Summary.

The solubility data contained in this article have been summarized in Tables II, IX and XIII, and are presented graphically in the accompanying figure, in which solubilities are plotted as formula weights per liter and the concentrations of the added salts as equivalents per liter. The article also contains the results of some conductance measurements for a number of salts, from which the corresponding ionization values have been calculated. The quantitative discussion of the results is reserved for a later article.

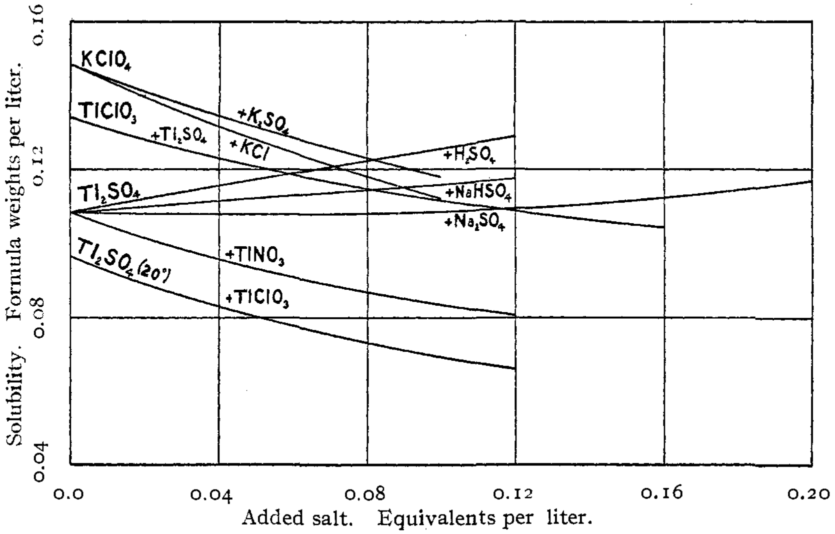

Fig. 1.

[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 74.]

THE EFFECT OF SALTS ON THE SOLUBILITY OF OTHER SALTS. III. SOLUBILITY OF THALLOUS CHLORIDE IN SOLUTIONS OF POTASSIUM NITRATE, POTASSIUM SULFATE, AND THALLOUS SULFATE AT 25°.

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This investigation was undertaken to determin the effect on the solubility of thallous chloride of the presence of thallous sulfate, a unibivalent salt with a common ion, and of potassium nitrate and potassium sulfate, salts without a common ion. These experiments supplement those of Noyes[1] on the solubility of thallous chloride in the presence of

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[1] A. A. Noyes, *Z. physik. Chem.*, 9, 603 (1892).

thallous nitrate, thallous chlorate, and a large number of chlorides and thus render possible the examination of the effect on the solubility of thallous chloride of typical uni-univalent and uni-bivalent salts both with and without a common ion.

The potassium nitrate, potassium sulfate, and thallous sulfate were prepared by recrystallizing Kahlbaum's salts from conductivity water and were dried at 120–150°, 260–280° and 300–350° respectively. Each of the various solutions was prepared by dissolving the required amount of the salt and diluting at 25° to a known volume. The specific conductance of the water was usually less than 1×10^{-6}. International atomic weights of 1910 were used in calculating concentrations and buoyancy corrections were applied throughout.

The thallous chloride was at first precipitated by adding hydrochloric acid to hot concentrated solutions of Kahlbaum's thallous sulfate or thallous nitrate. In the later work it was prepared from the residues of the earlier experiments (after removing silver as chloride and sulfide) by evaporating with sulfuric acid to fuming, dissolving in water, adding sulfurous acid to reduce any thallic salt, and precipitating as before with hydrochloric acid from a hot solution. The acid was washed out by rotating the solid salt for some time with successive small portions of water, and this treatment was shown to be satisfactory by the fact that the concentration and conductance of the saturated solution was the same as in the case of a sample of thallous chloride which had been recrystallized twice from conductivity water. After the experiments with potassium nitrate and with potassium sulfate these substances were washed out by the same treatment, and the saturated aqueous solutions were found to have the same conductance and concentration as before.

