[CONTRIBUTIONS FROM THE RESEARCH LABORATORY OF PHYSICAL CHEMISTRY OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY. NO. 75.]

THE EFFECT OF SALTS ON THE SOLUBILITY OF OTHER SALTS. IV. QUANTITATIVE DISCUSSION OF THE SOLUBILITY OF UNI-UNIVALENT SALTS IN THE PRESENCE OF OTHER SALTS.

BY WILLIAM C. BRAY.

Received September 22, 1911.

In the two preceding articles, a number of examples of the effect of salts on the solubility of uni-univalent salts were presented, and it was pointed out that the solubility-lowering produced by salts with a common ion was qualitatively in agreement with the principle of the constancy of the ionic solubility product. The increase of solubility of thallous chloride in the presence of potassium sulfate is also in qualitative agreement with this principle, and undoubtedly furnishes a typical illustration of the effect of salts without a common ion. In the present article these examples will be discussed quantitatively by the method outlined in the introductory article of this series.

1. The Solubility of Thallous Chloride in the Presence of Various Salts.[1]

The values of the degree of ionization (γ), as given by the conductance ratio Λ/Λ_0, and of the ionization function $k = \frac{(B^+)(A^-)}{(BA)} = \frac{(C\gamma)(\gamma)}{(1-\gamma)}$ for a single salt, given in Tables III to VI of the preceding article, were plotted against the equivalent ion-concentration, $(\Sigma i) = C\gamma$. In the case of barium chloride the values of γ were calculated from the conductance data of Kohlrausch and Grüneisen[2] at 18°. From these plots were derived the data presented in Tables I and II. The method of extrapolation by which the values of γ and k above 0.01 N (Σi) for thallous chloride and above 0.1 N for $TlNO_3$ and Tl_2SO_4 were obtained was explained in the preceding article.

TABLE I.— VALUES OF 100 γ FOR VARIOUS SALTS AT 25°.

$(\Sigma i.)$	KCl.	KNO_3.	$TlNO_3$.	TlCl.	$BaCl_2$.	K_2SO_4.	Tl_2SO_4.
0.01	93.7	93.2	92.4	91.0	87.6	85.9	81.7
0.02	91.7	90.7	89.25	86.95	83.8	81.3	74.8
0.03	90.3	88.85	86.9	83.95	81.2	78.1	70.2
0.05	88.2	86.05	83.2	79.4	77.8	73.9	64.0
0.07	86.65	83.9	80.4	75.9	75.6	71.0	59.8
0.10	84.9	81.3	77.0	71.75	73.0	67.9	55.4
0.15	82.9	78.3	72.5	66.5	70.0	64.2	50.4
0.20	81.4	75.7	69.1	62.5	68.0	61.5	46.7
0.25	80.0	73.4	66.2	59.4	....	....	....

---

[1] For the data see Article III of this series.

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

TABLE II.—VALUES OF 100 k FOR VARIOUS SALTS AT 25°.

(Σi).	KCl.	KNO_3.	$TlNO_3$.	TlCl.	K_2SO_4.	Tl_2SO_4.
0.01	14.8	13.70	12.15	10.10	6.10	4.46
0.02	22.2	19.50	16.60	13.30	8.70	5.96
0.03	28.0	23.85	19.90	15.70	10.70	7.06
0.05	37.3	30.8	24.8	19.25	14.15	8.89
0.07	45.5	36.4	28.7	22.00	17.15	10.41
0.10	56.2	43.5	33.4	25.40	21.20	12.41
0.15	72.8	54.1	39.5	29.75	26.90	15.23
0 20	87.7	62.3	44.6	33.6	31.90	17.52
0 25	100.3	68.9	49.1	36.6	...	...

The composition of the various solutions saturated with thallous chloride was calculated on the assumption that for each salt the values of γ in mixtures with a common ion, and of k in mixtures without a common ion depend only on the total equivalent ion-concentration (Σi). The results of the calculation are presented in the last ten columns of Table III. In the first column are given the names and concentrations of the

TABLE III.—COMPOSITION OF SATURATED TlCl SOLUTIONS.

(Concentrations in milliequivalents per liter.)

Added salt. ($\frac{1}{2}K_2SO_4$).	(ΣCl).	(Σi).	$(\overset{+}{K})$.	$(\overset{+}{Tl})$.	$(\overset{-}{Cl})$.	$(\frac{1}{2}\overset{--}{SO_4})$.	($\frac{1}{2}K_2SO_4$).	($\frac{1}{2}Tl_2SO_4$).	(KCl).	(TlCl).	$(\overset{+}{Tl})(\overset{-}{Cl})$.
0.0	16.07	14.32	0.0	14.32	14.32	0.0	0.0	0.0	0.0	1.755	204.9
19.96	17.79	20.33	16.73	13.60	15.52	14.81	2.30	2.85	0.93	1.338	211.0
49.96	19.42	51.96	38.80	13.16	16.61	35.35	9.47	5.14	1.69	1.120	218.3
99.89	21.37	85.03	72.17	12.86	17.87	67.16	25.19	7.54	2.53	0.966	229.7
299.6	26.00	200.9	188.5	12.45	20.77	180.2	106.6	12.78	4.46	0.768	258.6
($\frac{1}{2}Tl_2SO_4$).											
0.0	16.07	14.32	...	14.32	14.32	0.0	...	0.0	...	1.755	204.9
19.99	10.34	23.46	...	23.46	18.88	14.58	...	5.41	...	1.465	208.1
49.99	6.77	39.00	...	39.00	5.53	33.47	...	16.52	...	1.239	215.7
99.97	4.68	64.42	...	64.42	3.59	60.83	...	39.14	...	1.087	231.3

