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THE EFFECT OF SALTS ON THE SOLUBILITY OF OTHER SALTS. II.

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A. SOLUBILITY OF POTASSIUM PERCHLORATE IN THE PRESENCE OF POTASSIUM CHLORIDE AND OF POTASSIUM SULFATE. Experiments by C. R. Boggs.

B. SOLUBILITY OF THALLOUS CHLORATE AND THALLOUS SULFATE IN THE PRESENCE OF EACH OTHER. Experiments by F. S. Farrell.

C. SOLUBILITY OF THALLOUS SULFATE IN THE PRESENCE OF THALLOUS NITRATE, SODIUM SULFATE AND SULFURIC ACID. Experiments by M. A. Stewart.

A. Solubility of Potassium Perchlorate in the Presence of Potassium Chloride and of Potassium Sulfate.

EXPERIMENTS BY C. R. BOGGS.

Preparation of the Salts and Solutions.—The samples of potassium chloride and sulfate used were obtained by crystallizing the commercially pure salt from hot water. They were ignited in porcelain crucibles over a gas flame.

The potassium perchlorate employed was prepared by recrystallizing the commercially pure salt from boiling water six times. The presence of potassium chlorate was tested for by treating about half a gram of it for fifteen minutes with a zinc-copper couple in boiling-hot concentrated solution and adding silver nitrate. There was a faint turbidity after the fifth crystallization, but none after the sixth. Its purity was also confirmed by rotating portions of it with two successive quantities of water, with the result that the same solubility values were obtained, as will be seen from Table I.

The water used was ordinary distilled water, but its specific conductance did not exceed 5×10^{-6}. Approximately 0.1 and 0.2 normal solutions of potassium chloride and of potassium sulfate were prepared by dissolving the weights of the salts given below in a true liter of water at 25°. An approximately 0.05 normal solution of each salt was prepared by weighing out 251.86 g. of the 0.1 N KCl solution, or 252.18 g. of the 0.1 N K_2SO_4 solution, and adding in each case 250 g. water. All weights are those in air (uncorrected for air buoyancy). The compositions[1] by weight of these solutions were as follows:

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[1] The corresponding concentrations of these solutions expressed in equivalents per liter of solution at 25° were calculated (using 1910 atomic weights) for use in connection with the conductance measurements given below:

	KCl.	K_2SO_4.
Approx. 0.05 N	0.04998 N	0.0500 N
Approx. 0.1 N	0.0998 N	0.0999 N
Approx. 0.2 N	0.1991 N	0.1995 N

To enable these calculations to be made the densities of the 0.2 and 0.1 normal solu-

	KCl. Grams.	K_2SO_4. Grams.	H_2O. Grams.
Approx. 0.05 *N*	1.8712	2.1872	500.0
Approx. 0.1 *N*	7.456	8.715	996.1
Approx. 0.2 *N*	14.912	17.429	996.1

Method of Determining the Solubility.—The bottles containing the solutions to be saturated were rotated by means of the apparatus previously described[1] for four hours in a thermostat kept within 0.02° or 25°. The temperature was determined with a thermometer that had been compared with a Reichsanstalt standard. These solutions were allowed to settle, while standing in the thermostat, and 100.2 cc. portions were drawn out of each bottle through a cotton filter which had first been washed with a little of the same solution. The portions of the saturated solutions were run into platinum dishes and weighed. Saturation was reached in each case, since the values of the solubility were obtained from experiments in which equilibrium was approached both from above and below 25°, and the results by these two processes check within the error of the determination. The solutions were evaporated to dryness on the steam bath, the residues were heated for fifteen minutes as 200°, then cooled in a desiccator for half an hour, and weighed as quickly as possible. The residues were again heated to 200° and weighed, this process being repeated till the weights were constant within 0.5 milligram.

The weight of water in the portion of solution taken was next determined by difference and the corresponding amount of potassium chloride or potassium sulfate calculated from the composition of the original solution. Finally by subtracting this weight from the total weight of the residue the weight of the potassium perchlorate was determined.[2]

The Solubility Data.—The experimental data are given in Table I.

