

THE SOLUBILITY OF IODINE IN AQUEOUS SALT SOLUTIONS.

A THESIS

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THE SOLUBILITY OF IODINE IN AQUEOUS SALT SOLUTIONS.

HISTORICAL

Many investigators have found that the solubility of non-electrolytes in water is lowered by the addition of electrolytes, and various empirical or semi-empirical equations have been suggested to show the relation between the change in the solubility and the concentration of the electrolyte. In most of the earlier work, this latter concentration rarely exceeded one gram-equivalent per liter, and over this range the solubility lowering is approximately proportional to the concentration of the electrolyte.

According to Carter

Jour. Chem. Soc. 127. 2861 (1925)

experiments in which the electrolyte concentration was varied over a wider range, show, however, that this proportionality by no means holds.

A survey of the literature shows that many attempts have been made to study the effect of salts on the solubility of neutral substances.

Setschenow,

Z. phys. Chem. 4. 117 (1889)

as early as 1889, in working with carbon dioxide, succeeded in distinguishing between the chemical influence due to a partial displacement of salts of weak acids by carbon dioxide, and the physical change in absorption in case of salts of

strong acids. He set up the following formula for the influence of the salts on the solubility of carbon dioxide

$$y = y_0 e^{-\frac{k}{x}}$$

where y and y_0 are the absorption coefficients in salt solution and pure water respectively, e is the base of natural logarithms, x is the volume of the solution, and k is a constant. The expression is practically identical with the more familiar form in use today:

$$-\log \frac{S}{S_0} = k c$$

Euler

Z. phys. Chem. 31, 360 (1889)

concluded that the salting-out effect (that is, the decrease in the solubility of a substance to whose saturated solution a salt has been added) is greater the more soluble the substance originally. He advanced the theory that this salting-out effect was caused by an increased internal pressure of the solvent.

Rothmund

Z. phys. Chem. 33, 401 (1900)

made an extensive study of the effects of salts on the solubility of phenyl thiourea. He concluded that the anion of the salt has by far the greater effect upon the solubility. His results seem to indicate that the salting-out effect depends upon the extent to which the ions of the added salt combine with the solvent. He pointed out that the degree of hydration parallels the salting-out effect.

Geffcken

Z. phys. Chem. 49, 257 (1904)

decided that the magnitude of the salting-out effect is very

much dependent upon the nature of the saturating substance although the salting-out order of the added substances is almost the same in each case. While he agreed that the decrease in solubility is due to a change in the internal pressure of the solvent, he stated that Euler and Rothmund were both mistaken in assuming that the magnitude of the salting-out effect increases with an increased original solubility of the saturating substance.

Bray and MacKay

J. A. C. S. 32. 914 (1910)

Found that in potassium iodide solutions saturated with iodine the ratio $\frac{C_I}{C_{I_3}}$, which, according to the law of mass action should be a constant, decreases from 1.16 to 0.99 between 0.0 and 0.1 normal; thus showing that an effect due to the presence of potassium iodide, which has been known to exist in more concentrated solutions, is not negligible even in these very dilute solutions.

Brönsted and Pederson

Z. phys. Chem. 103. 309 (1923)

made some measurements of the tri-iodide equilibrium by the solubility method and assumed that iodine dissolved in the aqueous solution of potassium chloride is entirely present as free iodine.

Baxter

J. A. C. S. 48. 615 (1926)

tested the theory of solubility experiments at higher temperatures. He determined the solubility of silver iodate at 75° C., in pure water and in the presence of different salts in various concentrations. The results conform, up to an ionic concen-

tration of 0.01 M., with the limiting equation of Debye and Huckel, and afford a verification of the ion attraction theory at very small concentrations. The results also afford a confirmation of the theoretical effect of varying the temperature and of the simultaneous variation of the dielectric constant when water is the solvent.

Carter

Jour. Chem. Soc. 127, 2861 (1925)

made a comparison of the observed and the calculated solubilities of iodine and found that there is a close agreement over the entire range of possible salt solutions in the case of sodium nitrate and sulphate- and also in the case of sodium dihydrogen phosphate, excepting the two most concentrated solutions, for which the measured solubilities are smaller than the calculated values. He found that the expression

$$\log S = \log S_0 - kc$$

holds true especially when the concentration is expressed in moles per thousand moles of water. The divergence mentioned above for the more concentrated solutions suggested the operation of some factor other than that responsible for the normal salting-out effect. He suggested that an explanation might be found in the acid character of the electrolyte in this case, for, as he found later, the behavior of the nitric and sulphuric acids is quite different from that of the corresponding salts.

In a later paper

Jour. Chem. Soc. 2227 (1928)

Carter gave an account of a study of the polyiodide equilibrium in aqueous and salt solutions. Jones

J. Phys. Chem. 34, 673 (1930)

has shown that there is abundant evidence that the solution of iodine in solutions of iodides involves the formation of polyiodides, and that in dilute solutions the whole of the combined iodine is present as tri-iodide.

Carter's data seemed to indicate the presence of polyiodides more complex than the tri-iodide in the more concentrated solutions.

In a more recent paper, Carter

Jour. Chem. Soc. 580 (1929)

gives his conclusions drawn from a study of the solubility of iodine in solutions of halides. Measurements of the electrolytes have shown that, in the absence of interaction between the two, the relation between the solubility S and the electrolyte concentration C is represented by the exponential equation

$$s = s_0 e^{-aC},$$

where s has a value equal to or approximating to the solubility in the pure solvent and a is a constant which measures the salting-out effect of the electrolyte. When the non-electrolyte and the electrolyte react to form a soluble complex, the salting-out effect is opposed by a tendency towards increased solubility, and the solubility actually observed will depend on the relative magnitudes of the two opposing effects. If the equilibrium involved in the formation of the complex is known, it should be possible, by making allowance for the salting-out effect, to obtain constancy of the mass-law expression concerned. He found that his value for K obtained from experiment, after making due allowance for the salting-out effect, was relatively constant.

More recently Haeseler

Dissertation, Columbia Univ. 1929.

has studied the solubility of benzoic acid in salt solutions and the following conclusions were drawn from the experimental results.