The thallous chloride was not dried and was kept in the dark. When first prepared it was pure white, but turned pink if heated at 110°, and the wet salt also became pink and finally purple when exposed to the light. In nearly all the experiments the bottles were covered with black cloth to guard against this action of the light, but some special experiments showed that the conductance and concentration of saturated solutions were exactly the same for the purple and white salts.

In each solubility determination 10 to 20 grams thallous chloride were rotated for at least 12 hours at 25° in a 250 cc. "Resistenz" glass bottle nearly filled with conductivity water or a salt solution of known concentration. The bottles were rotated end over end in order to mix the heavy salt with the solution. The stoppers were paraffined and protected by rubber tubing in the usual way. Equilibrium was approached from undersaturation and supersaturation, the latter state being reached by shaking the bottles in hot water at 50° or 60°. The measurements with each salt were made successively from the dilute to the concentrated solutions. Before each determination with a given salt solution the thallous chloride was rotated for 3 or 4 hours with about 150 cc. of the salt solution; this was poured off, and the bottle filled with the same solution.

A portion of each saturated solution was first forced directly into a conductance cell of the pipet form and its conductance measured at 25° in the usual way.[1] The density at 25° was then determined with this same solution or sometimes with a fresh portion of the solution in an Ostwald pycnometer[2] of about 20 cc. capacity. The conductances of the salt solutions used in these experiments and of some dilute thallous chloride solutions were also measured and are compared with existing data in Tables III and IV below.

After the conductance had been measured the remainder of each saturated solution (about 200 cc.) was forced through a small asbestos filter into a weighed glass-stoppered flask, weighed, washed into a beaker, and analyzed for chloride by adding a few drops of nitric acid and silver nitrate solution. A nearly equivalent amount of 0.1 normal silver nitrate was added slowly, with vigorous stirring, to the cold solution in the dark, the mixture was allowed to stand about twenty hours in the dark and a 20 per cent. excess of silver nitrate added. After standing over night the precipitate was collected in a Gooch crucible, washed with about 150 cc. water, heated at 100° for an hour and then at 150° for 4 to 12 hours, cooled in a desiccator for one hour and weighed, and finally heated again at 150° and again weighed.

Solubility Data.—The results of the final measurements of the solubility and conductance of saturated thallous chloride solutions are given in Table I. The concentrations in equivalents per liter were calculated

TABLE I.—SOLUBILITY AND CONDUCTANCE OF SATURATED THALLOUS CHLORIDE SOLUTIONS AT 25°.

No.	Conc. × 10^3. Under.	Conc. × 10^3. Super.	Spec. cond. × 10^3.	Equiv. cond. Λ.
1	16.09	.	2.180	135.5
2	.	16.07	2.176	135.4
3	16.07	.	2.176	135.4
4	.	16.05	2.180	135.8
5	16.07	.	2.175	135.4
6	16.07	.	2.175	135.4
7	.	16.04	2.179	135.9
8	16.07	.	2.175	135.4
9	.	16.09	2.175	135.2
10	16.09	.	2.178	135.3
11	.	.	2.175	.
Mean values,	16.07		2.176	135.4

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[1] THIS JOURNAL, **33**, 796 (1911).

[2] Ostwald-Luther, *Physico-chemische Messungen*, **142** (1902).

from the experimental data by means of the absolute density $d25°/4° = 0.9994$ (Table II). The first four measurements were made before the experiments with potassium nitrate, the next three before those with potassium sulfate, and the last four before those with thallous sulfate. The results in the seventh experiment were rejected in calculating the mean values. A number of preliminary experiments which are not included in the table gave the same mean value for the concentration and a 0.1 per cent. higher value for the equivalent conductance. The latter value was probably due to the presence of a trace of acid and was rejected.

The final value for the solubility at 25°, 0.01607 mol. per liter, is only 0.13 per cent. lower than an early result of Noyes[1] but differs by 1.4 per cent. from a recent result of Hill,[2] 0.01629. The latter value, however, is based on a volumetric method of analysis and no record of test analyses at the time of the determination is given.

The results of the solubility determinations in the presence of potassium nitrate, potassium sulfate and thallous sulfate are given in Table II. The initial concentration (milliequivalents per liter) and the ab-

TABLE II.—SOLUBILITY OF THALLOUS CHLORIDE IN THE SALT SOLUTIONS.