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tions were measured by using a Mohr-Westphal balance, which had been adjusted at 25°, and the corresponding values for the 0.05 normal solutions were determined by extrapolation. The reduction from 25°/25° to 25°/4° was made by multiplying by the factor 0.9971, the density of water at 25°. The values obtained were as follows:

Solution. KCl.	Density referred to water.		Solution. K_2SO_4.	Density referred to water.	
	25°/25°.	25°/4°.		25°/25°.	25°/4°.
0.05 *N*	(1.0023)	(0.9994)	0.05 *N*	(1.0034)	(1.0005)
0.1 *N*	1.0046	1.0017	0.1 *N*	1.0069	1.0040
0.2 *N*	1.0093	1.0064	0.2 *N*	1.0138	1.0109

[1] *Z. physik. Chem.*, 9, 606 (1892). Ostwald-Luther, *Physiko-Chemische Messungen* (1902), page 281.

[2] This method was tested by dissolving a weighed amount of perchlorate in the 0.1 normal solution of potassium chloride:

$KClO_4$ taken	0.6926 gram	1.2580 grams.
$KClO_4$ found	0.6914 gram	1.2608 grams.

It will be noted that one weight decreased about 0.2 per cent. while the other increased by about the same amount.

The numbers are the weights in grams contained in 100.2 cc. of the saturated solutions. The third column shows the mean values of the weights of solution taken in each set of experiments; the variation of the separate values from the mean did not exceed 0.1 per cent. The mean values of the total weights of the salts are printed in italics.

TABLE I.—SOLUBILITY DATA FOR POTASSIUM PERCHLORATE.

No. Solvent.	Mean weight of solution.	Total weight of the salts. Equilibrium from		Weight of water.	Weight of KCl or K_2SO_4.	Weight of $KClO_4$.
		Oversatd.	Undersatd.			
1. Water	..	2.0568	2.0560	..	..	..
	..	2.0567	2.0568	..	..	..
	..	*2.0566*		..	..	2.0566
2. KCl solution approx. 0.05*N*	..	..	2.1494	..	..	..
	..	2.1538	2.1490	..	..	..
	101.42	*2.1515*		99.27	0.3715	1.7800
3. KCl solution approx. 0.1 *N*	..	..	2.3025	..	..	..
	..	2.2977	2.3034	..	..	..
	..	2.3044	2.3010	..	..	..
	101.45	*2.3018*		99.15	0.7421	1.5597
4. K_2SO_4 solution approx. 0.05 *N*	..	2.2593	2.2625	..	..	..
	..	2.2587	2.2598	..	..	..
	101.47	*2.2601*		99.21	0.4339	1.8262
5. K_2SO_4 solution approx. 0.1 *N*	..	2.5053	2.5060	..	..	..
	..	2.5075	2.5057	..	..	..
	101.55	*2.5061*		99.04	0.8665	1.6396

The final values of the solubility of the perchlorate and of the concentration of potassium chloride or potassium sulfate in these saturated solutions are given in Table II, in equivalents per liter. The International atomic weights for 1910 were used.

TABLE II.—FINAL VALUES OF THE SOLUBILITY OF POTASSIUM PERCHLORATE AT 25°
(EQUIVALENTS PER LITER).

No.	Salt added.	Concentration of salt.	Solubility of $KClO_4$.
1	none	0	0.1481
2	KCl	0.04973	0.1282
3	KCl	0.09933	0.1123
4	K_2SO_4	0.04970	0.1315
5	K_2SO_4	0.09922	0.1181

Discussion of the Solubility Data.—From an examination of Table I, it will be seen that there is no systematic difference between the results obtained by approaching equilibrium from the two opposit directions; also that the divergence of the separate values from the mean does not exceed 0.15 per cent., except in one instance. It may also be mentioned that the value (0.1481) of the solubility in pure water here obtained and that (0.1478) derived by interpolation from the results of Noyes and Sammet[1] at 10, 20 and 30° agree within the errors of experiment and interpolation.

It will be observed that potassium sulfate, in correspondence with its smaller ionization, has a somewhat less effect than potassium chloride in reducing the solubility of the perchlorate. The quantitative discussion of the solubility effects will be presented in a later article. The conductance measurements, which are needed for checking these calculations and for determining the ionization values involved, are presented in the following section.

Conductance Measurements.—All conductance measurements were made at 25° by the usual Kohlrausch method. A cylindrical cell with horizontal electrodes was used. The conductance capacity was determined by means of a potassium chloride solution, 0.1 normal at 18°, made by dissolving 3.715 grams potassium chloride (weighed in air) in 500 grams of solution.[2] The specific conductance of this solution at 25° was taken as 0.01289 in accordance with the value found by Kohlrausch and Maltby at 18° (0.01120) and Déguisne's temperature coefficients. From this value (0.01289) the specific conductance at 25° of a potassium chloride solution, 0.1 normal at 25° (using 1910 atomic weights), was calculated to be 0.01290, which agrees perfectly with the value found in this laboratory by Mr. A. C. Melcher.

