

ART. XXXVI.—*Ionization and Polymerization in Cadmium Iodide Solutions*; by R. G. VAN NAME and W. G. BROWN.

[Contributions from the Kent Chemical Laboratory of Yale Univ.—ccxcv.]

It is a well known fact that water solutions of cadmium iodide show an abnormally low electrical conductivity and freezing point lowering as compared with other salts of like type. This is generally ascribed to the presence in the solution of complex molecules and ions. In a previous article* we have described a method, based on the measurement of distribution coefficients of iodine between such a solution and a non-aqueous phase, by which it is possible, by extrapolation, to calculate the percentage of simple molecules and ions in a pure solution of cadmium iodide. The application of this method led to the conclusion that in 0.5-molar cadmium iodide at 25° about 6 per cent was present in the form of simple CdI_2 molecules, ionized and non-ionized, in 0.25-molar solution 10.6 per cent, in 0.125-molar solution 16.8 per cent, and in 0.01-molar solution 55 per cent.

These results may be compared with those of Walton,† who showed in 1904 that the rate of decomposition of hydrogen peroxide in a neutral solution containing an iodide is proportional to the concentration of the iodine ion, and used this kinetic method to determine the proportion of iodine ion in a series of rather dilute cadmium iodide solutions. With due allowance for ionization and for differences in concentration, our results, as will be shown later, are consistent with those of Walton, at least as to order of magnitude.

McBain‡ on the other hand, by a mathematical analysis of the data in the literature concerning conductivity, freezing points, and transport numbers of cadmium iodide solutions, has arrived at quite a different result. McBain concludes that in a 0.1 molar cadmium iodide solution, the only concentration quantitatively dealt with, most of the salt is in the form of simple non-ionized CdI_2 molecules, and that the complexes make up only about 8 per cent of the whole.

In the present investigation we have attempted to throw further light upon this question by a study of solutions of cadmium iodide containing dissolved iodine, by means of measurements of electromotive force and of freezing point lowering.

Electromotive Force Measurements.

The reversibility and reproducibility of iodine electrodes composed of platinum immersed in an iodide solution contain.

* This Journal (4), xlv, 105, 1917.

† Zeitschr. phys. Chem., xlvii, 185, 1904.

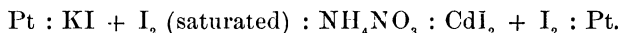
‡ Zeitschr. f. Elektrochem., xi, 215, 1905.

ing free iodine, have been proved by the work of a number of investigators.* In its relation to the present problem the work of Laurie† is especially important. Laurie used the electromotive force of concentration cells composed of two such iodine electrodes as a means of calculating the iodine ion concentration in a potassium iodide solution saturated with iodine. The Nernst equation for the electromotive force of such a cell at 25° may be written

$$(1). \quad \pi = 0.02955 \left\{ \left(\log \frac{(I_2)}{(I)^2} \right)_{\text{Sol. 1}} - \left(\log \frac{(I_2)}{(I)^2} \right)_{\text{Sol. 2}} \right\}.$$

The electromotive force is thus stated in terms of four concentrations. Under the conditions of Laurie's experiments three of these four concentrations were calculable from known data, and the fourth, the desired iodine-ion concentration, was calculated from the observed electromotive force. Concentrated ammonium nitrate solution was used to eliminate diffusion potentials.

The method pursued in our own experiments was similar to that of Laurie. The cells measured were of the type



Each cadmium iodide electrode was measured against two different potassium iodide electrodes of different concentrations, designated hereafter as electrodes A, and B, respectively, the former containing 0.1 molar KI, the latter 0.01 molar KI, both saturated with iodine. These two electrodes were then measured against each other, thus furnishing a check upon the results. All necessary data concerning these iodine-potassium iodide solutions have been given by Bray and MacKay.‡

As intermediate solution to eliminate diffusion potentials, a concentrated solution of ammonium nitrate was employed, to which, following a suggestion due to Luther,§ enough sodium nitrate was added to make the mean cation velocity the same as that of the anion. This solution contained 8.3 mols NH_4NO_3 and 1 mol NaNO_3 per liter. For comparison a few measurements were made in which saturated potassium chloride solution was substituted for the mixed nitrates, but the results failed to show any difference large enough to be of importance in the present work. The nitrate solution was used in all the experiments recorded below.