	Salt solution.		Soly. of TlCl × 10³.					
Salt.	Equiv. conc. × 10³.	$d25°/4°$.	Under.	Super.	Mean.	Mean spec. cond. × 10³.	$d25°/4°$.	Conc. of salt × 10³.
None	...	..	...	...	16.07	2.176	0.9994	..
KNO_3	20.01	0.9973	17.15 17.15	17.17 17.16	17.16	4.807	1.0009	20.00
	50.00	0.9992	18.27 18.25	18.24 18.29	18.26	8.466	1.0028	49.97
	100.05	1.0023	19.62 19.58	19.62 ...	19.61	14.18	1.0063	99.98
	300.2	1.0145	23.13	23.14	23.13	34.62	1.0194	300.0
	1000.5	1.0568	30.76	30.68	30.72	..	1.0632	999.6
K_2SO_4	19.97	0.9975	17.80 17.76	17.83 17.77	17.79	4.644	1.0012	19.96
	50.00	0.9995	19.45 19.39	19.41 19.44	19.42	7.962	1.0037	49.96
	100.0	1.0030	21.36 21.35	21.41 21.35	21.37	13.02	1.0074	99.89
	300.0	1.0167	26.00	25.99	26.00	..	1.0221	299.66
	1000.0	1.0628	34.16 33.86	34.11 34.22	34.16	..	1.0698	998.6
Tl_2SO_4	20.00	1.0007	10.33 10.34	10.35 10.33	10.34	3.620	1.0028	19.99
	50.00	1.0076	6.764 6.777	6.781 6.764	6.772	6.052	1.0090	49.99
	100.0	1.0191	4.673 4.683	4.681 4.678	4.679	10.01	1.0200	99.97

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[1] *Z. physik. Chem.*, **9**, 609 (1892).

[2] THIS JOURNAL, **32**, 1189 (1910).

solute density ($d25°/4°$) of the salt solutions used are given in the second and third columns of the table, and the concentration of the salt in the saturated solution (after correcting for the slight increase of volume on dissolving thallous chloride) is given in the last column. The solubilities (in millimoles per liter) in columns four and five were derived from the analytical results by means of the densities (column eight). The mean solubilities are given in column six and the specific conductance of the saturated solutions in column seven.

Conductance and Ionization Data.—The results of the conductance measurements at 25° for the potassium nitrate, potassium sulfate, and thallous sulfate solutions were reduced when necessary to round concentrations, and are presented in the following table. The values for the 0.3 normal solutions are less accurate than the results in more dilute solutions. Λ is the equivalent conductance and $C \times 10^3$ the concentration in milliequivalents per liter. These results and those of other investigators[1] (third column) were plotted in $1/\Lambda$ $(C\Lambda)^{n-1}$ diagrams in the usual way, and values were finally chosen for each salt (fourth

TABLE III.—CONDUCTANCE AND IONIZATION DATA AT 25°.

$C \times 10^3$.	Values of Λ.						
	B. & W.	J., M., or H.	Λfinal.	100 γ.	$\Sigma C_i \times 10^8$.	$K=\frac{(C\gamma)^{1.50}}{C(1-\gamma)}$.	$k=\frac{(C\gamma)(\gamma)}{(1-\gamma)}$.
(KNO_3)							
0.0	..	..	(145.4)	100.0	..	..	..
12.5	..	134.9	134.9	92.8	11.60	1.390	0.1495
20.0	132.5	(132.5)	132.5	91.1	18.24	1.400	0.1866
50.0	126.1	126.3	126.3	86.85	43.43	1.378	0.2870
100.0	120.3	120.3	120.3	82.7	82.7	1.375	0.3950
200.0	113.5[2]	..	113.4	78.0	156.0	1.400	0.553
300.0	108.3	..	108.6	74.7	224.1	1.400	0.656
($^1/_2K_2SO_4$)							
0.0	..	..	(154.8)	100.0	..	..	..
20.0	127.9	128.1	127.9	82.6	16.53	..	0.0784
50.0	117.95	118.15	117.95	76.2	38.10	..	0.1220
100.0	109.8	109.9	109.8	70.9	70.9	..	0.1727
200.0	(101.4)	101.4	101.4	65.5	131.0	..	0.2488
300.0	96.15	..	96.15	62.1	186.4	..	0.3055
($^1/_2Tl_2SO_4$)							
0.0	..	..	(156.2)	100.0	..	..	..
10.0	130.0	130.0	130.0	83.2	8.32	0.4517	0.0412
20.0	120.95	120.9	120.95	77.45	15.49	0.4275	0.0532
50.0	107.1	107.1	107.1	68.54	34.27	0.4033	0.0746
100.0	95.95	96.0	95.95	61.42	61.42	0.3946	0.0978
200.0	..	85.0	85.0	54.4	108.8	0.3935	0.1298
(300.0)	..	..	..	(50.3)	(150.9)	0.3931	0.1527
(400.0)	..	..	..	(47.4)	(189.6)	0.3924	0.1708