The following table contains the results of the conductance measurements with the saturated solutions. C denotes the equivalent concentration, and L the specific conductance. The equivalent conductance Λ of the $KClO_4$ solution is also included in the table.

TABLE III.—CONDUCTANCE OF SOLUTIONS SATURATED WITH $KClO_4$.

Exp. No.	C_{KClO_4}.	C_{KCl}.	$C_{K_2SO_4}$.	L.	Λ.
1	0.1481	...	...	0.01650	111.4
2	0.1282	0.04973	...	0.02029	..
3	0.1123	0.09933	...	0.02484	..
4	0.1315	...	0.04970	0.01946*	..
5	0.1181	...	0.09922	0.02263**	..

* Mean of two concordant determinations.

** Mean of two independent determinations which gave 0.02265 and 0.02260.

The conductance at 25° of the approximately 0.1 and 0.2 normal potassium chloride and sulfate solutions was also measured. In Table IV these results are compared with the more recent (unpublished) values obtained by Mr. Melcher, and it is evident that the error in the earlier measurements does not exceed 0.25 per cent.

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[1] Noyes and Sammet, *Z. physik. Chem.*, 43, 534 (1903).

[2] Kohlrausch and Holborn, Leitvermögen (1898), page 77.

TABLE IV.—CONDUCTANCE OF KCl AND K_2SO_4 SOLUTIONS.

Exp. No.	Salt.	C.	L.	Λ(Boggs).	Λ(Melcher).
1............	KCl	0.0998	0.01291	129.3	129.0
2............	K_2SO_4	0.0999	0.01096	109.7	109.9
3............	K_2SO_4	0.1995	0.02028	101.7	101.4

Ionization Values.—In order to calculate the degree of ionization of potassium perchlorate in its saturated solution the value at 25° of Λ_0, the conductance at zero concentration, was derived by interpolation from the values of Noyes and Sammet at 10°, 20° and 30° and found to be 143.0. The degree of ionization (γ) is therefore $111.4/143.0 = 0.779$ at the concentration $C = 0.1481$.

In order to check this result Noyes and Sammet's conductance measurements at 20° and 30° were plotted in the familiar $1/\Lambda$, $(C\Lambda)^{n-1}$ diagram and n was assured to be 1.50; the degree of ionization at the concentration 0.1481 was then calculated to be 0.779 at 30° and 0.776 at 20°. Accordingly the exponent $n = 1.50$ was used and the value

$$K = (C\gamma)^n/C(1\text{-}\gamma) = 1.194$$

calculated. From this function the percentage ionizations (100γ) at the concentrations 0.1 and 0.2 normal were calculated and are given in Table V.

Table V also contains ionization values for potassium chloride and potassium sulfate derived from Mr. Melcher's conductance data by means of the Λ_0 values, 150.6 and 154.8 respectively.

TABLE V.—IONIZATION VALUES OF KCl, $KClO_4$ AND K_2SO_4 AT 25°.

	KCl.		$KClO_4$ (calc.).		K_2SO_4.	
Equiv. conc.	Percent. ioniz.	Ion-conc.	Percent. ioniz.	Ion-conc.	Per cent. ioniz.	Ion-conc.
0.4	78.9	0.3156	..	..	60.1	0.2404
0.2	82.47	0.1649	75.5	0.1510	65.5	0.1310
0.1	85.65	0.08565	80.8	0.0808	71.0	0.0710
0.05	88.75	0.04437	..	..	76.33	0.03817

B. Solubility of Thallous Chlorate and Thallous Sulfate in the Presence of Each Other.

EXPERIMENTS BY F. S. FARRELL.

In this part are presented the results of experiments on the solubility at 20° of thallous sulfate and thallous chlorate when each salt is present in water alone and when both are present together as solid phases. Conductance measurements with the saturated solutions and with very dilute solutions of these salts are also described.

Preparation of the Salts.—The thallous sulfate was made from metallic thallium by digesting the finely cut metal with fairly strong sulfuric acid (1.65 sp. gr.), diluting the solution and precipitating the salt with alcohol. It was then recrystallized four times from boiling water till the last traces of acid had disappeared.