Calculation of the diffusion potential by the Planck or the Henderson equation was practicable only when the ion concen-

* See, for example, Maitland, *Zeitschr. f. Elektrochem.*, xii, 263, 1906; also, Jones and Hartmann, *Jour. Am. Chem. Soc.*, xxxvii, 757, 1915.

† *Zeitschr. phys. Chem.*, lxvii, 627, 1909.

‡ *Jour. Am. Chem. Soc.*, xxxii, 914, 1910.

§ See Bjerrum, *Zeitschr. phys. Chem.*, liii, 438, 1905.

trations of both solutions were known, which was true in the case of the cell made up of the two potassium iodide electrodes, but not for a cell with a cadmium iodide electrode. For the potassium iodide concentration cell the value of the diffusion potential was calculated with the aid of the following data taken from the article of Bray and MacKay:

	Solution 1 0.1 molar	Solution 2 0.01 molar		Migration velocities
(K ⁺)	0.0865	0.00941	:	74.8
(I ⁻)	0.0430	0.00484	:	76.5
(I ₃ ⁻)	0.0435	0.00457	:	41.5

Using the Planck formula the value of the potential so obtained was 0.0070 volt, while the Henderson formula gave from the same data the value 0.0069 volt. The measured value, as given by the difference between the electromotive force as observed with and without the use of the intermediate nitrate solution, was approximately 0.003 volt.

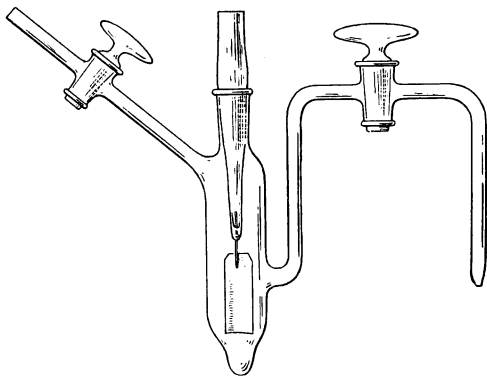
In the opinion of the writers this difference between the measured and calculated values of the diffusion potential is too large to be explained by experimental error, or by uncertainty in the data employed in the calculation, and is to be ascribed to some peculiarity in the behavior of liquid junctions which involve the tri-iodide equilibrium. Support for this view is given by the fact that the diffusion of iodine in an iodide solution is abnormal in at least one important respect, for the rate of diffusion of iodine in potassium iodide is known to increase with increasing concentration of the latter, while by the rule of Abegg and Bose* we should expect just the reverse. That the discrepancy is in all probability not due to the incomplete elimination of the diffusion potential by the nitrate solution is shown by the fact that the electromotive force of this concentration cell as measured with the nitrate solution as intermediate liquid (mean value of many determinations, 0.0560 volt), was in close agreement with the value calculated from Equation 1 (0.0561 volt).

Apparatus.—The type of half-cell used is shown in the figure. The tube carrying the electrode (of bright platinum foil) was fitted into the neck of the half-cell by a ground joint, so that the iodine solution came in contact with nothing but platinum and glass. Two such cells were clamped in a frame with their siphon tubes dipping into opposite arms of a U tube containing the intermediate solution, and the whole was immersed up to the necks of the half-cells in a thermostat kept at 25°. With stop-cocks closed the cell could be left set up for many days without danger of contamination of the solu-

* Zeitschr. phys. Chem., xxx, 551, 1899.

tion, and could quickly be put into commission again by emptying the siphon arms and renewing the intermediate liquid. The stop-cocks in the siphon arms were generally left open during the actual measurement. In the earlier experiments, contact between dissimilar solutions was brought about in the U tube in a layer of sea-sand, as recommended by Bjerrum,* but the use of sand was later abandoned as troublesome and unnecessary for the present purpose.

The measurements were made by the Poggendorf compensation method with the aid of a galvanometer sensitive to



4×10^{-9} amperes. Owing, however, to the high resistance of the cells measured, the accuracy of a single bridge-reading did not much exceed one millivolt.