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[1] Potassium nitrate, Noyes and Johnston, THIS JOURNAL, 31, 979 (1909). Potassium sulfate, preliminary values obtained by Mr. A. C. Melcher, of this laboratory. Thallous sulfate, Hunt, THIS JOURNAL, 33, 802 (1911).

[2] This value of Λ for 0.2 N KNO_3 was measured by Dr. W. D. Harkins.

column) which were concordant at the different concentrations. From the latter the values of the percentage ionization 100 γ were calculated (fifth column). The corresponding ion concentrations (in milliequivalents), 1000 $\Sigma C_i = 1000\ C\gamma$, are given in the sixth column. Data obtained by interpolation or extrapolation are enclosed in parentheses in Table III to VI. Values of $K = (C\gamma)^n/C(1-\gamma)$ and of $k = (C\gamma)(\gamma)/(1-\gamma)$, which will be used in the later calculations, are also given in the last columns of these tables.

The experimental results for thallous sulfate and potassium agree almost exactly with those of Hunt and of Noyes and Johnston respectively, while the results for potassium sulfate are only 0.1 to 0.2 per cent. less than Melcher's preliminary values.

The data for thallous chloride are given in Table IV. The dilute solutions were prepared by diluting known weights of saturated solutions (specific conductance = 0.002176) to known volumes. The results are shown to be concordant with those of Kohlrausch and Steinwehr at 18°[1] by the comparison of the ionization values at 18° ($\Lambda_0 = 131.4$) with those at 25° (columns three and four).[2] The values of the ion concentration ($\Sigma C_i = C\gamma$) are given in the fifth column. These results were shown to obey the law $(\Sigma C\gamma)^{1.6}/C(1-\gamma) = K$, and the calculated values of K are given in the second last column. Ionization values at higher concentrations were calculated by means of this relationship and are included in the table.

TABLE IV.—CONDUCTANCE AND IONIZATION OF TlCl AT 25°.

1000C.	$\Lambda_{\text{measured}}$.	100γ(18°).	100γ(25°).	1000(ΣC_i).	$K = \frac{(C\gamma)^{1.6}}{C(1-\gamma)}$.	$k = \frac{(\Sigma C_i)(\gamma)}{(1-\gamma)}$.
0.0	(152.0)	..	100.0	..	..	..
5.07	143.1	94.1	94.1	4.78	0.649	..
6.04	142.25	93.5	93.6	5.64	0.644	..
10.00	139.0	91.5	91.5	9.14	0.641	..
11.08	138.35	91.02	91.0	10.08	0.642	0.102
16.07	135.4	89.1	89.1	14.32	0.640	0.117
(40.0)	..	..	(83.1)	(33.24)	0.636	0.1637
(60.0)	..	..	(79.8)	(47.88)	0.637	0.1891
(80.0)	..	..	(77.2)	(61.76)	0.636	0.2090
(100.0)	..	..	(75.1)	(75.1)	0.638	0.2264
(139.7)	..	..	(71.7)	(100.2)	0.637	0.2540
(200.0)	..	..	(67.8)	(135.6)	0.635	0.2847
(300.0)	..	..	(63.4)	(190.2)	0.637	0.3290
(400.0)	..	..	(60.0)	(240.0)	0.637	0.360

[1] *Landolt-Börnstein-Meyerhoffer, Tabellen* 744 (1905).