The equation

$$\log f(\text{benzoic acid}) = kc + lc^2$$

in which c is the concentration of added salt, and k and l are constants whose value depends upon the nature of the added salt as well as the temperature, agrees with the experimental data obtained. This is true of the salt concentrations above one molar only, for below that concentration other factors such as the effect of the salt on the ionization of benzoic acids overshadows the salting-out effect.

The order of salting-out of the ions used in this investigation was found to be: lithium, sodium, potassium, for the cations, and chloride, bromide, iodide, nitrate, for the anions. It was shown that the position of lithium is subject to change at different concentrations.

2. PURPOSE OF THE PRESENT WORK.

The purpose of the present work was to determine the solubility and thence the activity coefficient of iodine as a function of concentration of added neutral salt, by the solubility method. In accordance with the behavior of other non-electrolytes mentioned in the introduction, the solubility of iodine is markedly changed by the addition of electrolytes. The desirability of knowing the activity coefficient, which is a measure of the change in solubility, has been pointed out by La Mer and Friedman

J. A. C. S. 52, 883 (1930)

in connection with some other work.

Working along these lines, one might think it most logical to obtain the desired values by comparing the solubility of iodine in various salt solutions at the several concentrations, to its solubility in pure water at the same temperature. However, iodine is only slightly soluble in water and owing to its high vapor pressure and its tendency to hydrolyze, chemical literature is full of different values for its solubility ranging from the low value of Carter to the high value of Noyes and Seidensticker. The following are the values at 25°C. of different workers as found in the literature.

Carter----- .001319 mol/liter

Jour. Chem. Sec. 127, 2861 (1925)

Bray----- .001320 mols/liter

J. A. C. S. 32, 937 (1910)

Hartley and Campbell----- .001334 mols/liter

Jour. Chem. Soc. Trans. 93. 741 (1908)

Jakowkin----- .001337 mols/liter

Z. phys. Chem. 13. 539
Sammet----- .001341 mols/liter

Z. phys. Chem. 53. 687 (1903)

Noyes and Seidensticker----- .001342 mols/liter

J. A. C. S. 21. 217 (1899)

Our method of attacking this problem, was, briefly, as follows: The iodine was shaken with water (.001 N. with sulphuric acid to prevent hydrolysis of the iodine) and with salt solutions of different concentrations, and its solubility in each case determined by titration with standard thiosulphate solution. From the data obtained in this way we calculated the values of $\log \frac{S}{S_0}$.

3. PREPARATION OF MATERIALS

The chemicals used in this work were purified in a very careful manner. In all cases, freshly distilled water was used. This water was boiled just before using to remove any dissolved gases.

, The iodine used was C.P. resublimed iodine which was further purified by sublimation from C.P. potassium iodide to remove any traces of the other halogens. After this the iodine was subjected to two more sublimations to assure the complete removal of the potassium iodide. Only the middle portions of these last two sublimations were saved for use.

The Oxalsäures Natrium nach Sørensen ($\text{Na}_2\text{C}_2\text{O}_4$) used as a standard against the potassium permanganate was dried in an oven at 145°C ., for twelve hours. It was then kept in a dessicator over anhydrous sulphuric acid.

, The potassium permanganate was C.P. salt and the solution made from it was allowed to stand for a week before filtering. After being filtered through washed asbestos, it was allowed to stand for a few days before standardization. The normality of the permanganate solution was checked at frequent intervals.

The sodium thiosulphate used was C.P. salt for quantitative work. The solution was made up and allowed to stand a week before standardization. Both the sodium thiosulphate and potassium permanganate solutions were kept in brown glass-stopped bottles because, according to Kilpatrick,

J. A. C. S. 45. 2132 (1923)

sunlight hastens their decomposition.

Sodium iodide was used as the titrating medium. The best C.P. grade was used for this purpose. Blanks were run on this

salt and no test for iodate was obtained.

The starch solution used as an iodine indicator was made up fresh each day from C.P. starch. A one-percent solution was used for this work.

All of the salts used were of the best C.P. grade obtainable. With the exception of the sodium chloride and the potassium chloride, they were further purified by two recrystallizations and then dried at 140°C., for at least twelve hours. They were kept in paraffin sealed glass-stoppered bottles until used.

The potassium and sodium chlorides were precipitated from their saturated solutions by passing pure hydrogen chloride gas into the respective solutions.

The aqueous solutions as well as the salt solutions were made 0.001 N., with sulphuric acid to prevent the hydrolysis of the iodine, since it has been found by Bray

J. A. C. S. 32, 937 (1910)

that the iodine tends to hydrolyze in neutral aqueous solution. However, this hydrolysis



is driven back almost completely in acid solutions.

4. EXPERIMENTAL METHOD.

A large electrically heated and controlled water-bath regulated to $25^{\circ}\text{C} \pm .01$ (ordinarily $\pm 0.005^{\circ}\text{C}.$) was used in this work. The thermo-regulator, which was placed at the opposite side of the bath from the stirring apparatus, was of the approved toluene-mercury expansion type with a mercury relay working in an inert atmosphere to prevent oxidation of the mercury. The regulator was shunted with a condenser to prevent sparking and the consequent oxidation of the mercury in it. The water level surrounding the regulator was kept constant to insure uniform regulation at all time. The temperature of the bath was checked very accurately with a U. S. Bureau of Standards thermometer and the variations of the temperature were observed by means of two Beckmann Thermometers checked against the Bureau of Standards Thermometer. One of these Beckmann's was kept in the bath at all times and the temperature of the bath was taken before each run was made.

The heating of the bath was accomplished by means of two Cenco Knife-blade Heaters placed in series, after it was found that one heater gave too rapid heating for uniform control.

The stirring of the bath was accomplished by a propeller type of stirrer driven by a quarter horsepower electric motor. This stirring was augmented by the system of shaking the bottles of solutions in the bath. This stirring was found to be sufficient to keep the bath uniform.

We first attempted to obtain saturation of the solution by putting an excess of iodine in the acidulated water and then shaking the mixture in the bath. Different bottles showed

different degrees of saturation when prepared in this manner and so a new method of saturation was sought. A stirring apparatus was set up in the bath to stir the solutions as they were shaken but this did not prove satisfactory.