The thallous chlorate was made by mixing hot, neutral solutions containing equivalent quantities of barium chlorate and thallous sulfate. The barium sulfate was filtered from the hot solution. The salt which crystallized out on cooling was then purified by four successive crystallizations.

Method of Determining the Solubility.—The solubility determinations were made by rotating from two to three hours 5–6 grams of each of the finely crystallized but not powdered salts with water in oil-sample bottles of about 125 cc. capacity. The thermostat was kept at 20° (± 0.03°), the thermometer used having been compared with two independently standardized ones. In order to insure the attainment of equilibrium, saturation was approached from both the under- and the supersaturated side. Supersaturation was reached by shaking the mixtures at a higher temperature. The contents of the bottle were allowed to settle, and one or two 50 cc. portions were drawn out through a filter consisting of a piece of cotton wool held over the end of the pipet by a piece of rubber tubing.

When only one of the salts was present, the analysis was made by evaporating the portion in a platinum dish on a steam bath, and drying the residue to a constant weight at 150–160° in the case of the sulfate and 130° in the case of the chlorate.

When both sulfate and chlorate were present, two 50 cc. portions of the solution were separately analyzed in the following manner: One portion was evaporated to dryness in a weighed platinum dish and dried at 130° till its weight was constant. The residue was dissolved in 400 cc. water, the solution heated to boiling and an excess of 0.1 normal barium chloride solution added. The precipitated barium sulfate was allowed to settle out on the steam bath, and it was then filtered out, washed, dried, and ignited to a constant weight in a platinum crucible.

The other portion was transferred to a 100 cc. Erlenmeyer flask, the bottom of which was covered with chloride-free metallic zinc. The flask was now placed on the steam bath and enough sulfuric acid (sp. gr. 1.20) added, from time to time, to keep up a moderate evolution of gas. Trial analyses[1] showed that the time necessary for complete reduction is about 8–10 hours, but for security the reduction was continued for at least twelve hours. The zinc was then filtered off and washed,

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[1] The results of these trial analyses were as follows:

Expt. No.	Time of reduction in hours.	Wt. of $TlClO_3$ taken.	Wt. of AgCl obtained.	Percent. of Cl in $TlClO_3$.	
				Calc.	Found.
1	4	1.9200	0.9421	12.32	12.13
2	4	1.9343	0.9548	12.32	12.21
3	8–10	1.9220	0.9576	12.32	12.32
4	8–10	1.9380	0.9637	12.32	12.29

and a slight excess of silver nitrate added to the filtrate. The silver chloride was filtered off, dried at 130°, and weighed in a platinum Gooch crucible.

The Solubility Data.—The following tables contain the data of the solubility experiments. The letters *u* and *s* denote that equilibrium was approached from undersaturation and supersaturation respectively. The International atomic weights for 1910 were employed in all the calculations.

TABLE VI.—SOLUBILITY DATA FOR Tl_2SO_4 AND $TlClO_3$ AT 20°.

Cc. of solution.	Grams of Tl_2SO_4.	Grams of Tl_2SO_4 per liter.	Cc. of solution.	Grams of $TlClO_3$.	Grams of salt per liter.
50.07	2.4341	48.61 *u*	50.01	1.9200	38.39 *u*
50.07	2.4294	48.50 *u*	50.13	1.9343	38.59 *s*
49.97	2.4292	48.61 *s*	50.01	1.9220	38.41 *u*
49.97	2.4263	48.56 *s*	50.13	1.9380	38.67 *s*
49.97	2.4325	48.68 *s*	50.07	1.9220	38.38 *u*
			50.13	1.9330	38.57 *s*
Mean, 48.59; a. d. = 0.05			49.97	1.9219	38.47 *u*
			50.01	1.9332	38.65 *s*
			50.07	1.9266	38.44 *u*
			49 97	1.9312	38.65 *s*
					Mean 38.51 a. d. = 0.10

TABLE VII.—DATA ON THE SOLUBILITY OF $TlClO_3$ AND Tl_2SO_4 WHEN PRESENT TOGETHER AT 20°.