(KNO_3).	(ΣCl).	(Σi).	$(\overset{+}{K})$.	$(\overset{+}{Tl})$.	$(\overset{-}{Cl})$.	$(\overset{-}{NO_3})$.	(KNO_3).	($TlNO_3$).	(KCl).	(TlCl).	$(\overset{+}{Tl})(\overset{-}{Cl})$.
0.0	16.07	14.32	0.0	14.32	14.32	0.0	0.0	0.0	0.0	1.755	204.9
20.00	17.16	32.42	17.84	14.58	14.91	17.51	1.25	1.24	0.91	1.343	217.4
49.97	18.26	57.65	42.87	14.78	15.50	42.15	5.46	2.36	1.64	1.124	229.1
99.98	19.61	97.08	82.11	14.97	16.23	80.85	15.56	3.67	2.41	0.968	243.0
300.0	231.3	238.3	233.0	15.34	18.20	220.1	72.9	7.02	4.16	0.775	279.2
($TlNO_3$).											
0.0	16.07	14.32	....	14.32	14.32	0.0	...	0.0	...	1.755	204.9
25.0	8.80	29.17	....	29.17	7.405	21.76	...	3.24	...	1.395	216.0
50.0	6.24	46.87	....	46.87	4.99	41.88	...	8.12	...	1.248	233.9
100.0	4.22	82.05	....	82.05	3.13	78.92	...	21.08	...	1.093	256.8

Added salt. (KCl).	(ΣTl).	(Σi).	(K^+).	(Tl^+).	(Cl^-).	$(\frac{1}{2}Ba^{++})$.	$(\frac{1}{2}BaCl_2)$.	(KCl).	(TlCl).	$(Tl^+)(Cl^-)$.
0.0	16.07	14.32	0.0	14.32	14.32	...	...	0.0	1.755	204.9
25.0	8.69	29.88	22.58	7.30	29.88	...	...	2.42	1.390	218.1
50.0	5.90	48.85	44.15	4.70	48.85	...	...	5.85	1.204	229.6
100.0	3.96	88.40	85.5	2.90	88.40	...	...	14.5	1.061	256.3
200.0	2.68	166.54	164.8	1.74	166.54	...	...	35.2	0.94	290.0
$(\frac{1}{2}BaCl_2)$.										
0.0	16.07	14.32	....	14.32	14.32	0.0	0.0	...	1.755	204.9
25.0	8.98	28.00	....	7.59	28.00	20.41	4.59	...	1.392	212.5
50.0	6.18	44.30	....	4.98	44.30	39.32	10.68	...	1.203	220.6
100.0	4.16	77.97	....	3.11	77.97	74.86	25.14	...	1.052	242.4
200.0	2.82	142.7	....	1.89	142.7	140.8	59.2	...	0.93	270.0

added salts, and in the second the corresponding solubilities of thallous chloride (see Tables II and VII in the preceding article). In the third column are the equivalent ion-concentrations $(\Sigma i) \times 10^3$, and in the last two columns the concentrations of the unionized portion of thallous chloride (TlCl) $\times$ 10^3, and of the ionic solubility product $(Tl^+)(Cl^-) \times 10^6$.

The specific conductances, L, of a number of these mixtures were calculated from the ionic concentrations by means of the following ionic conductances: Tl^+, 76.2; K^+, 74.8; Cl^-, 75.8; NO_3^-, 70.6; $\frac{1}{2}$ $SO_4^=$, 80.0; and are compared in Table IV with the experimentally determined values (see Table II of the preceding article). The concentrations of the added salts are given in the first, fourth and seventh columns:

TABLE IV.—SPECIFIC CONDUCTANCES OF THE MIXTURES.

	1000 L.			1000 L.			1000 L.	
$(\frac{1}{2} K_2SO_4)$.	Meas.	Calc.	$(\frac{1}{2} Tl_2SO_4)$.	Meas.	Calc.	(KNO_3).	Meas.	Calc.
0.01998	4.644	4.647	0.01999	3.620	3.625	0.02000	4.807	4.811
0.04996	7.96	7.99	0.04999	6.05	6.07	0.04997	8.47	8.49
0.09989	13.02	13.10	0.09997	10.01	10.05	0.09998	14.18	14.22
						0.3000	34.62	34.77

The agreement between the calculated and the measured specific conductances is very satisfactory, but this is only another confirmation of the principle of the conductance of mixtures referred to in the introduction. The observed agreement is also a check on the accuracy of the experimental data and of the calculations. Another check on the calculations was obtained by comparing the values of $K = \frac{[(Tl^+)(Cl^-)]}{(TlCl)(\Sigma i)^{0.4}}$ given with those of $K = \frac{(C\gamma)^{1.6}}{C(1-\gamma)}$ given for thallous chloride solutions in Table IV of the preceding article. The agreement was complete.

In Fig. 1*a* the values of the iodic solubility product and of the concentrations of the un-ionized portion of thallous chloride (Table III) are plotted as ordinates against the total ion-concentrations, $(\Sigma i) \times 10^3$, as abscissas. In order that the same ordinate scale might be used, the values plotted are $(Tl^+)(Cl^-) \times 10^5$ and $(TlCl) \times 10^4$. The diagram thus shows directly the relative variations of these two quantities with the ion-concentration.

