6. Ion Conductances.—From the "best" values given in Table X the differences in ion conductances for the four pairs of ions shown in Table XI have been calculated. From the mean values of these differences, together with the other Λ_0 values given in Table X, the set of ion conductances shown in Table XII has been calculated. These values are based upon 0.4960 as the cation transference number for potassium chloride.

TABLE XII.

Ion Conductances at 18°.

Ion	K.	Na.	Li.	Rb.	Cs.	Ag.	Cl.	NO_3.
Λ	64.30	43.23	33.07	67.6	67.56	53.9	65.34	61.71
Ion	IO_3.	Br.	I.	SCN.	ClO_3.	BrO_3.		
Λ	33.83	67.41	66.35	56.5	54.95	47.7		

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA.]

EQUILIBRIUM DATA ON THE POLYBROMIDES AND POLYIODIDES OF POTASSIUM.

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I. The Equilibrium between Bromine and Potassium Bromide Solutions at Different Temperatures.

In connection with an investigation dealing with the polyiodides of potassium, it was of interest to calculate for comparison the values for the equilibrium constants of the polybromides from Worley's data[1] at 26.5° and compare them with those obtained by Jones & Hartmann[2] at 0°. From these values at 0° and 26.5°, were then calculated equilibrium constants for 32.6° and compared with those calculated from Worley's data for 32.6°. In Table I are given Worley's data at 26.5° and the equilibrium constants calculated from them with the aid of the following relations:

$$\frac{(Br^-)}{\gamma} + \frac{(Br_3^-)}{\gamma} + \frac{(Br_5^-)}{\gamma} = \Sigma(KBr), \ (1);$$

$$\frac{(Br_3^-)}{\gamma} + \frac{2(Br_5^-)}{\gamma} + (Br_2) = \Sigma(Br_2), \ (2);$$

$$\frac{(Br_3^-)}{(Br^-)(Br_2)} = K', \ (3); \quad \frac{(Br_5^-)}{(Br_3^-)(Br_2)} = K'', \ (4)$$

Combining (2) and (4) we have,

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[1] *J. Chem. Soc.* (*London*), 87, 1107 (1905).

[2] *Trans. Am. Electrochem. Soc.*, 30, 295 (1916).

$$\frac{(Br_5^-)}{\gamma} = \frac{\Sigma(Br_2)-(Br_2)}{\left(\dfrac{1}{K''\,(Br_2)} + 2\right)} \quad (5).$$

It is here assumed that for moderate concentrations of KBr, KBr_3 and KBr_5, the thermodynamic degrees of dissociation, γ, of these substances are the same in the mixture, and also that the activity of the free bromine is proportional to its concentration. The validity of this latter assumption is substantiated by the vapor-pressure measurements of Br_2 aq. by Winkler.[1] It is to be noted that the constants so calculated are fairly concordant.

It was found by trial that if 1.2 is taken for the value of K'',[2] the following values were obtained for K':

$K'' = 1.20$. TABLE I. $t = 26.5°$ C.

Series A.

ΣKBr = 0.5 gram-mol per liter.

$\Sigma(Br_2)$.	Free (Br_2).	K'.
0.51829	0.12507	15.8
0.48217	0.10583	17.5
0.46720	0.10431	16.8
0.45997	0.09712	17.7
0.42581	0.08508	17.6
0.42246	0.08714	16.5
0.37041	0.07352	15.2
0.32753	0.06008	15.6
0.29450	0.04999	16.2
0.28966	0.04818	14.9
0.21097	0.03249	15.5
0.14892	0.02000	16.5
0.11400	0.01515	15.6
0.05700	0.00751	14.3

Series B.

ΣKBr = 0.1 gram-mol per liter.