Expt. No.	Cc. of solution.	Weight of both salts.	Weight of $BaSO_4$.	Cc. of solution.	Weight of AgCl.
1	50.07	3.2477	0.7984	49.97	0.7544
2	50.13	3.2464	0.7997	50.01	0.7504
3	50.13	3.2527	0.7999	50.01	0.7594
4	50.07	3.2380	lost	49.97	0.7594
5	50.13	3.2529	0.8014	50.01	0.7596
6	50.07	3.2498	0.7993	49.97	0.7585
7	50.13	3.2427	0.8009	50.01	0.7566

TABLE VIII.—DATA ON THE SOLUBILITY OF $TlClO_3$ AND Tl_2SO_4 WHEN PRESENT TOGETHER (EXPRESSED IN GRAMS PER LITER).

Expt. No.	Total salt.	Tl_2SO_4 (by anal.).	Tl_2SO_4 (by diff.).	$TlClO_3$ (by anal.).	$TlClO_3$ (by diff.).
1	64.86	34.43	34.59*	30.27*	30.43
2	64.76	34.44	34.67*	30.09*	30.32
3	64.88	34.45	34.43	30.45	30.43
4	64.67*	lost	34.19*	30.48	lost
5	64.89	34.52	34.43	30.46	30.37
6	64.90	34.47	34.36	30.44	30.43
7	64.69	34.51	34.35	30.34	30.18
Mean,	64.83	34.47	34.39	30.43	30.36

* Omitted in calculation of the mean.

SUMMARY.

	Tl_2SO_4.	$TlClO_3$.
Mean weight (by analysis)	34.47	30.43
Mean weight (by difference)	34.39	30.36
Final weight	34.43	30.40

TABLE IX.—FINAL VALUES OF THE SOLUBILITIES OF THALLOUS CHLORATE AND THALLOUS SULFATE AT 20° (EQUIVALENTS PER LITER).

$TlClO_3$	0.1340	0.0	0.1058
Tl_2SO_4	0.0	0.1928	0.1366

The summary of the results in Table IX shows to what extent the solubility of each of the salts in water alone is reduced by the presence of the other salt. An examination of the experimental data indicates that the results are probably accurate to about 0.1 per cent. This conclusion is confirmed by the fact that an entirely independent determination of the solubility of thallous sulfate in this laboratory by Dr. H. T. Kalmus[1] gave the value 0.09642 mol. per liter at 20°, which is identical with the present value.

Conductance Measurements.—The conductance measurements were made in duplicate at 20° by the usual bridge method, employing a U-shaped resistance cell of 50 cc. capacity for the saturated solutions and a cylindrical cell for the dilute ones. The saturated solutions and also 0.001 normal solutions of the separate salts were measured, and all these solutions were prepared by dissolving weighed amounts of the salt in calibrated flasks. The results of the measurements are given in Table X.

TABLE X.—CONDUCTANCE OF SOLUTIONS OF THALLOUS SULFATE AND THALLOUS CHLORATE AT 20°.

Concs. Tl_2SO_4.	(Milli-equiv.). $TlClO_3$.	Specific cond. $\times 10^4$.			Equiv. cond.
		Separate values		Mean.	
192.8	0.0	149.5	149.3	14.94	77.5
1.001	0.0	1.330	1.332	1.331	133.0
0.0	134.0	135.5	135.3	135.4	101.0
0.0	1.001	1.241	1.242	1.242	124.1
136.6	105.8	200.7			

A check on these results is furnished in the case of thallous sulfate by a more recent, extended series of measurements at 18° and 25° made by Mr. F. L. Hunt[2] in this laboratory. From these results, by assuming a slightly smaller degree of ionization at 20° than at 18°, the values of the equivalent conductance at 0.001 and 0.1928 normal were calculated to be 133.0 and 77.43 respectively, in good agreement with the present results. Further excellent checks are furnished by independent de-

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[1] *Physics Theses M. I. T.* (1904).

[2] THIS JOURNAL, **33**, 802 (1911).

terminations of the conductance of a saturated solution at 20° by H. T. Kalmus[1] and by W. H. Whitcomb[2] in this laboratory; after correcting to 1910 atomic weights the values are 77.6 and 77.44 respectively.

Ionization Values.—The ionization values for thallous sulfate at 20°, given in Table XI, were calculated from the data of Hunt at 18° and 25° by extrapolating to concentrations higher than 0.2 normal by means of a $1/\Lambda$, $(C\Lambda)^{0.5}$ plot. These values are almost identical with those obtained at an earlier date by means of a similar plot based on the two available measurements at 20° (Table X). The values of Λ_0 were assumed to be 134.4, 140.4 and 156.2 at 18°, 20° and 25° respectively.