Next the solutions were saturated at 50°C., by means of a water-bath and an electric stirrer. The saturated solutions were then put in the bath and allowed to come to equilibrium before analysis. When this procedure was followed, the different solutions gave very good checks so the above procedure was followed for the rest of the work.

All of the solutions worked with were kept 0.001 N. in sulphuric acid to prevent any hydrolysis.

The titrations were carried out using the new type of weight burettes designed by Friedman and La Mer.

Jour. Ind. and Eng. Chem. Anal. Ed. 2, 54 (1930)

These burettes were kept perfectly clean and were washed out three times with the titrating solution each time before use. This method of analysis necessitated the determining of the densities of each solution used in the burettes. For this work an approved type of pycnometer was used. The density of the solution was determined by dividing the net weight of the solution by the volume of the pycnometer.

The weighings were made on a Chain-O-Matic balance. The balance was read to three decimal places but only two places were retained in this work.

The iodine dissolved in the solutions was determined by titrating a 100 cc. sample with standard thiosulphate solution according to the directions given by Fales.

Fales' Inorganic Quant. Analysis. Century. pg. 72. 1925.

Exceptionally large values in every case were discarded as containing solid iodine. Fales advises the discarding of any values whose deviation from the mean is as much as four times the average deviation.

The samples were extracted by forcing the solution into a 100 cc. pipette. It had been found that suction lowered the content of iodine dissolved in the sample. It was also found that a filter necessitated the use of such a high pressure of air that the solubility was increased. Consequently the bottles were shaken in the bath and then allowed to stand at rest for at least two hours at which time the samples were drawn off from the upper portion of the bottle. Dorfmann and Hildebrand,

J. A. C. S. 49. 729 (1927)

in their work on the "Solubility Relation of Stannic Iodide", use and recommend this method of procuring samples.

The thiosulphate was standardized by means of standard permanganate according to directions in Fales.

Fales' Inorganic Quant. Analysis. Century. 1925.

Following the recommendation of the U. S. Bureau of Standards, sodium oxalate was used for standardizing the permanganate solutions. Directions as given by Fales were followed in this standardization.

5. EXPERIMENTAL DATA.

Density of Solutions Used:

Solution	Density at 25°C.
(1) Na ₂ S ₂ O ₃ -----	.9981
(2) Na ₂ S ₂ O ₃ -----	1.0013
(3) Na ₂ S ₂ O ₃ -----	1.0034
(4) Na ₂ S ₂ O ₃ -----	1.0034
Water-----	.99707 (Chem. Handbook)
(1) KMnO ₄ -----	Went Bad.
(2) KMnO ₄ -----	.99975
(3) KMnO ₄ -----	.99903
(4) KMnO ₄ -----	.99903
(5) KMnO ₄ -----	.99952

Results of Permanganate Standardizations:

Solution (2) KMnO₄ vs Na₂C₂O₄

				Color
				Check.
Wt. Na ₂ C ₂ O ₄ --	.2386	.2432	.2512	
Wt. B. KMnO ₄ -	73.788	89.707	104.650	57.941
" " "	<u>42.592</u>	<u>57.941</u>	<u>71.835</u>	<u>57.913</u>
Wt. KMnO ₄ -	<u>31.196</u>	31.766	32.815	.028
Color Corr. -	<u>.028</u>	<u>.028</u>	<u>000.028</u>	
	31.168	31.738	32.787	



Let "a" = wt. of sample Na₂C₂O₄

$$\frac{a}{66.997} = \frac{\text{gm. KMnO}_4 \text{ sol'n} \times \text{cc./gm.} \times \frac{1}{1000}}{1000}$$

$$N_{\text{KMnO}_4} = \frac{1000a}{66.997 \times \text{gm. KMnO}_4 \times \text{cc./gm.}}$$

(1)	log N_1 = 9.05778-10	N_1 = 0.11423 - .00006
(2)	log N_2 = 9.05819-10	N_2 = 0.11431 + .00002
(3)	log N_3 = 9.05815-10	N_3 = 0.11433 + .00003

Av. N = 0.11429 ± .000036

Solution (3) $KMnO_4$ vs $Na_2C_2O_4$

(1)	log N_1 = 8.96826-10	N_1 = .092952 - .000021
(2)	log N_2 = 8.96836-10	N_2 = .092974 + .000001
(3)	log N_3 = 8.96845-10	N_3 = .092993 + .000020

Av. N = .092973 ± .000014

Solution (4) $KMnO_4$ vs $Na_2C_2O_4$

(1)	log N_1 = 8.96877-10	N_1 = .093062 + .000005
(2)	log N_2 = 8.96805-10	N_2 = .092908 - .000010
(3)	log N_3 = 8.96877-10	N_3 = .093062 + .000005

Av. N = .09301 ± .000007

Solution (5) $KMnO_4$ vs $Na_2C_2O_4$

(1)	log N_1 = 9.03639-10	N_1 = .10874 - .000003
(2)	log N_2 = 9.03690-10	N_2 = .10887 + .000010
(3)	log N_3 = 9.03609-10	N_3 = .10867 - .000010
(4)	log N_4 = 9.03665-10	N_4 = .10880 + .000003

Av. N = .10877 ± .000065

Results of Thiosulphate Standardizations:

Solution (1) $Na_2S_2O_3$ vs Solution (2) $KMnO_4$

(Thiosulphate too dilute for standardization)

Solution (2) $Na_2S_2O_3$ vs Solution (3) $KMnO_4$

Wt. B. + $KMnO_4$ -	105.724-89.371-99.827-103.803-92.609-82.530
" " " "	- 89.371-73.231-86.791- 92.609-82.530-75.416
Wt. $KMnO_4$ Used	16.353-16.140-13.036- 11.194-10.079- 7.114

Wt. B. + $Na_2S_2O_3$ -	104.249-104.114-104.085-103.644-70.465-101.934
" " " "	- 56.180- 56.659- 65.550- 70.465-40.777- 80.905
	48.069 47.455 38.535 33.179 29.688 21.029

$$N_{\text{Na}_2\text{S}_2\text{O}_3} = \frac{\text{gm. KMnO}_4 \text{ Sol'n} \times N_{\text{KMnO}_4} \times \text{gm./cc. of Na}_2\text{S}_2\text{O}_3}{\text{gm./cc. of KMnO}_4 \times \text{gm. Na}_2\text{S}_2\text{O}_3 \text{ Sol'n}}$$