In the curves on the right-hand side of the same diagram (Fig. 1*b*),

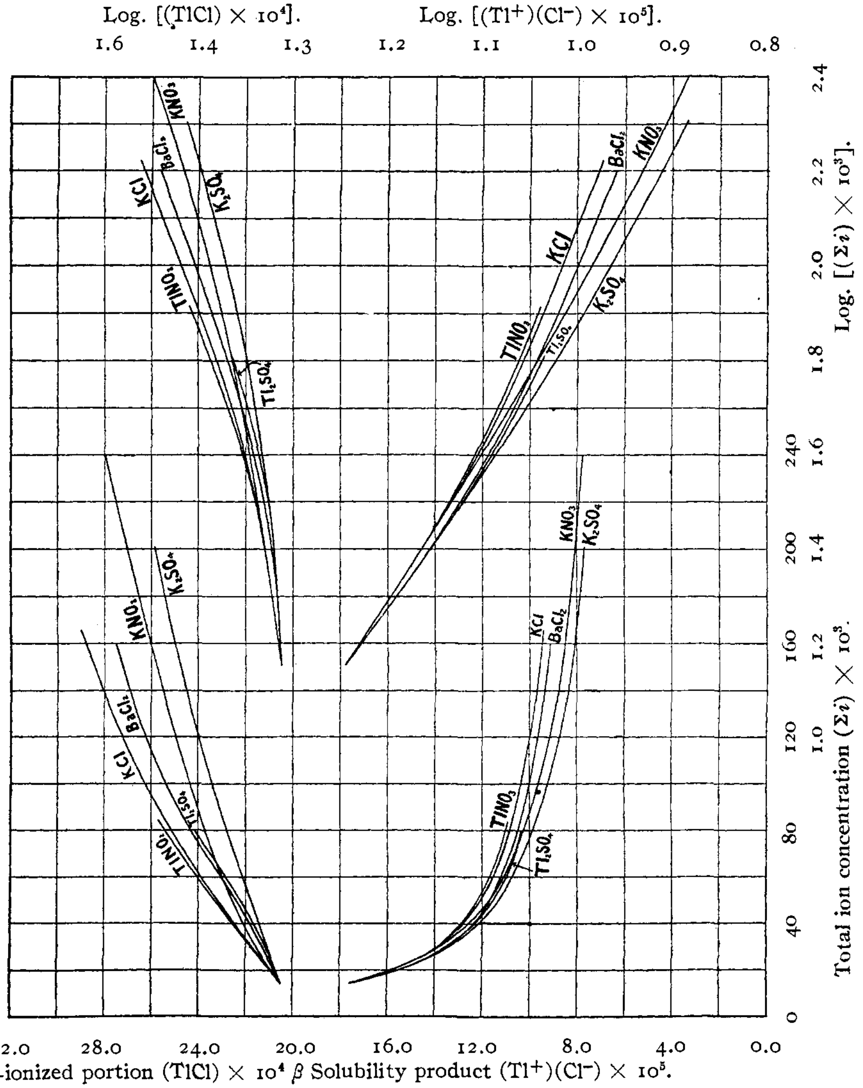

Fig. 1*b*.—Values of Log. $[10^5 \times (Tl^+)(Cl^-)]$ and log. $[10^4 \times (TlCl)]$.

Fig. 1*a*.—Values of $(Tl^+)(Cl^-) \times 10^5$ and $(TlCl) \times 10^4$.

the logarithms of the quantities $[10^5(\text{Tl}^+)(\text{Cl}^-)]$ and 10^4 (TlCl) are plotted against the logarithm of 10^3 (Σi), the data themselves being given in Table V. The various curves have, of course, the same relative positions in the two cases, but the logarithmic plot has the advantage of showing the relationships in dilute solutions more clearly. The points corresponding to 0.02 *N* $BaCl_2$ and 0.05 *N* $TlNO_3$ were found to lie above the curves through the remaining points and were neglected, but the possible errors in the original experimental data were sufficiently great to account for such variations.

TABLE V.—DATA FOR THE LOGARITHMIC PLOT, FIG. 1*b*.

Added salt.	Log $10^3 \times$ (Σi).	Log $10^4 \times$ (TlCl).	Log $10^5 \times$ $(\text{Tl}^+)(\text{Cl}^-)$.	Added salt.	Log $10^3 \times$ (Σi).	Log $10^4 \times$ (TlCl).	Log $10^5 \times$ $(\text{Tl}^+)(\text{Cl}^-)$.
None......	1.1559	1.2443	1.3115	K_2SO_4...	1.4819	1.1265	1.3243
Tl_2SO_4.....	1.3703	1.6158	1.3183		1.7157	1.0492	1.3401
	1.5911	1.0931	1.3339		1.9296	0.9850	1.3612
	1.8090	1.0362	1.3642		2.3030	0.8854	1.4126
$TlNO_3$.....	1.4649	1.1446	1.3345	KNO_3...	1.5108	1.1281	1.3373
	1.6709	1.0962	1.3690		1.7608	1.0508	1.3600
	1.9141	1.0386	1.4096		1.9871	0.9859	1.3856
					2.3771	0.8893	1.4459
$BaCl_2$......	1.4472	1.1436	1.3274	KCl.....	1.4754	1.1430	1.3387
	1.6464	1.0803	1.3436		1.6889	1.0806	1.3610
	1.8919	1.0220	1.3846		1.9465	1.0257	1.4088
	2.1544	0.9685	1.4314		2.2215	0.9721	1.4624

It will be seen from the figure that neither the concentration of unionized TlCl nor the ionic solubility product is constant. In all cases, as the ion-concentration (Σi) increases, the value of (TlCl) decreases rapidly, and that of $(\text{Tl}^+)(\text{Cl}^-)$ increases steadily, although much more slowly. When we consider that (Σi) increases seventeen-fold (from 0.014 to 0.238), and that the results are based on experiments with uni-univalent and uni-bivalent salts with and without a common ion, it is very remarkable that the curves in each group lie as closely together as they do. The uniformity of the results therefore confirms the assumption that it is the total ion-concentration in the mixture which primarily determins the ionization of uni-univalent salts.