Preparation of the Reference Electrodes.—The complete saturation of the iodide solutions with iodine was accomplished by sealing the solution with powdered iodine in a large glass tube, which was attached to the stirring axle of the thermostat and rotated for a period of at least 24 hours. With solutions so prepared the two reference electrodes, when measured against one another, usually gave a constant potential difference within 12 hours, which retained its value practically unchanged for many days. Occasional shaking of the half-cells (which contained a little solid iodine) was found to favor constant results. The liquid in the siphon arms was emptied periodically, and the half-cell when necessary could be refilled with a portion of the original (iodine saturated) solution without altering the measured electromotive force. All measurements were at 25° C.

Experimental Procedure.—A cell composed of the two reference electrodes was first set up and its electromotive force

* Zeitschr. f. Elektrochem., xvii, 58 and 389, 1911.

measured from time to time until the constant value 0.056 volt was reached. A half-cell was then filled with the iodine-cadmium iodide solution to be investigated, and measured in turn against each of the reference electrodes. Finally, as a check, the reference electrodes were again combined and measured. Obviously the difference between the electromotive forces of the two cells in which the iodine-cadmium iodide electrode was used should agree with the electromotive force of the cell made up of the two reference electrodes (0.056 volt). All measurements in which the difference above mentioned was within ± 0.001 volt of 0.056 volts were considered trustworthy.

The cadmium iodide solutions used were of four different concentrations: 0.5, 0.25, 0.125 and 0.01 molar, from each of which a number of electrodes containing varying amounts of dissolved iodine were prepared and measured against electrodes A and B. Since these concentrations of cadmium iodide were the same as employed in the determinations of distribution coefficients described in our previous article* the results of that work were used in calculating (I_2), the concentration of uncombined iodine, from the concentration of dissolved iodine as found by direct titration. For electrodes A and B (I_2) was obviously equal to 0.00132, the solubility of iodine in pure water, and the values of (I') for these two solutions were those given on p. 455 of this article. It was, therefore, possible to calculate (I') for each cadmium iodide solution from the observed electromotive force by means of Equation 1.

A summary of the results is given in Table I. Except where otherwise stated, concentrations in this and the following tables are expressed in millimols per liter. In the third column are the potential differences given by each iodine-cadmium iodide electrode against reference electrode A, while the potential difference for the same electrode against reference electrode B is found in the fourth column on the horizontal line next below. A negative sign prefixed to the recorded potential indicates that the reference electrode formed the negative pole. Usually the reverse was true. The iodine-ion concentrations calculated from these potential differences are recorded in the fifth and sixth columns, the former giving the two independent values for each solution, derived from the two potentials measured, and the latter the mean of the two. Finally, by graphical extrapolation of the values in column six to zero concentration of iodine, a value has been obtained for each cadmium iodide solution which should represent the concentration of iodine ion in the given cadmium iodide solution if it contained no dissolved iodine. These four extrapolated values are the important ones for our present purpose. Since

* This Journal (4), xlv, 105, 1917.

TABLE I.

	Dissolved iodine	(I ₂)	E. M. F. volt		(I')	(I' mean
			against A	against B		
0.5 molar CdI ₂	*55.5	1.32	0.0423		25.1	25.3
				—0.0134	25.5	
	39.29	0.955	0.0504		29.3	30.0
				—0.0046	30.7	
	26.06	0.605	0.0536		26.5	26.9
				—0.0029	27.3	
	21.63	0.505	0.0589		29.7	30.2
				0.0037	30.8	
	13.44	0.315	0.0648		29.5	29.7
0.25 molar CdI ₂				0.0090	29.8	
	7.57	0.175	0.0725		29.7	30.6
				0.0178	31.5	
	6.02	0.140	0.0751		29.4	30.2
				0.0203	30.9	
	0.0	0.0				30.4
	*45.35	1.32	0.0470		30.2	29.7
				—0.0099	29.2	
	36.24	0.99	0.0490		28.3	28.8
0.125 molar CdI ₂				—0.0063	29.2	
	20.4	0.538	0.0592		31.0	30.8
				0.0027	30.5	
	9.69	0.255	0.0689		31.1	30.9
				0.0124	30.7	
	6.02	0.160	0.0745		30.4	31.1
				0.0193	31.8	
	3.387	0.090	0.0818		30.6	31.2
				0.0267	31.8	
0.125 molar CdI ₂	0.0	0.0				31.2
	*35.7	1.32	0.0423		25.1	25.6
				—0.0137	26.0	
	18.63	0.648	0.0531		26.9	27.4
				—0.0021	27.8	
	7.26	0.250	0.0675		29.2	29.1
				0.0112	29.0	
	3.443	0.110	0.0770		28.1	28.3
				0.0213	28.5	
0.125 molar CdI ₂	1.641	0.051	0.0870		28.3	28.5
				0.0313	28.7	
	0.792	0.022	0.0962		26.5	27.0
				0.0410	27.5	
	0.0	0.0				27.5