(1)	log N ₁ = 8.50106-10	N ₁ = .03170 +.00011
(2)	log N ₂ = 8.50093-10	N ₂ = .03169 +.00010
(3)	log N ₃ = 8.49860-10	N ₃ = .03152 -.00009
(4)	log N ₄ = 8.49761-10	N ₄ = .03145 -.00014
(5)	log N ₅ = 8.50033-10	N ₅ = .03165 +.00006
(6)	log N ₆ = 8.49878-10	N ₆ = .03153 -.00006

Av. N = .03159 ±.00009

Solution (3) Na₂S₂O₃ vs Solution (4) KMnO₄

(1)	log N ₁ = 8.64718-10	N ₁ = .044377 +.00003
(2)	log N ₂ = 8.64732-10	N ₂ = .04430 +.00004
(3)	log N ₃ = 8.64709-10	N ₃ = .04437 +.00002
(4)	log N ₄ = 8.64640-10	N ₄ = .04430 -.00005
(5)	log N ₅ = 8.64664-10	N ₅ = .04432 -.00003

Av. N = .04435 ±.00003

Solution (4) Na₂S₂O₃ vs Solution (5) KMnO₄

(1)	log N ₁ = 8.64491-10	N ₁ = .04415 -.00007
(2)	log N ₂ = 8.64668-10	N ₂ = .04433 +.00011
(3)	log N ₃ = 8.64481-10	N ₃ = .04414 -.00008
(4)	log N ₄ = 8.64604-10	N ₄ = .04427 +.00005

Av. N = .04422 ±.00008

Solubility of Iodine in Water at 25° C. ± .01

Data Obtained	Normality	Mols/liter	No. Det'ns. included in average
3-18-31	.0026433	.0013217	8
3-18-31	.0026600	.0013300	
3-18-31	.0026682	.0013341	
3-20-31	.0026454	.0013227	
3-25-31	.0026385	.0013193	
3-25-31	.0026543	.0013272	
3-26-31	.0026468	.0013234	
3-29-31	.0026546	.0013273	
Average	.0026514	.0013257 = S ₀	

Solubility of Iodine in Sodium Nitrate.

1 Molar

N _I	Mols/liter	No. Det'ns. included in average	S/S ₀
.0023053	.0011527	4	.87902
.0023732	.0011866		
.0023617	.0011809		
.0022819	.0011410		
.0023305 - Av.	.0011653		

Solubility of Iodine in Sodium Nitrate. (cont'd.)

<u>2 Molar</u>			
N _I	Mols/liter	No. det'ns included in Average	S/S _o
.002149	.001075		
.002096	.001048		
.001974	.000987		
.002016	.001008		
<u>.002059</u>	<u>.001030</u>	4	.77696
-----Av.-----			

<u>3 Molar</u>			
.001593	.000797		
.001605	.000803		
.001544	.000772		
.001574	.000787		
.001554	.000777		
.001561	.000781		
<u>.001572</u>	<u>.000786</u>	6	.5929
-----Av.-----			

Solubility of Iodine in Potassium Nitrate.

<u>1 Molar</u>			
.002390	.001195		
.002375	.001188		
.002384	.001192		
<u>.002383</u>	<u>.001192</u>	3	.89916
-----Av.-----			

<u>2 Molar</u>			
.002080	.001040		
.002120	.001060		
.002136	.001068		
.002090	.001045		
<u>.002106</u>	<u>.001053</u>	4	.79432
-----Av.-----			

<u>3 Molar</u>			
.0019016	.0009508		
.0019168	.0009584		
.0019089	.0009545		
.0019246	.0009623		
.0018997	.0009499		
<u>.0019103</u>	<u>.0009552</u>	5	.72053
-----Av.-----			

Solubility of Iodine in Sodium Chloride.

1 Molar

N_I	Mols/liter	No. Det'ns included in Average	S/S _o
.005785	.002893		
.005782	.002891		
.005277	.002639		
.005397	.002699		
.005379	.002690		
<u>.005489</u>	<u>.002745</u>		
.005518	.002759	6	2.0812

2 Molar

.006560	.003280		
.006696	.003348		
.006719	.003360		
.007083	.003542		
<u>.007027</u>	<u>.003514</u>		
.006817	.003409	5	2.5715

3 Molar

.006798	.003399		
.006879	.003440		
<u>.006865</u>	<u>.003433</u>		
.006848	.003424	3	2.5828

Solubility of Iodine in Potassium Chloride.

1 Molar

.005796	.002893		
.005721	.002861		
<u>.005706</u>	<u>.002853</u>		
.005741	.002871	3	2.1657

2 Molar

.007698	.003849		
.007874	.003937		
.008337	.004169		
<u>.007672</u>	<u>.003836</u>		
.007895	.003948	4	2.9781

3 Molar

.008773	.004387		
.008859	.004430		
.008774	.004387		
<u>.008756</u>	<u>.004378</u>		
.008791	.004395	4	3.3153

Solubility of Iodine in Sodium Sulphate.

N_{I_2}	<u>.2 Molar</u> Mols/liter	No. of Deths included in average.	S/S _o
.002289	.001145		
.002234	.001117		
.002285	.001143		
.002258	.001129		
.002253	.001127		
<u>.002209</u>	<u>.001105</u>		
.002255---Av.-----	.001128-----	6 -----	.85088

.3 Molar

.002030	.001015		
.002054	.001027		
.002072	.001036		
<u>.002104</u>	<u>.001052</u>		
.002065---Av.-----	.001033-----	4 -----	.77922

.4 Molar

.001923	.000962		
.001918	.000959		
.001914	.000957		
.002014	.001007		
<u>.001878</u>	<u>.000939</u>		
.001930---Av.-----	.000965-----	5 -----	.72793

Solubility of Iodine in Potassium Sulphate.

.2 Molar

.002282	.001141		
.002270	.001135		
.002294	.001147		
.002321	.001161		
<u>.002279</u>	<u>.001140</u>		
.002289---Av.-----	.001145-----	5 -----	.86372

.3 Molar

.002130	.001065		
.002140	.001070		
.002141	.001071		
.002116	.001058		
<u>.002179</u>	<u>.001089</u>		
.002141---Av.-----	.001071-----	5 -----	.80788

Solubility of Iodine in Potassium Sulphate. (cont.)