Ionization values for thallous sulfate (Table XI) were also obtained by means of a $1/\Lambda$, $(C\Lambda)^{0.5}$ plot based on the above conductance data at 20° (assuming $\Lambda_0 = 126.2$ at 20°), but there is at present no means of checking the calculations as in the case of thallous sulfate. It is interesting to note that thallous chlorate is slightly less ionized than potassium chlorate or potassium nitrate, but is more highly ionized than thallous nitrate.

TABLE XI.—IONIZATION VALUES OF Tl_2SO_4 AND $TlClO_3$ AT 20°.

Equiv. conc.	Percentage ionization.	Ion conc.	Equiv. conc.	Percentage ionization.	Ion conc.
0.20	54.8	0.1096	0.1340	80.1	0.1073
0.25	52.5	0.1313	0.1844	77.6	0.1431
0.30	50.7	0.1521	0.2421	75.4	0.1826
0.35	49.2	0.1720			
0.40	48.0	0.1920			

C. Solubility of Thallous Sulfate in the Presence of Thallous Nitrate Sodium Sulfate and Sulfuric Acid.

EXPERIMENTS BY M. A. STEWART.

In this part experiments are described on the solubility of thallous sulfate at 25° in water and in the following solutions: 0.1 formal $TlNO_3$, 0.2 and 0.5 formal Na_2SO_4, 0.1 formal $NaHSO_4$, and 0.1 and 0.5 formal H_2SO_4. The effect of the last two substances was investigated in connection with the research on the ionization relations of sulfuric acid,[3] and the discussion of the results will be postponed until after the solubility relations of other uni-bivalent salts have been examined.

The conductivity of the saturated solutions was also measured; and the density of the solutions before and after saturation was determined in order to obtain the change in concentration of the original solute due to the increase in volume attending the saturation with thallous sulfate.

Preparation of the Substances and Solutions.—The thallous sulfate was prepared substantially as described in the previous article by F. S. Farrell.

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[1] *M. I. T. Physics Theses* (1904).

[2] *M. I. T. Chemical Theses* (1906).

[3] THIS JOURNAL, **32**, 1133 (1910).

Two separate preparations designated below, Sample I and Sample II, were used.

The water used in this investigation was conductivity water with a specific conductance between 1 and 2 × 10^{-6}. All concentrations are expressed in formula weights per liter referred to the International atomic weights for 1907 but are only 0.04 to 0.06 per cent. smaller than if 1911 atomic weights had been used.

The 0.2 formal sulfate solution was prepared by weighing out the ignited salt and making it up to the proper volume at 25°. The 0.05 formal solution was made from this one by dilution. The sodium sulfate was purified by heating a solution saturated at 33° to boiling and filtering out the precipitate, which was washed with a little hot water and heated for two hours at a dull red heat. Tests made upon it showed no trace of potassium or chloride.

The 0.1 F $NaHSO_4$ solution was one of the solutions used in the transference measurements.[1]

The sulfuric acid solutions were made by diluting a 0.2 formal acid, which had been prepared from Baker and Adamson's chemically pure sulfuric acid, and which had been standardized by titration with well ignited sodium carbonate.

The thallium nitrate was prepared by dissolving the metal, cut up into small pieces, in hot nitric acid (1.10 sp. gr.). On cooling, the greater part of the thallous nitrate crystallized out, and the remainder was precipitated by the addition of alcohol. The salt was filtered off, washed with alcohol, recrystallized twice from hot water, washed once with cold water and dried for three hours at 120–140°. The thallium nitrate solution was prepared by making up a weighed amount of thallium nitrate to the proper volume at 25°. The thallous content of the solution was also determined by two titrations with potassium permanganate by the method described below, the results obtained being 0.10013 and 0.10009, showing the absence of thallic salt.

Description of the Experiments.—The solutions were saturated with thallous sulfate by placing an excess of it with the desired solution in tightly stoppered bottles, and rotating them for four to twenty hours in a thermostat at 25° ± 0.02°. In some cases saturation was approached from a higher and in other cases from a lower temperature.

The amount of thallous sulfate dissolved was determined as follows: A sample from the bottle was drawn into a clean, dry pipet (of 14.754 cc. capacity) through a cotton plug placed in a cap on the end of the pipet, and the liquid was made up to 500 cc.; 100 cc. of this solution were diluted to about 500 cc., 40 cc. of HCl (1.20) added, and the mixture was

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[1] THIS JOURNAL, **32**, 1151 (1910).

titrated with dilute potassium permanganate solution, whereby the thallous is converted to the thallic salt. The permanganate solution was standardized against thallous sulfate that had been heated at 230° for four hours.