The figure shows the nature of the variation of (TlCl) and of (Tl^+) (Cl^-) with (Σi). The curves obtained by plotting log (TlCl) against log (Σi) are more clearly linear than those obtained by plotting (TlCl) directly against (Σi), but the converse is true for the $(\text{Tl}^+)(\text{Cl}^-)$ curves. We will examin the logarithmic curves more closely on account of the following simple relationship between their slopes and the deviations from the law of mass action.

Any small portion of one of the curves may be considered to be a straight line whose equation is:

$\log (\mathrm{TlCl}) = m_u \log (\Sigma i) + \log k_u$ or $\log (\mathrm{Tl}^+)(\mathrm{Cl}^-) = m_i \log (\Sigma i) + \log k_i$. These equations when written in another form become:

$$(\mathrm{TlCl}) = k_u(\Sigma i)^{m_u} \text{ and } (\mathrm{Tl}^+)(\mathrm{Cl}^-) = k_i(\Sigma i)^{m_i},$$

and the exponents m_u and m_i may be determined directly from the slopes of the tangents to the curves. It is obvious that the last two equations correspond to the general ionization function used in the calculations $\frac{(\mathrm{Tl}^+)(\mathrm{Cl}^-)}{(\mathrm{TlCl})} = K(\Sigma i)^{0.4}$, and that $m_i - m_u = 0.4$ and $k_i/k_u = K$. From the slope of the curves it is evident that in each case m_i is a small positive number which increases with increasing ion concentration, and that m_u is a negative number which is numerically greater than m_i and therefore appears to change less rapidly. The approximate values of m_i for each added salt at the ion concentrations $(\Sigma i) = 0.016$ and 0.100 normal are as follows:

TABLE VI.—VALUES OF THE EXPONENT m_i IN VARIOUS SALT SOLUTIONS.

$10^3(\Sigma i)$.	Log $10^3(\Sigma i)$.	K_2SO_4.	Tl_2SO_4.	$BaCl_2$.	KNO_3.	KCl.	$TlNO_3$.
16	1.20	0.03	0.03	0.03	0.07	0.07	0.07
100	2.00	0.12	0.17	0.18	0.12	0.19	0.20

The corresponding values of m_u were obtained by subtracting 0.40 from each of these numbers and were found to check with those derived directly from the (TlCl) curves. Thus the values of m_u at $(\Sigma i) = 0.016$ normal are —0.37 and —0.33 for the unibivalent and the uni-univalent salts, respectively.[1]

The values of m_i decrease with increasing ion-concentration and show a tendency to approach zero if the curves be produced toward zero concentration. This signifies that in the case of thallous chloride the

---

[1] Reference was made in the previous article to the possible inaccuracy of the ionization values of thallous chloride obtained by extrapolation, and to the calculation, by means of the expression $(C\gamma)^{1.55}/C(1-\gamma) = K'$, of values which were larger than those corresponding to the exponent $n = 1.60$. Thus at 0.1 normal γ was 0.766 instead of 0.751. The present calculations with K_2SO_4, Tl_2SO_4 and KNO_3 were repeated, using these higher values of γ for TlCl, and the data obtained were plotted in a diagram similar to Fig. 1. The results and curves did not differ in character from those presented above. The values of m_i were slightly larger than those given in Table VI, which was to have been expected, since $m_i - m_u = 0.45$ instead of 0.40.

A change in the ionization values of one of the added salts would, on the other hand, have specific effects on the results, but such effects are relatively small. Thus in the 0.1 normal KCl solution a 2 per cent. decrease in the degree of ionization of KCl causes a 2.0 per cent. decrease of (Σi), a 1.7 per cent. decrease of $(\mathrm{Tl}^+)(\mathrm{Cl}^-)$ and a 1.0 per cent. increase of (TlCl); and this would have the effect of only slightly lowering the (Tl^+) (Cl^-) curves and slightly raising the TlCl curves. It is therefore evident that the conclusions reached in this article would not be appreciably altered as a result of introducing a correction in the ionization values, such as that for viscosity, which is negligible in the very dilute solutions and does not exceed a few per cent. in the more concentrated ones.

solubility product is more nearly constant in the dilute than in concentrated salt solutions, and furnishes some indications that the solubility product would be more exactly constant for a less soluble substance than thallous chloride.