.4 Molar

I_2	Mols/liter	No. Det's included in Average.	S/S ₀
.001995	.000998		
.002013	.001007		
.002007	.001004		
.002123	.001062		
<u>.002416</u>	<u>.001208</u>		
.002111---Av.-----	.001056-----	5 -----	.79656

6. DISCUSSION AND SUMMARY

Curves were drawn from the experimental data obtained. These curves bear out the theory that there is a decided salting-out effect and that this effect is dependent both upon the anion and the cation of the added salt. The order of salting-out of the ions in the investigation was found to be in the same order as that found by Haeseler,

Loc. Cit.

Sodium, potassium for cations, and sulphate, nitrate, and chloride, for the anions. Chloride seems to be out of place according to Haeseler's order but this is due to the fact that this work was done with iodine and there seems to be some indication of compound formation which increases the solubility of the iodine in the chloride solution. As shown by Carter,

Loc. Cit.

"Thus the salting-out effect is opposed by a tendency towards increased solubility, and the solubility actually observed will depend on the relative magnitudes of the two opposing effects."

Quoting Eucken Jette & La Mer

Fundamentals of Physical Chemistry, Pg.341 McGraw-Hill (1925)

"It is well known that the addition of neutral salts to an aqueous solution containing an electrically neutral substance like ether, H_2 , or N_2O gas usually results in a decrease in the solubility of the neutral substance.

The specific solubility effects, which concentrated solutions of $NaCl$, $(NH_4)_2 SO_4$ and Na_2SO_4 exert, are made use of in the separation of proteins and in the commercial manufacture of dyestuffs and soaps. Although, in general, this phenomenon

is a complicated one depending upon the specific properties of the neutral molecule and of the added salts, it has been found empirically that a linear relation between the logarithm of the solubility ration and the concentration of added salt often holds for a considerable range (up to about 4.0 N.) of salt additions- namely

$$\log \frac{S}{S_0} = k_s C \quad (193x)$$

where k_s , the salting-out coefficient, is a constant for each each particular salt when salting out a given neutral substance. S is the solubility in the salt solution of a concentration c and S_0 is the solubility in pure water.

Now Eq. (193j) permits the substitution of $-\log F$ for $\log \frac{S}{S_0}$ and Eq. (193X) then becomes

$$-\log F = k_s C \quad (193X)$$

In Eq. (193X') negative values of k_s represent a positive salting-out effect- positive values, a dissolving power greater than that of pure water.

When the anion of the added salt is the same but the cation is varied, it is found that the values of k_s usually form the following series:-

Li. Na. K. Rb. Cs

Increasing negative values of k_s .
The general order of the anions of the potassium salts is

SO₄. Cl. Br. I. SCN

Increasing negative values of k_s .

It was found in this work that the order as outlined by the above authors held. As may be seen from the accompanying curves, the sodium salts had a larger negative value than the corresponding potassium salts.

Since it is the purpose of this work to determine the

solubility and thence the activity coefficient of iodine as a function of concentration of added neutral salt the following procedure was followed.

From thermodynamics we know that

$$\log \frac{S_0}{S_1} = \log \frac{\gamma_1}{\gamma_0}$$

where S_0 and S_1 are the solubilities in pure water and neutral salt solution respectively, while γ_1 and γ_0 are the activity coefficients in salt solution and pure water respectively. Rearranging the above equation we find

$$\log \frac{S_1}{S_0} = - \log \frac{\gamma_0}{\gamma_1} = - \log \gamma_0 + \log \gamma_1$$

but since the activity coefficient in pure water is always one the above equation becomes

$$\log \frac{S_1}{S_0} = \log \gamma_1 .$$

Since the S_0 and S_1 values were determined in this experiment it is a simple matter to calculate the activity coefficients of iodine at varying concentrations of added neutral salts. The values thus obtained are given in the tables under the heading S/S_0 .

The values obtained seem to give smooth curves although they are not straight line functions. There seems to be a decided drop in the curve of the sodium nitrate solution at a concentration of 3 mols per liter. The author has no reason for this as the value used was the average of six determinations.