$\Sigma(Br_2)$.	Free (Br_2).	K'.
0.23849	0.15455	14.4
0.21650	0.13515	15.9
0.18013	0.10647	16.3
0.17761	0.10532	15.7
0.16684	0.09644	16.3
0.14837	0.08516	14.6
0.13202	0.07215	15.9
0.08416	0.04173	15.6
0.06365	0.03027	15.2
0.04320	0.01938	15.3

The average of the 24 values for K' at 26.5° is 15.9 and the value for K' at 0° is 19.6,[3] whence ΔH, the heat of the reaction, $Br^- + Br_2(aq.) = Br_3^-$, equals —1290 cal., calculated by means of the equation

$$\ln K'_{T'}/K'_{T''} = \Delta H\ (T''-T')/RT''T', \qquad (6)$$

Similarly, ΔH for the reaction $Br_3^- + Br_2(aq.) = Br_5^-$ equals —3390 cal., where K'' at 26.5° equals 1.20 and K'' at 0° equals 2.08.[4] By means of these values, the corresponding equilibrium constants were then calculated for 32.6°, giving for K' 15.2 and for K'' 1.06, on the assumption that ΔH remains constant for the given range of temperature.

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[1] *Chem. Zeit.*, **23**, 687 (1899).

[2] Since the equation for K'' contains the term (Br_2) to the second power it is found more advantageous to maintain K'' constant throughout the two series and calculate: first, the value for KBr_5 by means of Equation 5.

[3] Jones and Hartmann, already cited (page 326).

[4] *Ibid.*

In Table III Col. 3 are given the values for K' at 32.6° calculated from Worley's data by means of Equations 5, 2, 1 and 3, keeping K'' constant at 1.06, which is the calculated value from equilibrium constants at 0° and 26.5° by means of Equation 6.

TABLE II.

$K'' = 1.06$. $t = 32.6°$ C.

$\Sigma KBr = 0.125$ gram-mol per liter.

$\Sigma(Br_2)$.	Free (Br_2).	K'.
0.22530	0.12800	15.7
0.21711	0.12094	16.5
0.18989	0.10202	15.7
0.13828	0.06838	14.7
0.11750	0.05446	15.9
0.07974	0.03423	15.3
0.04875	0.01974	14.6
0.01831	0.00698	14.0

The average value for K' at 32.6° (15.5) agrees fairly well with the value (15.2), calculated from K' at 0° and at 26.5°.

KBr Solutions Saturated with Respect to Bromine.—If we now apply the value 1.20 for the equilibrium constant K'' at 26.5° to Worley's data of KBr solutions saturated with bromine, the average value obtained for K' is found to be several per cent. too high. This may be due to the presence of another complex, KBr_7.[1] However, the oscillations of the ratios of the total combined bromine and total KBr to the extent of about 10% may account, in part, for this difference.

Summary.

(1) In Table III below are given values for the equilibrium constants K' and K'' calculated from experimental results at 0°, 26.5° and 32.6°, as well as calculated values for 25°.

TABLE III.

$t°$.	$\frac{(Br_3^-)}{(Br^-)(Br_2)}$.	$\frac{(Br_5^-)}{(Br_3^-)(Br_2)}$.
0.0	19.6	2.08
25.0	16.1	1.23
26.5	15.9	1.20
32.6	15.5	1.07

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[1] Since, in saturated solution, with reference to bromine, the combined bromine is practically a linear function of the total KBr in the solution, concordant constants would be obtained for any number of complexes of the type $KBr.nBr_2$, which we may assume to exist together in the same solution, but the constants so obtained would not necessarily be of the same magnitude as those given in Table I. Worley also calls particular attention to the fact that the function is not quite linear from the experiments at 18.5°. This discrepancy is apparent only, for a 1% error in the solubulity of bromine in water (which is quite within experimental error as contrasted with data of other investigators) would change the ratio when KBr = 0.01 from 1.86 to 2.30, while, when KBr = 0.9, the ratio would be changed only from 2.27 to 2.29.

(2) The heat of the reaction $Br^- + Br_2(aq.) = Br_3^-$ equals —1290 cal., and of the reaction $Br_3^- + Br_2(aq.) = Br_5^-$ equals —3390 cal.

