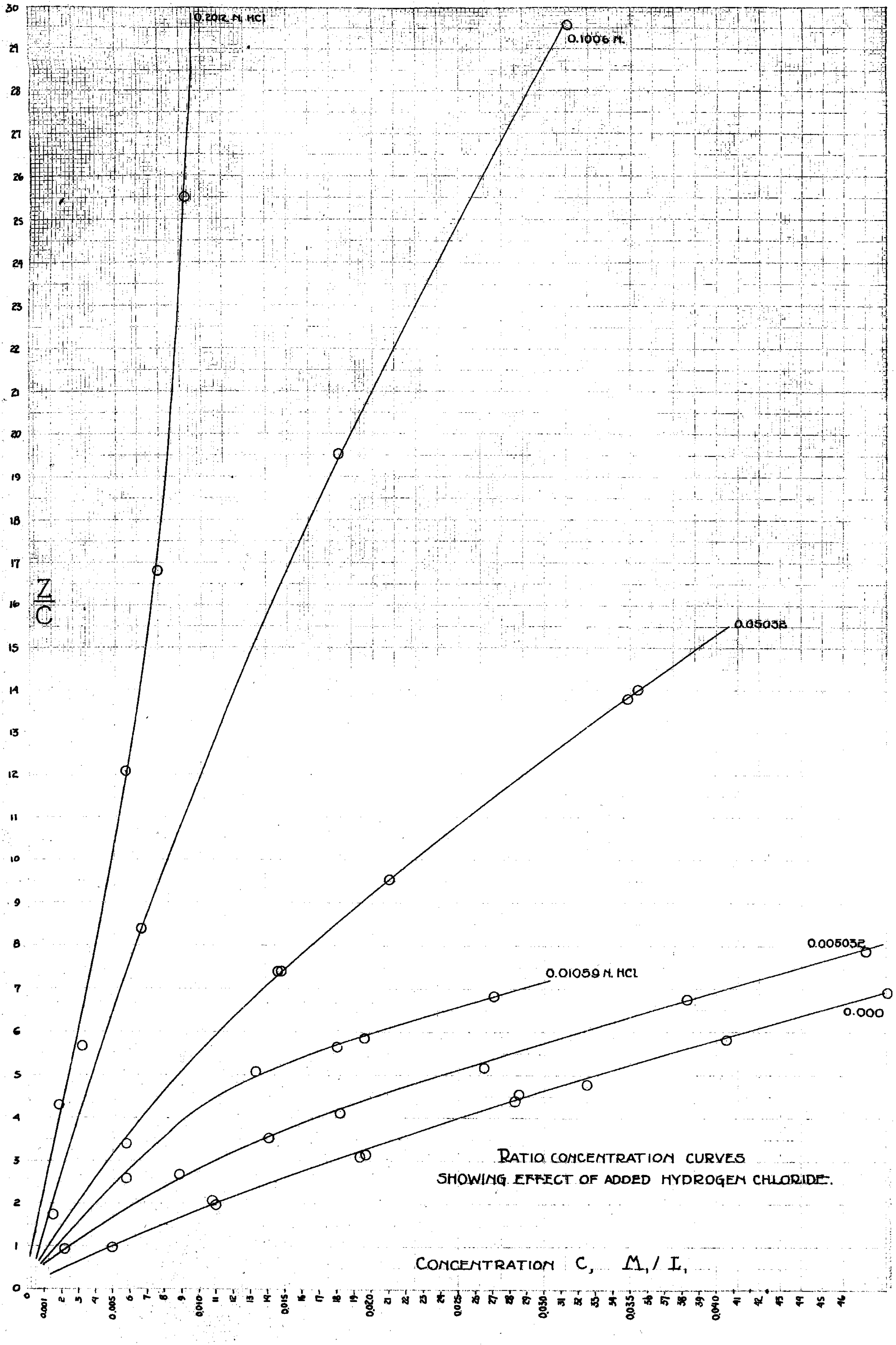
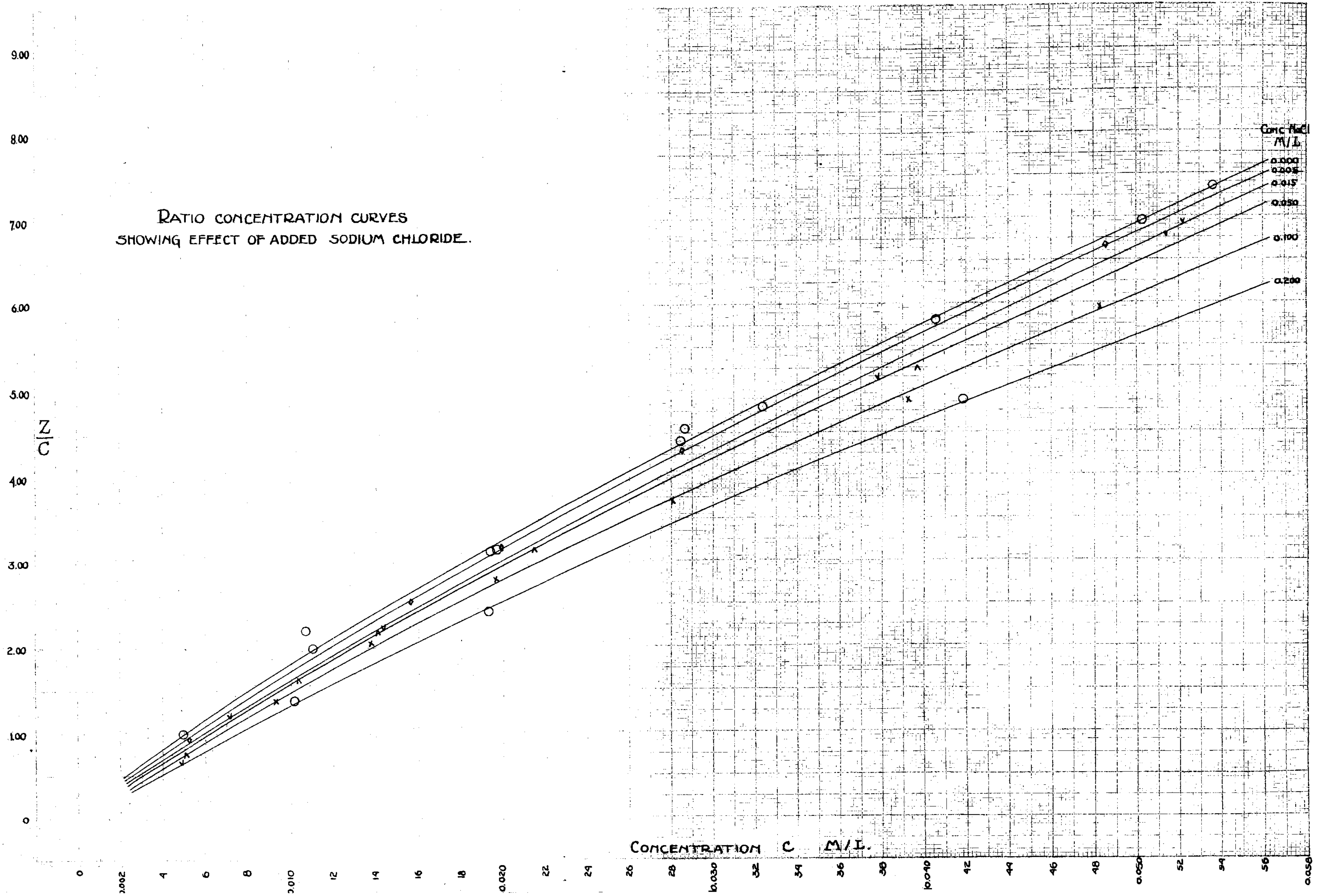
.130
.120
.110
0.100
90
80
70
60
50
40
30
20
10
0.005
0.000
Concentration of Added Salt.
0.000
0.002
4
6
8
0.010
12
14
16
18
0.020
Concentration of Picric Acid in C.



RATIO CONCENTRATION CURVES
SHOWING EFFECT OF ADDED HYDROGEN CHLORIDE.



RATIO CONCENTRATION CURVES
SHOWING EFFECT OF ADDED SODIUM CHLORIDE.