This titration requires certain precautions. After many trials the proper conditions were found to be as follows:

1. The concentration of hydrochloric acid[1] in the solution to be titrated must be that produced by the addition of between 38 cc. and 42 cc. of acid of specific gravity 1.20 to 500 cc. of the solution. Much less than 38 cc. is likely to allow a brown precipitate of hydrated manganese oxides to separate and therefore mask the end point. More than 42 cc. causes the end point to fade away very rapidly. 2. The solution must be diluted enough to insure the non-precipitation of thallous chloride on addition of the hydrochloric acid. 3. The standard potassium permanganate solution used, must be dilute, containing not more than 2.0 g. $KMnO_4$ per liter, best 1.0 to 1.5 g. 4. The permanganate solution must be run in very slowly (drop by drop) and the solution must be constantly and thoroughly stirred; for, otherwise, the hydrochloric acid will react with the permanganate, liberating chlorine, before it is all used up by the thallium. With these precautions, the method gives concordant results.

The conductance of the solutions was measured in a specially made U-shaped cell 8 cc. in volume and of suitable resistance. The conductance capacity was determined with a potassium chloride solution (0.02 normal at 25°), the specific conductance of which was assumed to be 0.002770.[2]

The Experimental Data.—The experimental data relating to the saturated solutions are presented in Table XII and the results summarized in Table XIII. The solubilities at 25° are expressed in formula weights Tl_2SO_4 per liter, and the symbols S_I and S_{II} refer to Sample I and Sample II respectively. In almost every case two or three separate portions of the same solution were titrated, and the separate results differed from the mean by less than 0.1 per cent. Only the mean value is given in the table. When the letter *s* is attached to the number, it indicates that equilibrium was approached from supersaturation. C_0 and C denote the formal concentrations of the salt solution before and after saturation with thallous sulfate; D_0 and D denote the corresponding densities. L is the specific conductance of the saturated solution.

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[1] Sulfuric acid can not be used, because, even a large amount of it will not prevent the precipitation of the brown precipitate.

[2] This value is a mean between that calculated from the results of Kohlrausch and Maltby at 18° and the temperature coefficient of Déguisne and corrected for the expansion of the solution between 18° and 25° (0.002767), and a recent result obtained by Mr. A. C. Melcher, of this laboratory (0.002773).

TABLE XII.—EXPERIMENTAL DATA.

S_I.	S_{II}.	$L \times 1000$.	D.	C.
		Water		
0.1084*	0.1084			
0.1083*	....			
0.1084*s	0.1081 s			
0.1085*s	0.1085*s			
(0.1081*)	(0.1081*)			
Mean, 0.1083				
	Na_2SO_4 soln.:	$C_0 = 0.2000$;	$D_0 = 1.0223$.	
0.1174*	0.1174*	42.08	1.0754	
0.1173*	....	42.09	1.0754	
0.1172*s	0.1173†s	42.15	1.0755	
0.1173*s	....	42.13	..	
Mean, 0.1173		42.11	1.0754	0.1988
	Na_2SO_4 soln.:	$C_0 = 0.04995$;	$D_0 = 1.0035$.	
0.1080*	0.1080*	24.20	1.0531	
0.1081*	....	24.21	1.0531	
0.1081*s	....	24.23	1.0531	
0.1080*s	....	..	1.0531	
Mean, 0.1080		24.21	1.0531	0.04971
	$NaHSO_4$ soln.:	$C_0 = 0.1015$;	$D_0 = 1.0066$.	
0.1161*	0.1161	39.67	1.0594	
0.1161	0.1161	39.66	..	
0.1162*s	0.1162	39.68	1.0597	
0.1161*s	0.1161 s	..	1.0597	
Mean, 0.1161		39.67	1.0596	0.10096
	H_2SO_4 soln.:	$C_0 = 0.09933$;	$D_0 = 1.0036$.	
0.1250*	0.1249*	53.52	..	
0.1249*	....	53.52	1.0604	
0.1249*s	....	53.52	1.0604	
0.1250*s	....	53.52	1.0604	
Mean, 0.1249		53.52	1.0604	0.09872
	H_2SO_4 soln.:	$C_0 = 0.04967$;	$D_0 = 1.0005$.	
0.1172†	0.1172*	35.27	1.0540	
0.1172*	0.1172	35.27	1.0540	
Mean, 0.1172		35.27	1.0504	0.04939

* Mean of two titrations of same solution.