Mols./liter Salt

0

2

3

4

5

 $\log \frac{S}{S_0}$

Harman

.001926

-.06378

-.09281

-.09987

-

McLauchlan

.00133

-.15263

1000

0000

 $\log \frac{S}{S_0}$

-1000

-2000

-3000

0

1

2

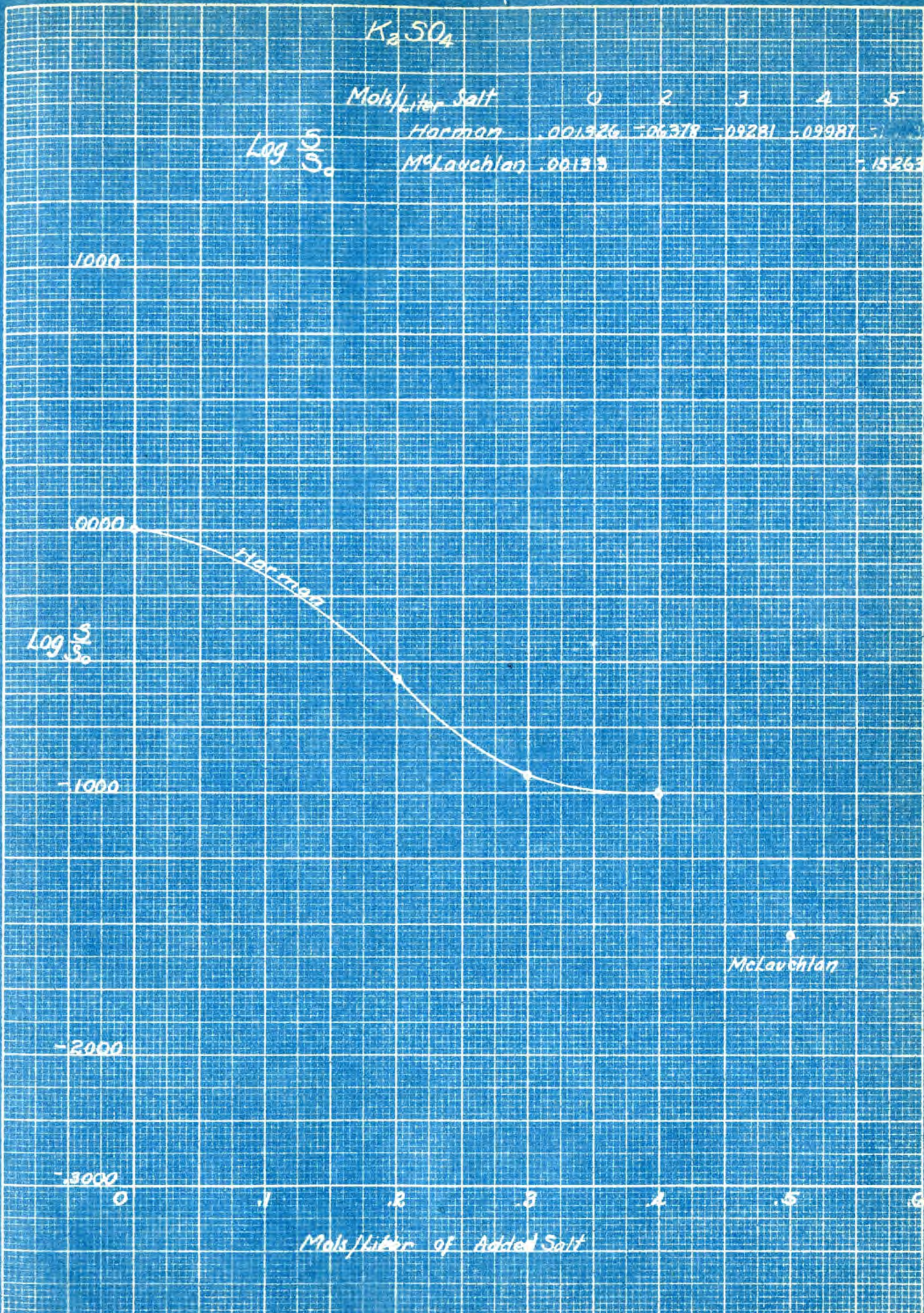
3

4

5

6

Mols./liter of Added Salt



Na₂SO₄

1000
900
800
700
600
500
400
300
200
100
0

1000

900

800