From the result that in the dilute solutions m_u is much larger than m_i it follows that the deviations from the law of mass action in the ionization of thallous chloride are more largely due to the abnormal behavior of the un-ionized substance than to the abnormal behavior of the ions.[1] If we make use of the concept of activity, which was explained in the first article of this series, we may say that the activity coefficient of un-ionized TlCl ($A_{\mathrm{TlCl}}/C_{\mathrm{TlCl}}$) increases rapidly as the total ion-concentration increases and is proportional to its 0.37 to 0.33 power in dilute solutions. Similarly the product $\left(\frac{A_{\mathrm{Tl}+}}{C_{\mathrm{Tl}+}}\right)\left(\frac{A_{\mathrm{Cl}-}}{C_{\mathrm{Cl}-}}\right)$ decreases slowly, and is at first inversely proportional to the 0.03 to 0.07 power of the total ion concentration. If it is legitimate to distribute this effect equally upon the two ions, then the activity coefficient of each ion must decrease in the proportion in which the 0.015 to 0.035 power of the ion concentration increases. This is really only a small deviation from direct proportionality; and if, as seems reasonable, we assume the same law in a solution of a single uni-univalent salt where the concentration of each ion is equal to (Σi), then we may conclude that in dilute solutions (say 0.01 to 0.03 normal) the activity of each ion is nearly, but not quite, proportional to its concentration and increases somewhat less rapidly than the concentration. By similar reasoning, the increase in m_i with increasing ion concentration (shown in Table VI) leads to the similar conclusion that in more concentrated solutions of a single salt the activity coefficient (A/C) decreases more rapidly with increasing concentration of the salt.

This conclusion is in agreement with the results of electromotive force measurements of concentration cells. Lewis and Von Ende[2] have shown, namely, in connection with their work with the thallous-ion concentration cell, that the ratio A/C for the thallous ion is constant at low concentrations and shows a distinct decrease at 0.1 normal. The measurements of Jahn[3] on the chloride-ion concentration cell show a similar but more pronounced decrease of the activity coefficient of chloride ion.

In the foregoing discussion the general effects produced by added salts have been discussed, but a number of interesting specific effects

---

[1] Compare Lewis, *Proc. Am. Acad.*, **43**, 288 (1907); *Z. physik. Chem.*, **61**, 160 (1907).

[2] Lewis and Von Ende, THIS JOURNAL, **32**, 737 (1910). See also Bray and Mackay, *Ibid.*, **32**, 930, 1213 (1910).

[3] Jahn, *Z. physik. Chem.*, **33**, 545 (1900).

may be easily seen by examining the figure and Table VI more closely. Thus from the effects produced by the first small portions of salts the six salts fall into two classes, the three uni-univalent salts, KNO_3, KCl and $TlNO_3$, and the three uni-bivalent salts, K_2SO_4, $BaCl_2$ and Tl_2SO_4. The initial portions of the three curves in each group practically coincide and the values of m_i are 0.07 and 0.03, respectively, for the uni-univalent and uni-bivalent salts. In each group of curves, as the solutions become more concentrated, the two curves corresponding to the salts with a common ion remain very close together, while the curve corresponding to the salt (KNO_3 or K_2SO_4) without a common ion diverges and always remains below the other two curves.

The fact that the effect of a uni-bivalent salt is consistently different from that of the corresponding uni-univalent salt shows that the mere presence of a bivalent ion has an effect on the ionization relations of thallous chloride which is somewhat different from that of an equivalent amount of the univalent ion. While such an effect is not improbable, it seems strange that the effect is in such a direction as to decrease m_i and thus make the activities of Tl^+ and Cl^- appear to be more nearly proportional to their concentrations in the uni-bivalent salt solution. On this account, and also to obtain if possible greater simplicity in the solubility relations of thallous chloride, it seems worth while to examin how the original assumptions may be altered in order to bring the two sets of effects into better agreement. This is the question which was referred to in the closing paragraph of the preceding article, and it was shown there that larger values would be calculated for the concentration of Cl^- in 0.1 N $BaCl_2$ and of Tl^+ in 0.1 N Tl_2SO_4 if the solubility product were assumed to be the same in 0.1 N Tl_2SO_4 as in 0.1 N $TlNO_3$ and the same in 0.1 N $BaCl_2$ as in 0.1 N KCl. A study of the $(Tl^+)(Cl^-)$ curves shows that we may now draw the corresponding general conclusion that these curves for the uni-bivalent salts would be raised if we assumed larger values for the total ion concentration in the uni-bivalent salt solutions. The corresponding effect on the concentration of the un-ionized TlCl would be to increase its value and thus bring the two groups of TlCl curves closer together. It is interesting to note that such a result suggests the presence of intermediate ions ($TlSO_4^-$ or $ClBa^+$) in the solutions of the uni-bivalent salts. The possibility of the existence of such ions has been mentioned in the introduction, and will be fully discussed by Dr. W. D. Harkins in a later article of this series.

2. The Solubility at 25° of $KClO_4$ in the Presence of KCl and K_2SO_4.[1]

The results of the calculations are given in Tables VII, the arrangement being the same as in Table III. The ionization values upon which the calculations are based were given in Table V of the second article

---

[1] Article II, A, of this series.

of this series. It may be recalled that the ionization function there assumed for potassium perchlorate was

$$K = \frac{(C\gamma)^{1.5}}{C(1-\gamma)} = \frac{(K^+)(ClO_4^-)}{(KClO_4)(\Sigma i)^{0.5}}.$$

Table VIII contains the measured specific conductances of the mixtures and the values calculated[1] from the ionic conductances K^+, 74.8; ClO_4^-, 68.2; Cl^-, 75.8; and $\frac{1}{2}SO_4^{--}$, 80.0.

TABLE VII.—COMPOSITION OF SATURATED $KClO_4$ SOLUTIONS.
(Concentrations in milliequivalents per liter.)