† Mean of three titrations of same solution.

TABLE XII (*continued*).

$TlNO_3$ soln.:[1] $C_0 = 0.1000$; $D_0 = 1.0917$.

S_I.	S_{II}.	$L \times 1000$.	D.	C.
0.08365*	0.08363*	23.73	..	
0.08364	0.08362*	23.73	1.0581	
0.08367**s*	....	..	1.0582	
0.08368**s*	....	23.73	1.0582	
Mean, 0.08365		23.73	1.0582	0.09964

* Mean of two titrations of same solution.

TABLE XIII.—SUMMARY OF SOLUBILITY AND CONDUCTANCE DATA.

Solution.	1000 *L*.	Conc. Tl_2SO_4.
Water	..	0.1083
0.0996 *F* $TlNO_3$	23.73	0.08365
0.0497 *F* Na_2SO_4	24.21	0.1080
0.1988 *F* Na_2SO_4	42.11	0.1173
0.1010 *F* $NaHSO_4$	39.67	0.1161
0.0494 *F* H_2SO_4	35.27	0.1172
0.0987 *F* H_2SO_4	53.52	0.1249

The results (except in two cases) are presented in the order in which the measurements were made. The exceptions are the measurements of the solubility of each sample of thallous sulfate in pure water from undersaturation, which were made after all the other determinations had been completed. Since these two concordant values (0.1081) are 0.3 percent less than the mean solubility obtained in the initial measurements (0.1084), it is impossible to claim an absolute accuracy of better than 0.2 or 0.3 per cent. for the final results. The separate determinations in each series are, however, remarkably concordant, and it seems probable that the relative accuracy of the solubilities in the first three series (in water and in sodium sulfate solutions) is about 0.1 per cent.

An examination of the results (Table XIII) shows that the solubility of thallous sulfate is greatly lowered by the presence of thallous nitrate, a salt with a common univalent ion, which is in qualitative agreement with the principle of the constancy of the ionic solubility product. On the other hand, the addition of sodium sulfate, a salt with a common bivalent ion, does not produce the expected lowering. The solubility is reduced only 0.3 per cent. in the 0.1 normal sodium sulfate solution and is actually increased in the more concentrated solution. That the solubilities of other uni-bivalent salts are affected in a similar manner by the addition of salts with common bivalent ions has already been pointed out in Part B of the first article.

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[1] Measurements of the conductance of this 0.1 *F* $TlNO_3$ solution gave the results: L_{25} = 0.01163, 0.01165, 0.01163, 0.01165; mean, 0.01164.

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.

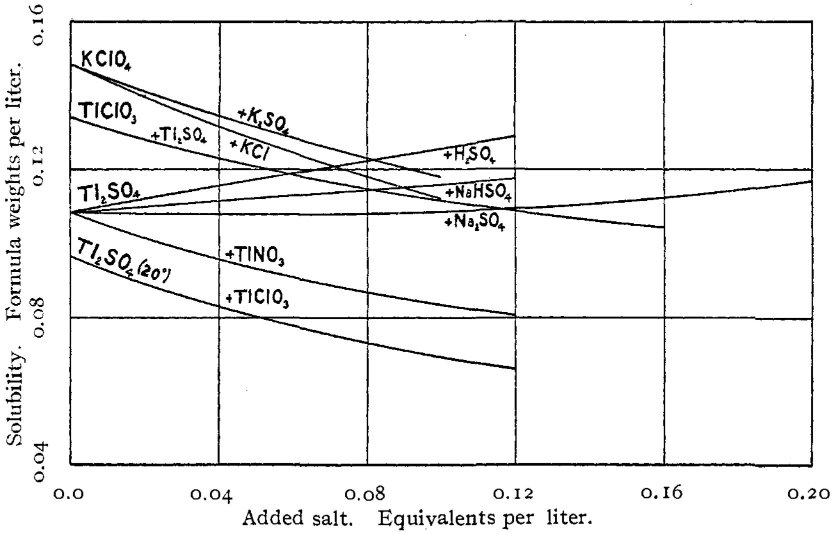

Fig. 1.

[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°.

By William C. Bray and W. J. Winninghoff.

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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 uni-bivalent 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).