[2] Hunt's value of the conductance of the thallium ion at 25°, 76.0 derived from thallous sulfate measurements, has been raised to 76.2 since otherwise the ionization of thallous chloride would have been found to increase with increasing temperature. The ionization values for thallous sulfate given in Table III are therefore somewhat less than those given by Hunt.

A comparison of the ionization values of thallous chloride with those of other salts (see for example Table I of the following article) shows that this salt is much less ionized than nearly all other uni-univalent salts. Since in the case of salts of a given type the ones least ionized have the largest values of the exponent n, there does not seem to be any reason for choosing a lower value than $n = 1.60$. In order, however, to determin to what extent the results of the extrapolation were influenced by the value assumed for the exponent, some calculations were made for $n = 1.55$, which was regarded as the lowest possible exponent at 0.1 normal concentration. At this concentration γ was found to be 0.766 instead of 0.751, as given in the table, and this difference is not large when the range of the extrapolation is considered.

Ionization values at 25° for use in later calculations were also desired for a number of salts. The values for KCl (Table V) are based on the preliminary conductance results of Mr. A. C. Melcher, of this laboratory, but the values of Λ were reduced by about 0.1 per cent. in two instances as a result of the comparison of the ionization values with those derived from the measurements of Kohlrausch and Maltby at 18°. The ionization values for thallous nitrate (Table VI) were derived from the conductance measurements of Kohlrausch and Steinwehr at 18°. The assumption that the ionization of thallous nitrate is the same at 18° and 25° is supported by a conductance measurement for 0.1 normal $TlNO_3$

TABLE V.—IONIZATION OF KCl AT 25°.

Conc. $\times 10^3$.	$\Lambda_{25°}$. Melcher.	Λused.	100γ.	$(C\gamma)\times 10^3$.	$K=\frac{(C\gamma)^{1.40}}{C(1-\gamma)}$.	$k=\frac{(C\gamma)(\gamma)}{(1-\gamma)}$.
0	..	(150.6)	100	..	..	..
10	141.4	141.4	93.9	9.39	2.380	0.1445
20	138.65	138.55	92.0	18.40	2.325	0.2117
50	133.65	133.6	88.7	44.35	2.258	0.3480
100	129.0	129.0	85.65	85.65	2.234	0.512
(146)	..	(126.4)	(83.9)	(122.6)	2.263	0.639
200	124.2	124.2	82.47	164.9	2.285	0.776
(300)	..	..	(80.3)	(240.9)	2.309	0.982

TABLE VI.—IONIZATION OF $TlNO_3$ AT 18° AND 25°.

Conc. $\times 10^3$.	$\Lambda_{18°}$.	100γ.	$(C\gamma)\times 10^3$.	$K=\frac{(C\gamma)^{1.55}}{C(1-\gamma)}$.	$k=\frac{(C\gamma)(\gamma)}{(1-\gamma)}$.
0	(127.7)	..	..	..	..
10	118.38	92.7	9.27	0.967	0.1176
(28.55)	..	(88.0)	(25.12)	0.965	0.1843
50	107.93	84.52	42.25	0.958	0.2307
(67.1)	..	(82.4)	(55.30)	0.954	0.2590
100	101.91	79.24	79.24	0.947	0.3026
(166.0)	..	(74.7)	(124.0)	0.937	0.366
(220.0)	..	(71.9)	(158.2)	0.928	0.404
(300.0)	..	(68.7)	(206.1)	0.921	0.452

made by Stewart[1] $\Lambda_{25^\circ} = 116.4$. since the corresponding degree of ionization, $116.4/146.8 = 0.793$, is practically the same as that given in the table, 0.7924.

Discussion of the Solubility Results with Thallous Chloride in the Presence of Other Salts.—The solubility values of thallous chloride in the presence of thallous sulfate, potassium nitrate, and potassium sulfate (Table II) are summarized in the last three columns of Table VII. The earlier results of A. A. Noyes[2] are also presented in this table, but the original numbers have been diminished by 0.3 per cent., since, as pointed out above, the corresponding solubility of thallous chloride exceeds our present value by this amount. The numbers in the third column headed KCl are mean values from the three sets of experiments in which the added salts were potassium, sodium, and ammonium chlorides; and no regular deviations from salt to salt were observed. Similarly the numbers in the fourth column are mean values from experiments with the chlorides of barium, calcium, magnesium, manganese, zinc and copper as in this case also the deviations of the values of the separate salts from the mean values are irregular. An examination of the original data shows, however, that the error in some of the individual results is over 1 per cent. The concentrations are all in milliequivalents per liter.