Added salt.	Conc.	(ΣClO_4).	$(\Sigma i)=(K^+)$.	(ClO_4^-).	(Cl^-).	(KCl).	$(KClO_4)$.	$(K^+)(ClO_4^-)$
KCl.......	0.0	148.1	115.3	115.3	0.0	0.0	32.8	13290
	49.73	128.2	139.1	97.7	41.43	8.30	30.5	13590
	99.33	112.3	165.7	83.8	81.90	17.43	28.5	13890
					$(\frac{1}{2}SO_4^{--})$.	$(\frac{1}{2}K_2SO_4)$.		
$^1/_2K_2SO_4$...	0.0	148.1	115.3	115.3	0.0	0.0	32.8	13290
	49.70	131.5	133.2	100.7	32.50	17.20	30.8	13410
	99.22	118.1	152.8	89.0	63.80	34.42	29.1	13600

TABLE VIII.—SPECIFIC CONDUCTANCES OF THE MIXTURES.

Added salt. (KCl).	1000 *L*.		Added salt. $(\frac{1}{2}K_2SO_4)$.	1000 *L*.	
	Meas.	Calc.		Meas.	Calc.
0.04973	20.29	20.21	0.04970	19.46	19.43
0.09933	24.84	24.31	0.09922	22.63	22.60

It will be seen from the table that as the ion-concentration increases, the concentration of un-ionized $KClO_4$ decreases steadily and that the ionic solubility product $(K^+)(ClO_4^-)$ increases steadily, though much less rapidly. This is similar to what was found above with thallous chloride, but in the present case the relations between (Σi) and $(KClO_4)$ and between (Σi) and $(K^+)(ClO_4^-)$ are almost linear. On account of the small range of these experiments, the corresponding logarithmic curves (shown in Fig. 2) are also almost linear. In order that the same scale might be used in drawing the different curves the increase of log (K^+) (ClO_4^-) and the decrease of log $(KClO_4)$ have been plotted against the increase of log (Σi). The data for Fig. 2 are given in Table IX.

TABLE IX.—DATA FOR THE LOGARITHMIC PLOT (FIG. 2).

Added salt.	Increase of log (Σi).	Increase of log $(K^+)(ClO_4^-)$.	Increase of log $(KClO_4)$.
KCl........................	0.0815	0.0097	—0.0316
	0.1575	0.0192	—0.0610
K_2SO_4....................	0.0627	0.0039	—0.0273
	0.1223	0.0100	—0.0520

---

[1] For the significance of the agreement of the calculated specific conductances with the measured values see the discussion following Table IV, above. In the present instance the disagreement in the 0.1 *N* KCl experiment is undoubtedly due to an error in the measured value, since this was not checked by a duplicate measurement.

Since the curves in the figure are nearly linear it follows that the exponents m_i and m_u (in the equations $(K^+)(ClO_4^-) = k_i(\Sigma i)^{m_i}$ and $(KClO_4) = k_u(\Sigma i)^{m_u}$) are nearly constant in the range of the experiments. When the added salt is potassium chloride $m_i = 0.11$ and $m_u = -0.39$, while for small additions of potassium sulfate $m_i = 0.07$ (and increases with increasing concentration) and $m_u = -0.43$. These results are thus seen to be very similar to those obtained with thallous chloride and may be interpreted in the same way.

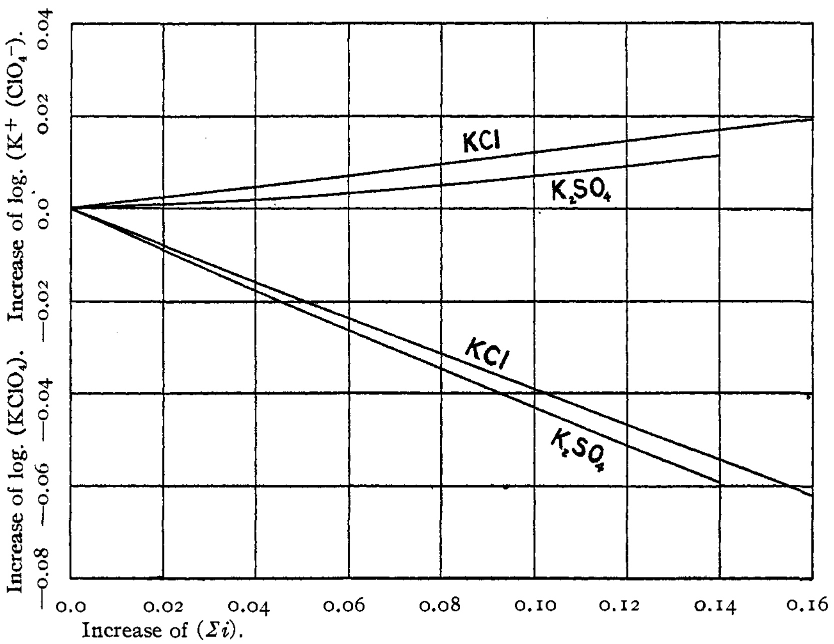

Fig. 2.—Variation of log. $(K^+)(ClO_4^-)$ and log. $(KClO_4)$ with log. (Σi).