II. Distribution of Iodine between CCl_4 and H_2O, at 25°.

Experimental.—A concentrated solution of pure iodine in pure carbon tetrachloride was diluted with the desired amount of carbon tetrachloride and introduced into resistance bottles, of about 600 cc. capacity, provided with ground glass stoppers. The bottles were then filled to overflowing[1] with conductivity water. The stoppers were inserted and the bottles suspended up to the necks in a thermostat. After the bottles attained the temperature of the bath, 25°, the stoppers were tightened. The bottles were frequently shaken during the day and left in the thermostat overnight to reach equilibrium. On removing a bottle for analysis it was placed up to the neck in a vessel of water of the same temperature as that of the thermostat. A portion of the water phase was then siphoned into a weighed Erlenmeyer flask provided with a ground glass stopper. The siphons used for the CCl_4 phase were sealed at the bottom, terminating in a small, thin bulb, easily broken when in contact with the bottom of the bottle. The iodine was estimated in the usual way by means of sodium thiosulfate. The results are given in table below.

TABLE IV.—EXPERIMENTAL RESULTS AT 25°.

	Grams solution for analysis.		Gram iodine found in.		Mol iodine to 1000 g.		
	H_2O phase.	CCl_4 phase.	H_2O phase.	CCl_4 phase.	CCl_4 phase.	H_2O phase.	Ratio.
(*a*)	370.215	48.335	0.037760	0.280586	0.022988	0.000402	57.2
(*b*)		50.913		0.295012	0.022945		57.1
(*a*)	372.175	48.350	0.058916	0.429174	0.035260	0.000623	56.6
(*b*)		51.005		0.452255	0.035220		56.6
(*a*)	369.175	48.349	0.067887	0.496254	0.040828	0.000724	56.4
(*b*)		50.965		0.522943	0.040815		56.4
(*a*)	419.405	48.248	0.080340	0.522943	0.043020	0.000754	57.1
(*b*)		51.075		0.550811	0.042921		56.9
(*a*)	357.975	48.503	0.082416	0.623925	0.051304	0.000907	56.6
(*b*)		51.005		0.656383	0.051325		56.6

Discussion of the Results.

It is interesting to note that when the measurements of the distribution of iodine between carbon tetrachloride and water are performed with the necessary precautions, concordant ratios are obtained for the entire range of concentration, and that this value is equal to the one obtained from the solubility of iodine in carbon tetrachloride and water, respectively.

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[1] This precaution was found necessary as the emulsion formed between the CCl_4 and the iodine, when the bottles were shaken, when there was an air space, led to erroneous results, because there was no equilibrium established even after the bottles had been left in the thermostat for several days, while, when there was no air space, the equilibrium was established very rapidly and the water phase became perfectly clear.

Thus, according to Jakowkin [1] the solubility of iodine in carbon tetrachloride at 25° is 0.11941 mol per liter of solution, and the solubility of iodine in water is 0.00134 mol per liter of solution. Dividing the amount of iodine in the tetrachloride phase by the amount in the water phase we obtain a ratio of 89. Comparing this value with the one obtained from Expt. 4 in which the volumes of the CCl_4 phase used for analysis were 30.0 cc. and 31.7 cc., respectively, we obtain 90.7 and 90.4 or 90.6[2] while the ratios given by Jakowkin range from 89 at saturation to 85 at extreme dilution.

On account of the small solubility of iodine in water or in carbon tetrachloride it is immaterial in what units the concentrations are expressed, as the ratios remain reasonably constant, whether computed to mol fractions, mol per liter of solution, or mols per thousand grams of solvent.

Summary.

The results here presented show that the activity of iodine is proportional to its concentration in water and in carbon tetrachloride, from extreme dilution to saturation. It does not, of course, necessarily follow that because the distribution ratio of a substance between two immiscible solvents is constant, the activity and therefore the vapor pressure of the substance in each solvent is proportional to the mol fraction; *i. e.*, the vapor pressure of the substance need not obey either Raoult's law or Henry's law in the two solvents but may vary proportionately in the same direction and thus give a constant partition ratio.