700

600

500

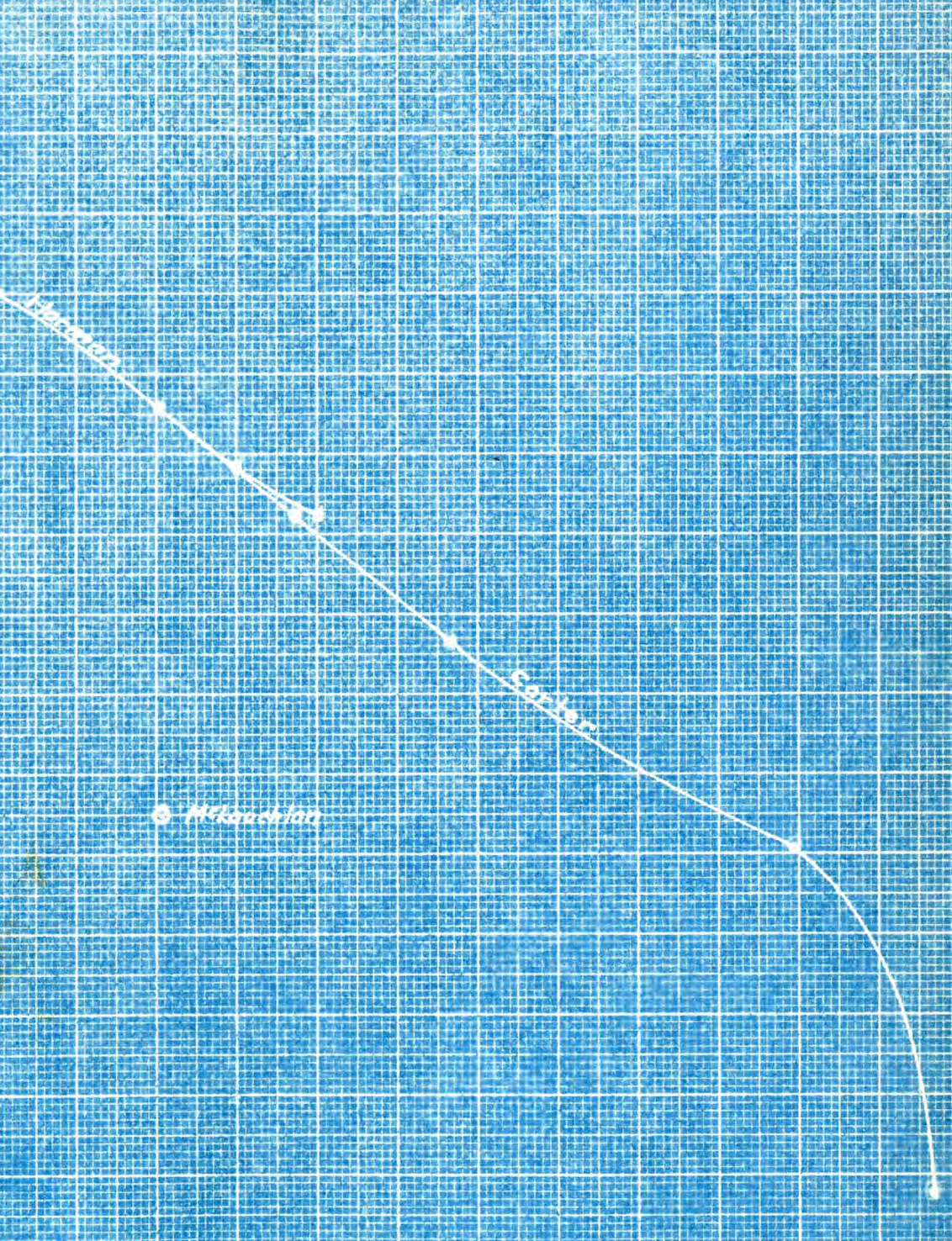
400

300

200

100

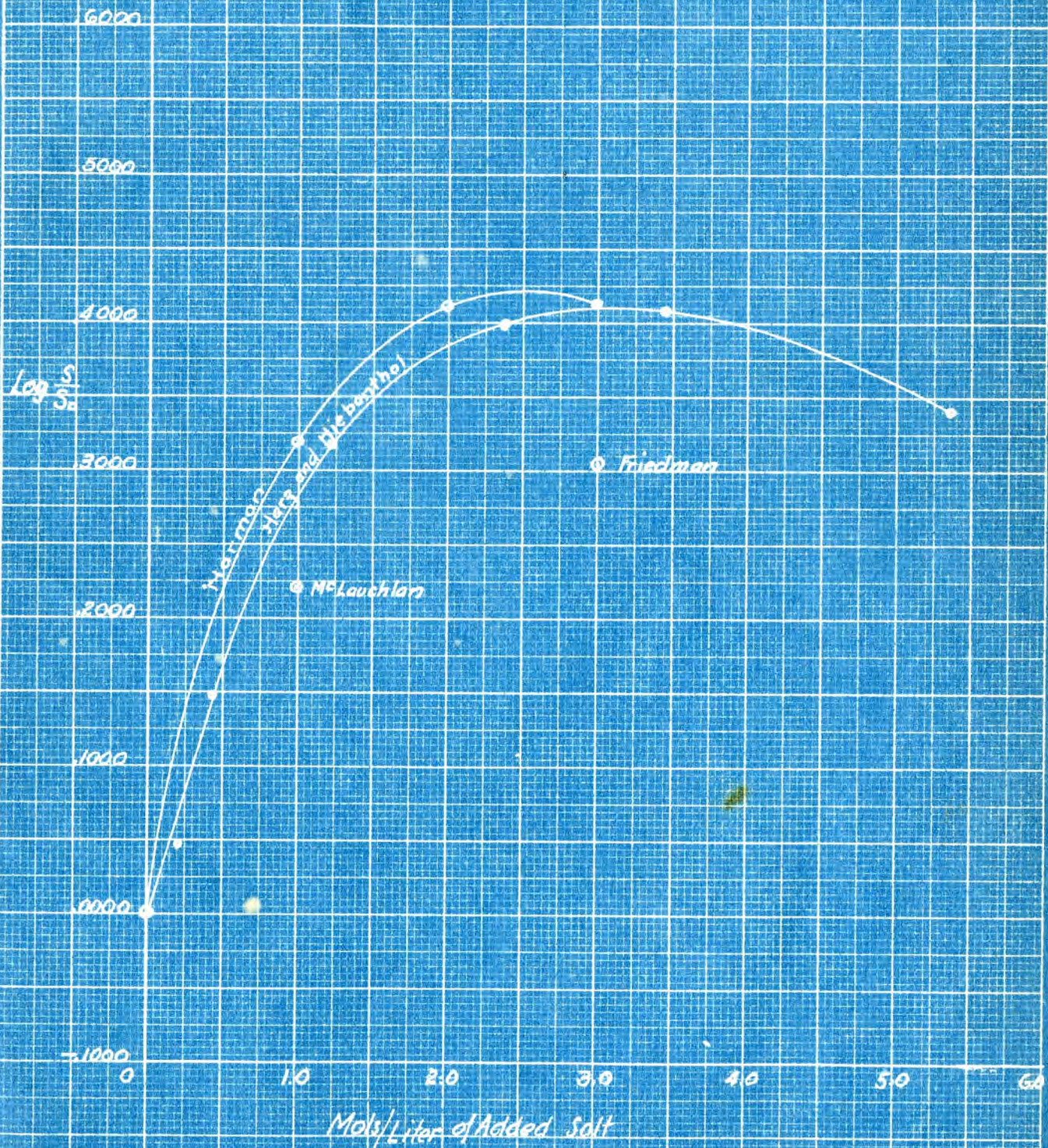
0



Melting of Added Salt

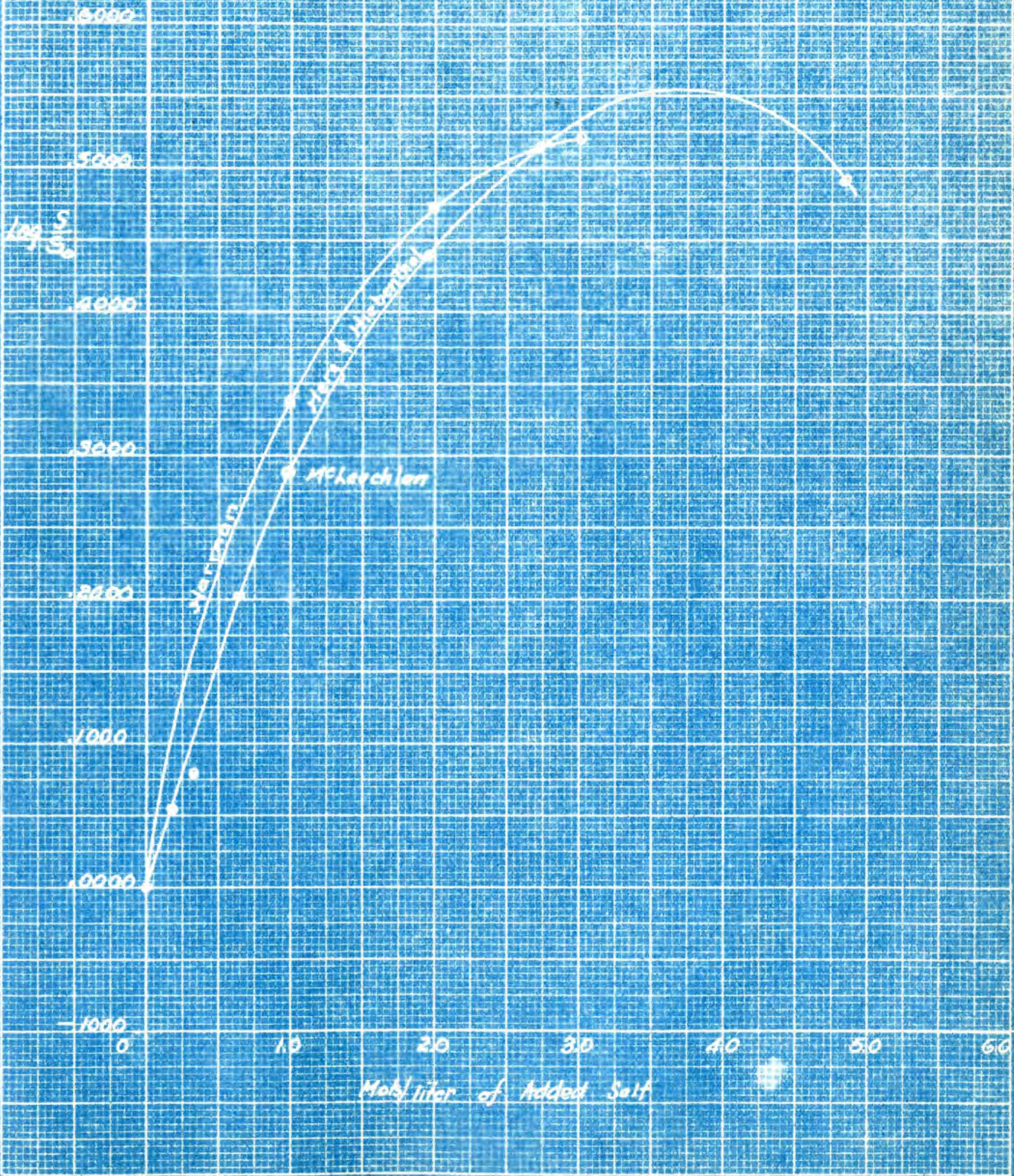
NaCl

Mols/Liter	0	20	44	1.0	1.23	2.0	2.39	3.0	3.45	5.34
Hartman	001326			.31831		.41013		.4207		
Hog & Hiebenthal	00122	.04718	.14917		.32018		.39936		.40078	.54015