A comparison with Table VI shows that the values of m_i in the $KClO_4$ experiments are greater than the corresponding values for small additions of salts in the TlCl experiments. This is undoubtedly due to the fact that $KClO_4$ is a much more soluble salt than TlCl, and corresponds to the increase, shown in Table VI, of m_i with increasing ion concentration and to the former conclusion that the activity coefficient (A/C) for univalent ions decreases with increasing ion concentration. Furthermore, if we consider the solubility product we see that it is more nearly constant in the thallous chloride experiments for small additions of salts than in the experiments with the more soluble substance, potassium perchlorate, so that we have further evidence that the principle of the constancy of the solubility product will hold in the case of difficultly soluble substances for small additions of salts.

3. The Solubility of $TlClO_3$ and Tl_2SO_4 in the Presence of Each Other.[1]

The results of the calculations are presented in Table X:

TABLE X.—COMPOSITION OF SATURATED $TlClO_3$ AND Tl_2SO_4 SOLUTIONS.
(Concentrations in equivalents per liter.)

($\Sigma \frac{1}{2}SO_4$).	(ΣClO_3).	(Σi)=(Tl^+).	(ClO_3^-).	($\frac{1}{2}SO_4^=$).	($\frac{1}{2}Tl_2SO_4$).	($TlClO_3$).	(Tl^+)(ClO_3^-).
0.0	0.1340	0.1073	0.1073	0.0	0.0	0.0267	0.01152
0.1366	0.1058	0.1511	0.0817	0.694	0.0672	0.0241	0.01234
0.1928	0.0	0.1064	0.0	0.1064	0.0864	0.0	.....

An examination of the first two lines[2] of the table shows that with increasing ion concentration the concentration of the un-ionized $TlCl_3$ decreases rapidly, and the ionic solubility product (Tl^+)(ClO_3^-) increases less rapidly. The values of the exponents m_i and m_u were calculated to be 0.20 and —0.30 respectively. The value of m_i is larger than that found in the $KClO_4$ experiments, but is about the same as the values found in the TlCl experiments in the more concentrated salt solutions (see Table VI). The three sets of results studied in this article are thus seen to yield corresponding results.

Discussion of the Results.

The results reached in the cases here investigated, that the concentration of the un-ionized substance in the saturated solution rapidly decreases with increasing concentration, is in perfect agreement with the conclusions drawn by Arrhenius and Stieglitz from the solubility determinations with the silver salts of certain organic acids in the presence of salts with common ions. It may therefore be accepted as a general principle.

The evidence in favor of regarding as a general law the increase of the solubility product with increasing ion-concentration is somewhat less conclusive; but the results presented in this article and the data on the electromotive force of concentration cells support such a conclusion. Stieglitz's calculations, it is true, show a general increase of the solubility product for the silver salts of organic acids, but the increase is much less rapid than in the TlCl experiments, even in the case of the silver salts which are more soluble than thallous chloride. For the silver salts of about the same or smaller solubility than thallous chloride the solubility product remains almost exactly constant over a large range of concentration of the added salts. We must therefore conclude for the present

---

[1] Article II, B. The ionization values are given in Table XI of this article.

[2] The last two lines of the table show the effect on the solubility of the uni-bivalent salt Tl_2SO_4 produced by $TlClO_3$, a uni-univalent salt with a common ion. In this case the concentration of the un-ionized Tl_2SO_4 is seen to decrease rapidly with increasing ion-concentration and the solubility product $(Tl^+)^2(SO_4^=)$ was found to increase rapidly. Additional more comprehensive examples will be presented in later articles of this series.

that the solubility product for uni-univalent salts remains nearly constant or increases steadily with increasing ion-concentration, and that the increase will probably be more marked the greater the solubility of the salt.

The inconstancy of the ionic solubility product has recently been discussed by Hill,[1] who concluded that there is a decrease and not an increase with increasing concentration of added electrolyte. His experiments show that the solubility of thallous chloride decreases rapidly in very concentrated solutions of acetic acid, and that the solubility of tetramethylammonium iodide decreases rapidly in very concentrated solutions of potassium hydroxide. The solubility product must decrease in these cases with increasing concentration of the added substance; but it is very doubtful whether Hill is justified in drawing general conclusions from these two cases, since acetic acid at least is not a typical strong electrolyte and since the behavior in dilute solutions has not been carefully examined. It seems more probable that these experiments indicate the mutual insolubility of acetic acid and thallous chloride, and of tetramethylammonium iodide and potassium hydroxide. That such "solvent effects" must be taken into consideration has been shown in a striking manner by Kendall[2] in a recent article.

Summary.

In this article the effects of six typical salts on the solubility of thallous chloride, of two salts on the solubility of potassium perchlorate, and of one salt on the solubility of thallous chlorate have been discussed quantitatively by the method described in the introduction to this series of articles. This method consists essentially in calculating, with the aid of ionization values derived from conductance, the concentration of the un-ionized portion and the product of the concentrations of the ions of the salt with which the solution is saturated for the case when it is present alone and for cases in which another salt is simultaneously present.

This "un-ionized" concentration and this "solubility product" should, according to the mass action law, be constant in any saturated solution. The actual variations of these quantities in the different cases are shown in the last two columns of Tables III, VII, and X, and in Fig. 1*a* of this article. In every case the un-ionized concentration (BA) decreases markedly and the solubility product $(B^+)(A^-)$ increases slightly, as the total concentrations of the salts and of the ions in the saturated solution increase.

A study of these variations by means of the logarithmic plots of Fig. 1*b* and 2 shows that they can be expressed approximately as a function

---

[1] Hill, This Journal, **32,** 1186 (1910).