III. The Equilibrium between Iodine and Potassium Iodide in Water Solution.

In Sec. I of this paper it is pointed out that the increase in the solubility of bromine in a water solution of KBr is proportional to the concentration of the KBr. This is not the case for the increase in the solubility of iodine in a water solution of KI. Thus, a liter of a 0.1 M KI solution dissolves about 0.05 M I_2, while a liter of a 1.0 M KI dissolves about 0.7 M I_2, the iodine separating out again on dilution with water. This may be explained by assuming that the higher complex compounds of KI and I_2 are chiefly of the type $2KI.nI_2$ instead of $KI.nI_2$ as in the case of the polybromides. In deciding on a value for n in the complex $2KI.nI_2$ it seemed most plausible as a first approximation to choose a value corresponding to the compound which has been investigated and identified by several investigators, *viz.*, 2KI, $6I_2$ or K_2I_{14}.[3] We then have,

$$\frac{(I^-)}{\gamma} + \frac{(I_3^-)}{\gamma} + \frac{2(I_{14}^{--})}{(\gamma)^2} = \Sigma KI, (1); \qquad \frac{(I_3^-)}{\gamma} + \frac{6(I_{14}^{--})}{(\gamma)^2} + I_2 = \Sigma I_2, (2);$$

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[1] *Z. physik. Chem.*, 20, 19 (1896).

[2] This agrees with the value given by Bray and MacKay, THIS JOURNAL, 32, 1208 (1910).

[3] *Z. anorg. Chem.*, 50, 403 (1906); Foote and Chalker, *Am. Chem. J.*, 39, 561 (1908).

$$\frac{I_3^-}{I^-} = (I_2)K', (3); \quad \frac{I_{14}^{--}}{(I_3^-)^2} = (I_2)^4K''.$$

Assuming that at 0.005 M KI the concentration of K_2I_{14} is zero, then $K'(I_2)K'$ equals 0.92. The values for K'' were then calculated, using the data given by Parsons and Whittemore for concentrated solutions. These are apparently the most reliable data on the solubility of iodine in concentrated water solution of KI with iodine as the solid phase. The data given by Abegg and Hamburger not only differ from those mentioned above, but are grossly inconsistent among themselves.

In the first column of Table V are given the concentrations of KI in mols per thousand grams of water; in the second column, the concentrations of the iodine also in mols per thousand grams of water; in the third column are given the equilibrium constants $(I_2)^4K''$.

TABLE V.

ΣKI.	ΣI_2.[1]	$(I_2)^4K''$. 25.°	
0.0050	0.00373	....	Bray & MacKay[2]
0.0500	0.02577	0.17	
0.1000	0.05135	0.18	
0.4136	0.2313	0.17	Linhart
0.5959	0.3538	0.18	
0.8065	0.5176	0.20	
1.0246	0.7079	0.21	
1.4747	1.1118	0.20	Parsons & Whittemore[3]
2.1952	1.9030	0.21	
3.3578	3.4595	0.23	
3.9349	4.4339	0.26	
6.9109	9.7669	0.29	
12.6880	20.9390	0.28	
17.2711	29.6126	0.24	

The concordance of the values in the last column is perhaps better than might be expected, when the mass law is applied to such concentrated solutions, and when it is assumed that the activity of the divalent salt K_2I_{14} is equal to the square of the activity of KI_3, which holds only approximately even for very dilute solutions.

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[1] 0.00132 mol, the solubility of iodine at 25° were subtracted from each value of column two. The corrected values were used in the calculation of the ratios given in column three.

[2] THIS JOURNAL, **32,** 919 (1910).

[3] Parsons and Whittemore, *Ibid.*, **33,** 1934 (1911).