TABLE VII.—SOLUBILITY OF THALLOUS CHLORIDE IN THE PRESENCE OF OTHER SALTS.

Conc. of added salt.	HCl.	KCl.	$BaCl_2$.	$TlNO_3$.	Tl_2SO_4.	KNO_3.	K_2SO_4.
10	16.07	16.07	16.07	16.07	16.07	16.07	16.07
20	.	.	.	.	10.34	17.16	17.79
25	8.66	8.69	8.98	8.80	.	.	.
50	5.83	5.90	6.18	6.24	6.77	18.26	19.42
100	3.83	3.96	4.16	4.22	4.68	19.61	21.37
200	2.53	2.68	2.82	.	.	.	.
300	.	.	. .	.	.	23.13	26.00
1000	.	.	.	.	.	30.72	34.16

These results are presented graphically in the accompanying diagram, but the HCl and $TlNO_3$ curves have not been drawn since they would lie close to the KCl and $BaCl_2$ curves respectively.

The solubility of thallous chloride is seen to increase in the presence of potassium nitrate and of potassium sulfate, the salts without a common ion. This was to be expected on account of the formation of un-ionized thallous nitrate and thallous sulfate by metathesis. The greater increase of solubility in the potassium sulfate solutions corresponds, moreover, to the fact that thallous sulfate is less ionized than thallous nitrate (Table III and VI).

The great decrease in the solubility of thallous chloride produced by

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[1] Article II of this series, Table XII, footnote.

[2] A. A. Noyes, *Z. physik. Chem.*, 9, 609–18 (1892).

the addition of salts with a common ion is in qualitative agreement with the principle of the constancy of the ionic solubility product, $(Tl^+)(Cl^-)$ = const. The relative solubilities at a given concentration of added salt are also in agreement with this principle. Thus the ionization values of the three chlorides increase in the order $BaCl_2$, KCl and HCl[1] and the solubilities of thallous chloride decrease in the same order. Similarly the ionization values increase and the solubilities decrease in the order