[2] Kendall, *Proc. Roy. Soc.*, **85,** 200 (1911).

of the total ion-concentration (Σi) in the solution by the exponential equations,

$$(BA) = k_u(\Sigma i)^{m_u} \text{ and } (B^+)(A^-) = k_i(\Sigma i)^{m_i},$$

in which k_u, k_i, m_u, and m_i are constants, which were separately determined for each substance in the presence of each added salt. These expressions are evidently closely related to the empirical dilution law $(B^+)(A^-)/(BA) = K(\Sigma i)^{2-n}$, K being equal to k_i/k_u and the exponent $2-n$ equal to $m_i - m_u$. In the case of thallous chloride, where the range of the concentrations of the added salts was very large, these exponential expressions do not fully express the results. As shown by the curvature of the logarithmic graphs, different values of the exponent m_i or m_u must be assumed at different concentrations.

The values of m_i and m_u were found to be as follows:

			m_i.	m_u.
TlCl	+ uni-univalent salts	at $(\Sigma i) = 0.016$....	0.07	—0.33
	+ uni-bivalent salts	at $(\Sigma i) = 0.016$....	0.03	—0.37
	+ uni-univalent salts	at $(\Sigma i) = 0.100$....	0.12 to 0.20	—0.28 to —0.20
	+ uni-bivalent salts	at $(\Sigma i) = 0.100$....	0.12 to 0.18	—0.28 to —0.22
$KClO_4$	+ KCl	at $(\Sigma i) = 0.12$	0.11	—0.39
	+ K_2SO_4	at $(\Sigma i) = 0.12$	0.07	—0.43
$TlClO_3$	+ Tl_2SO_4	at $(\Sigma i) = 0.12$....	0.20	—0.30

It will be seen that the values of m_i at the small concentration 0.016 normal are small and less than those at the higher concentrations. This seems to justify the conclusion that the solubility product would be practically constant in the case of less soluble salts in the presence of small quantities of other salts.

The fact that the values of m_i are much smaller than those of m_u at small concentrations shows that the deviation from the theoretical dilution law $(B^+)(A^-)/(BA) = k$ is mainly due to abnormal behavior of the un-ionized substance and only secondarily to abnormal behavior of the ions.

In terms of the activity concept, these results indicate that the ratio of the activity to the concentration of univalent ions is nearly constant below 0.016 normal, but that above this concentration it decreases with increasing concentration at first slowly and then more rapidly. The corresponding ratio for the un-ionized portion, on the other hand, increases very rapidly with increasing concentration throughout the whole range of concentration investigated.

The nearly uniform effect on the un-ionized concentration and on the solubility product exerted by the salts of the two different valence types and by those with and without a common ion confirms the original assumption that the ionization relations of uni-univalent salts are primarily determined by the total equivalent ion-concentration. There are, however, consistent differences of secondary order in the effects of the different kinds of salts, and especially between the uni-uni- and uni-bivalent salts.

In conclusion, I take pleasure in thanking Professor A. A. Noyes for his assistance in connection with this investigation.

[CONTRIBUTIONS FROM THE LABORATORY OF PHYSICAL CHEMISTRY, UNIVERSITY OF ILLINOIS.]

THE LAWS OF "CONCENTRATED" SOLUTIONS. III.[1] THE IONIZATION AND HYDRATION RELATIONS OF ELECTROLYTES IN AQUEOUS SOLUTION AT ZERO DEGREES: A. CESIUM NITRATE, POTASSIUM CHLORIDE AND LITHIUM CHLORIDE.

BY EDWARD W. WASHBURN AND DUNCAN A. MACINNES.

Received August 28, 1911.

1. Purpose and Outline of the Investigation.

In undertaking a systematic extension of our knowledge of aqueous solutions of strong electrolytes into the region of "concentrated" solutions, it is natural to begin the study with the simplest type of such electrolytes, the uni-univalent salts. The salts of this type range from those such as cesium nitrate and iodide, which are slightly or not at all hydrated in solution, to those of which lithium chloride is an example, which are combined with considerable amounts of the solvent. The present investigation includes the two salts cesium nitrate and lithium chloride, which represent extremes in this respect, together with one salt, potassium chloride, which occupies an intermediate position.

For investigating the condition of these salts in solution the freezing-point method was adopted. As pointed out in a previous paper,[3] this method possesses the disadvantage that one is obliged to change two variables simultaneously, the concentration and the temperature. This difficulty can be avoided either (1) by combining measurements of heat of dilution with those of freezing-point lowering, or (2) by replacing the freezing-point method by the method of vapor-pressure lowering. For higher temperatures the latter alternative is preferable and a parallel

---

[1] Contributions Nos. 1 and 2 of this series appeared in THIS JOURNAL, **32**, 653 and 1636 (1910), and **33**, 1461 (1911). Owing to the fact that the author was given no opportunity to correct the page proof of article No. 2, it is necessary to note the following corrections: p. 1462, for G. N. Lewis[4] read G. N. Lewis[1]; p. 1472, line 1, for (10) read (12); p. 1467, for (see p. ——) read (see p. 1471); p. 1473, Table IV, for 19° read 18°, and for f_0 read η_0, p. 1463, Note 2, next to last line, the figure 7 is omitted.

[2] Presented at the Indianapolis meeting of the Society, June 29, 1911. Abstract of a thesis presented by Mr. MacInnes to the Graduate School of the University of Illinois in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[3] *Technology Quarterly*, **21**, 379–80 (1908).