* Solution saturated with iodine.

TABLE I.—Continued.

	Dissolved iodine	(I ₂)	E. M. F. volt		(I')	(I') mean
			against A	against B		
0.01 molar CdI ₂	*8.16	1.32	0.0080		6.62	6.79
				— 0.0468	6.95	
	2.540	0.2967	0.0342		8.69	9.16
				— 0.0193	9.62	
	1.397	0.1569	0.0431		8.95	9.23
				— 0.0114	9.52	
	0.646	0.0713	0.0535		8.94	8.94
	0.3104	0.0343	0.0654		9.93	10.42
				0.0116	10.90	
	0.1411	0.0168	0.0755		10.36	10.77
				0.0216	11.27	
	0.0	0.0				10.50

* Solution saturated with iodine.

all these iodine-ion concentrations are very low we can certainly afford to disregard here the slight error involved in the assumption that the results of electromotive force measurements represent concentrations rather than "activities" as defined by Lewis.*

Discussion.—In the previous investigation, as has already been stated, values were obtained for the proportion of simple molecules, ionized and non-ionized, in a pure solution of cadmium iodide at various concentrations. This quantity we shall designate, as in our former article, by the term "active fraction." The rest of the cadmium iodide must consist of associated cadmium iodide molecules, and of the ions, simple or complex, formed therefrom.

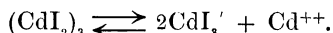
These values of the active fraction are calculated upon the assumption that the abnormally low power of cadmium iodide to unite with iodine is due entirely to the presence of complexes, a condition which may be only approximately fulfilled. The amount of iodine taken up by an iodide should be practically independent of its degree of ionization, provided that the tri-iodide is ionized to about the same extent, as is no doubt generally the case.† But although it is contrary to experience

* For a discussion of the relation between activity and concentration for the iodine ion in potassium iodide solutions, see Bray and MacKay (Jour. Am. Chem. Soc., xxxii, 925, 1910).

† This is confirmed by the fact that for all metallic iodides so far investigated, with the exception of those of cadmium and mercury, the value of the equilibrium constant $K_1 = (\Sigma I)(I_2) / (\Sigma I_2)$ is the same. The list includes the iodides of di- and trivalent metals, Ba, Sr, Zn, Ni, and La, whose degrees of ionization are certainly somewhat different from those of the univalent iodides.

that two metallic salts of like type and as closely related as are cadmium iodide and cadmium tri-iodide should show any large difference in ionization, the possibility of slight differences is not excluded, which if present would cause small positive or negative errors in the value of the active fraction, calculated as above.

According to McBain* the observed transport numbers indicate that the complex ion present in predominating amount is CdI_3' , formed by ionization of $(\text{CdI}_2)_3$ according to the reaction:



Whether or not this inference is correct it is probable that the above equilibrium is typical, and that the inactive fraction consists essentially of (a) associated molecules, (b) complex anions, and (c) simple Cd^{++} cations. It follows, therefore, that the degree of ionization of the simple CdI_2 molecules may be calculated, at least approximately, by dividing the concentration of the iodine ion, taken from Table I, by the equivalent concentration of the "active" cadmium iodide as derived from the data of the previous investigation.

Table II shows the results obtained in this way. The first three columns contain the concentrations of total cadmium iodide, of active cadmium iodide, and of the iodine ion, respectively. The fourth column gives the degree of ionization of the simple CdI_2 molecules as calculated from columns two and three, and the fifth shows, for comparison, the degrees of ionization of cadmium nitrate, a normally ionized salt of like type, at the same concentrations as those of $(\text{CdI}_2)_{\text{active}}$ in column two. The data for cadmium nitrate were obtained by interpolation from values given by Noyes and Falk.†

TABLE II.