Friedman	00134							.30523		
McLauchlan	001333			.22015						

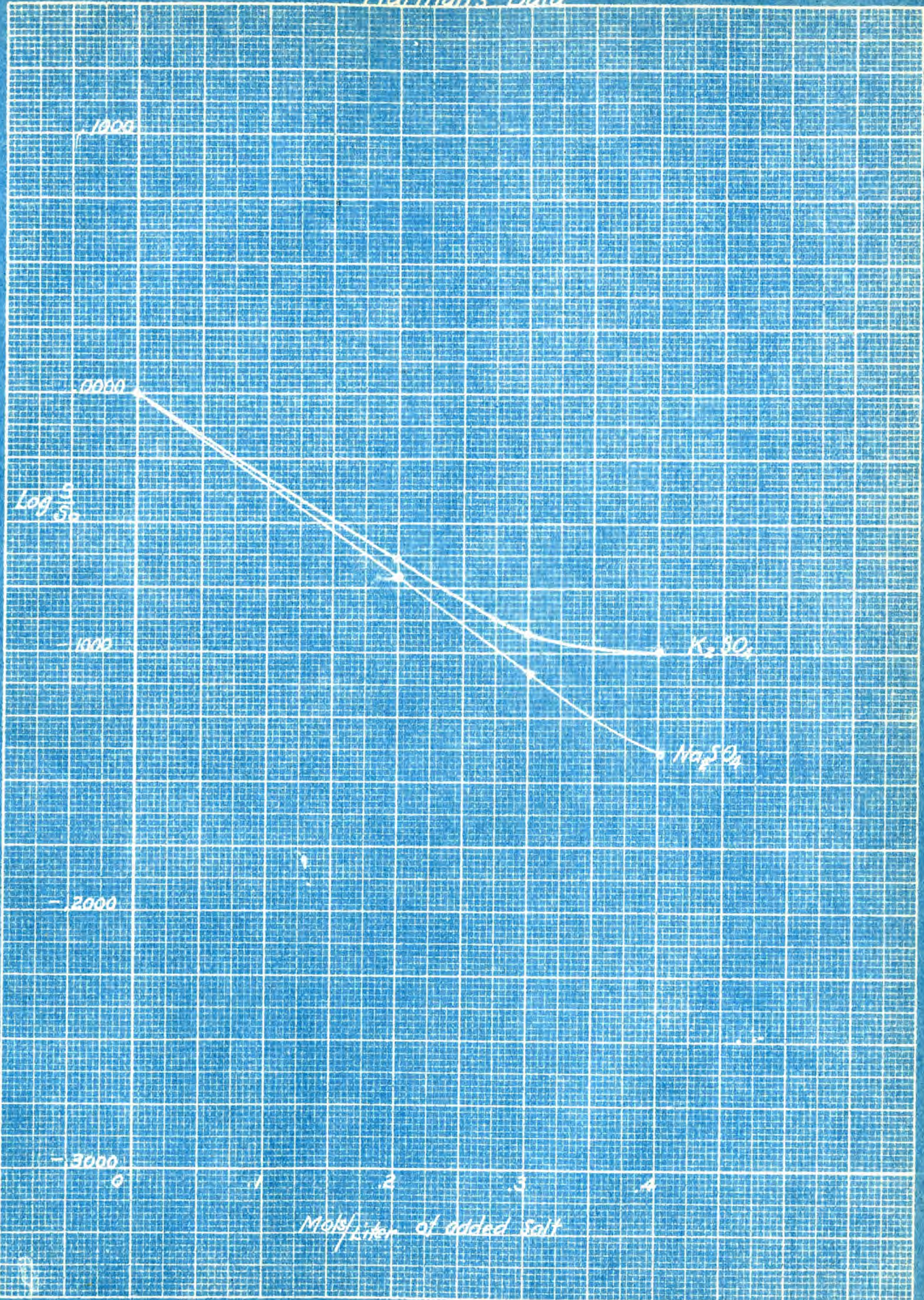


KCl

Author	Year	Temp	Concn	Concn	Concn	Concn	Concn	Concn	Concn
Kelly	1892	25	20	30	40	50	60	70	80
Holman	1892	25	20	30	40	50	60	70	80
Wahlund	1893	25	20	30	40	50	60	70	80
McKee	1893	25	20	30	40	50	60	70	80



Harman's Data



Hacman Data