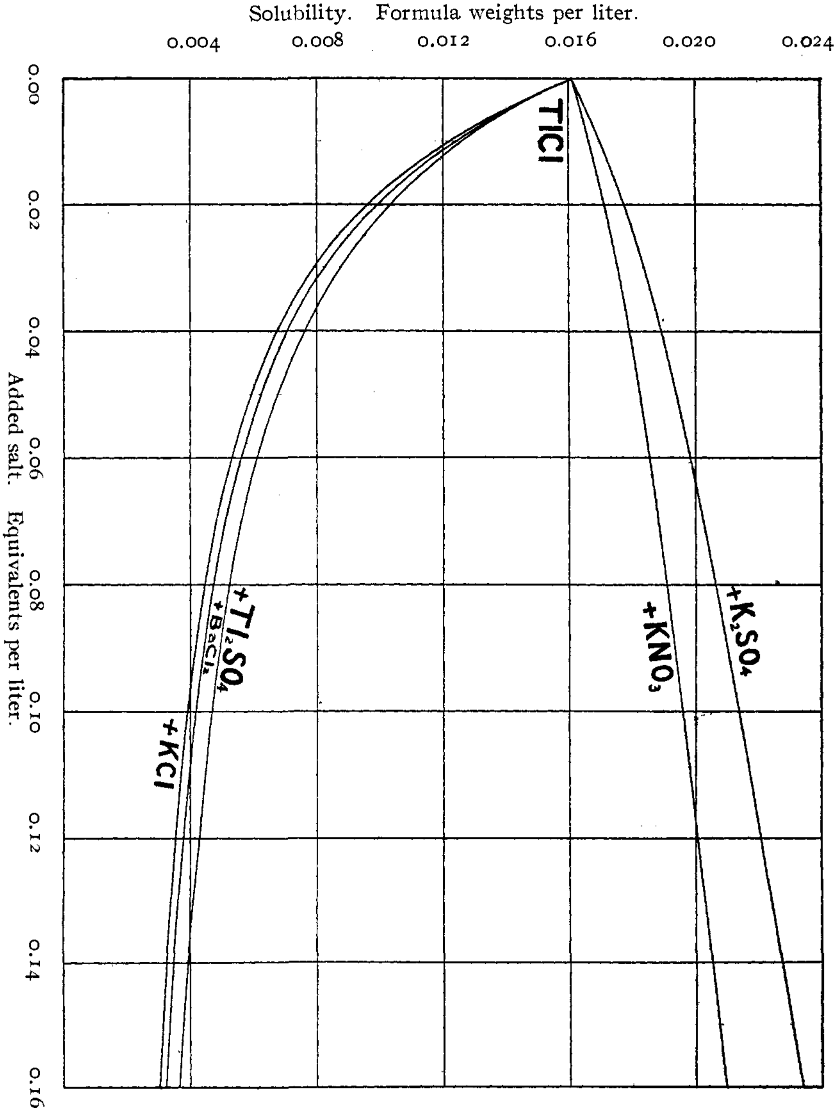

Fig. 1.

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[1] Bray and Hunt, This Journal, **33**, 787 (1911).

Tl_2SO_4, $TlNO_3$ and KCl. The striking agreement between the results obtained by Noyes with the three uni-univalent salts, KCl, NH_4Cl and NaCl, and with the six uni-bivalent salts indicates that the salts in each group are ionized to almost the same extent. This is in agreement with the results of conductance measurements, since in 0.1 normal solutions after correcting for viscosity the ionization values of KCl and NaCl differ by only 1 per cent. and those of $BaCl_2$, $CaCl_2$ and $MgCl_2$ differ by a slightly less amount.

With regard to the relative effect of HCl and KCl, if we accept the view that dilute solutions of these substances are equally ionized,[1] then the smaller solubility in the acid solution may be referred to a "salting out" effect of the hydrochloric acid, and we may say that hydrochloric acid is a poorer solvent for thallous chloride than is potassium chloride. In agreement with this view is the fact that at small concentrations of the two added substances the solubility curves practically coincide although the corresponding ionization values calculated from conductance measurements differ by considerable amounts.

The quantitative discussion of these results is presented in the following article, but it may be pointed out here that the different curves for salts with a common ion seem to lie somewhat more closely together than is to be expected from the widely different ionization values. Thus in the 0.1 normal salt solutions, where the concentrations of thallous chloride are small (0.0040 to 0.0047) in comparison with those of the added salts, the ratio of the concentrations of Tl^+ in the $TlNO_3$ and Tl_2SO_4 solutions is approximately equal to the ratio of their ionization values $0.792 : 0.614 = 1.29 : 1$, and similarly the ratio of the Cl^- values in KCl and $BaCl_2$ solutions[2] is approximately $0.856 : 0.751 = 1.14 : 1$, while the ratios of the solubilities of the TlCl are much smaller, $4.68/4.22 = 1.11$ and $4.16/3.96 = 1.05$ respectively. Since the concentration of the unionized TlCl is small (about 0.001) and nearly the same in each of these solutions, it is evident that the values of the ionic solubility product $(Tl^+)(Cl^-)$ must be smaller in the Tl_2SO_4 and $BaCl_2$ solutions than those in the $TlNO_3$ and KCl solutions. Conversely, if we assume that the ionization values for $TlNO_3$ are correct and that the solubility product has the same value in 0.1 N Tl_2SO_4 and $TlNO_3$ solutions, we would calculate from the solubility data that the concentration of Tl^+ in Tl_2SO_4 is larger than that assumed in the above calculations. Similarly, starting with 0.1 N KCl, the concentration of Cl^- in 0.1 N $BaCl_2$ would be found to be larger than that derived from conductance measurements.

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[1] Lewis and Sargent, THIS JOURNAL, **31**, 364 (1909); see also *Ibid.*, **33**, 792.

[2] Kohlrausch and Grüneisen, *Landolt-Börnstein-Meyerhoffer, Tabellen*, 745.