(CdI_2)	$(\text{CdI}_2)_{\text{active}}$	(I')	$\gamma = \frac{(I')}{2(\text{CdI}_2)_{\text{active}}}$	γ for $\text{Cd}(\text{NO}_3)_2$ at 18°
500	30·	30·4	·51	·78
250	26·5	31·2	·59	·79
125	21·	27·5	·65	·80
10	5·5	10·5	·95	·87

According to these results the degree of ionization of the CdI_2 molecules is considerably lower, except in the most dilute solution, than that of the cadmium nitrate. A difference in this direction, though smaller in amount, would be expected on account of the presence in the cadmium iodide solution of

* Zeitschr. f. Elektrochem., xi, 215, 1905.

† Jour. Am. Chem. Soc., xxxiv, 475, 1912.

an excess of Cd^{++} ions resulting from the ionization of the associated molecules, and it would also be expected that the difference, if due to this cause, would decrease with increasing dilution, as is in fact the case. It is probable, however, that the actual difference between the degrees of ionization of these two salts is considerably smaller than these results would indicate, for the error in determining γ by the above method may easily be rather large.

The work of Walton,* whose kinetic method for determining iodine ion concentrations has already been referred to, is of interest here, since his results yield values of (I') which can be compared with those in Table I. Unfortunately, Walton's experiments with cadmium iodide were confined to solutions more dilute than 0.05 molar. The comparison is shown in Table III, the second horizontal line giving the values of (I') calculated from Walton's results† while the third contains our values for the same quantity. Figures enclosed in parentheses were obtained by graphical interpolation.

TABLE III.

(CdI_2)	4.9	10	19.4	31.8	42.1
(I') Walton	6.5	(12)	19.3	26.5	31.2
(I') V. N. & B.		10.5	(14)		(20)

The two sets of results agree in order of magnitude, though Walton's values are higher and increase more rapidly with the concentration. Since Walton's method has not yet been very thoroughly studied, particularly as to its sensitiveness toward secondary catalytic influences, the results of the electromotive force measurements deserve the greater weight.

Freezing Point Measurements.

Since the purpose of these measurements was to determine the effect of successive additions of iodine upon the freezing point of a given cadmium iodide solution, it was necessary to employ a method of the "undercooling" type, the very convenient and accurate method of Roloff,‡ as improved by Richards,§ being excluded by the fact that it would not permit the concentration of the cadmium iodide to be kept constant. After unsuccessful attempts to obtain sufficient accuracy with the aid of a modified Beckmann apparatus, using a cryohydric mixture for the cooling bath, and other special precau-

* *Zeitschr. phys. Chem.*, xlvii, 185, 1904.

† These values were obtained by dividing the observed velocity constants in each case by 1.45, the average value of the ratio, *Velocity constant* / (I') , as found by Walton's experiments with KI, NaI, and NH_4I .

‡ *Zeitschr. phys. Chem.*, xviii, 572, 1895.

§ *Jour. Am. Chem. Soc.*, xxv, 291, 1903.

tions, an apparatus was finally devised which satisfactorily met the needs of the case. The construction and manipulation of this apparatus have been fully described in a former paper,* so that only the principal points in the procedure need be given here.

The different cadmium iodide solutions used were kept in thoroughly steamed bottles of Jena glass. The freezing point of the water was first taken. The water was then replaced by the cadmium iodide solution, which had been prepared by dissolving the carefully dried and weighed salt in a portion of the same water, and diluting to an exact volume. At least three determinations of the freezing point were made, using varying degrees of undercooling, and no result was accepted unless the final temperature held constant within 0.001° (the maximum sensitiveness of the temperature reading) for at least five minutes. The volume of solution used in the freezing point apparatus was either 200 or 250 cm^3 .

The pure cadmium iodide solution was next replaced by a portion of the same solution which had been shaken at room temperature with an excess of iodine in a Jena glass bottle for some hours. At 0° this solution was supersaturated with iodine. To insure equilibrium with both ice and solid iodine the liquid was allowed to partially freeze and was then kept at its freezing point with continual stirring for several hours. Equilibrium was assumed to have been reached when successive determinations of the freezing point agreed, and also successive titrations of the dissolved iodine. In this way the freezing points were obtained for solutions saturated with iodine, and for those containing no dissolved iodine. Data for the intermediate iodine concentrations were obtained by mixing varying amounts of the saturated solution with the original pure cadmium iodide solution, determining the freezing point as before, and, finally, estimating the iodine by titration.

In all these measurements care was taken to maintain the room temperature as constant as possible, and in a few cases where appreciable variation occurred the thermometer readings were corrected for change in the length of the projecting mercury thread with the aid of the usual formula, using the value 0.000156 for the apparent expansion coefficient for mercury in glass. This correction was applied only in working with the more dilute solutions where its importance was obviously greatest.

The results of these experiments are given in Table IV. The four concentrations of cadmium iodide studied are the same as in the measurements of electromotive force at 25° . Iodine concentrations are given in the second column, the starred values being those for solutions approximately saturated with iodine, having iodine present as a solid phase. In the

* This Journal (4), xliii, 110, 1917.

third column are the observed freezing point depressions, which in nearly every case are the mean of two or three separate determinations. The fourth and fifth columns contain the observed values, for the pure cadmium iodide solution, of the van't Hoff coefficient i , and of the apparent degree of ionization γ , as calculated in the ordinary way from i .

TABLE IV.

(CdI ₂)	Dissolved iodine	F. p. dep.	$i =$ van't Hoff coeff.	$\gamma = \frac{i-1}{2}$	Dep. due to iodine	Molec. dep. for iodine
500	0.0	1.067°	1.147	7.35%		
"	9.4	1.089			0.022°	2.34(?)
"	19.6	1.095			0.028	1.43
"	27.9	1.112			0.045	1.61
"	*40.4	1.125			0.058	1.44
250	0.0	0.533°	1.145	7.25%		
"	9.33	0.546			0.013°	1.40
"	19.4	0.558			0.025	1.29
"	24.9	0.567			0.034	1.37
"	*33.6	0.579			0.046	1.37
125	0.0	0.277°	1.193	9.65%		
"	5.93	0.285			0.008°	1.35
"	10.29	0.293			0.016	1.56
"	16.75	0.301			0.024	1.43
"	*27.5	0.317			0.040	1.46
10	0.0	0.0365°	1.962	48.1%		
"	2.344	0.0394			0.0029°	1.24
"	4.266	0.0424			0.0059	1.38
"	*7.53	0.0453			0.0088	1.17

Previous determinations of i for cadmium iodide by the freezing point method have been made by Arrhenius,* by H. C. Jones,† and by Chambers and Frazer.‡ Our values at the two lowest concentrations are in excellent agreement with those of Jones (whose results only cover concentrations up to 0.1 molar) and at the two higher concentrations they are close to the mean between the results of Arrhenius and those of Chambers and Frazer. No explanation is offered for the fact that i is slightly larger in 0.5 molar cadmium iodide than in the 0.25 molar solution, but the effect is real as it is even more evident in the results of the other investigators than in our own. Chambers and Frazer ascribe the phenomenon to hydration.

The last column of Table V shows the "molecular depression for iodine" as obtained by dividing the depression due to iodine (column six) by its total concentration as given in col-

* Zeitschr. phys. Chem., ii, 491, 1888.

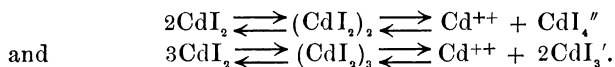
† Ibid., xi, 544, 1893.

‡ Am. Chem. Jour., xxiii, 512, 1900.

nmn two. This quantity proves to be roughly constant irrespective of the concentration and to have a value between 1.3 and 1.4, or about three-fourths of 1.86, the normal molecular lowering for a non-electrolyte in pure water.

The relatively large amount of this increase proves that the cadmium tri-iodide formed is derived ultimately from some source which previously contributed a much smaller number of molecules and ions to the solution. Unless, therefore, we are willing to admit that the cadmium tri-iodide may have in the solution a degree of ionization many times greater than that of the simple cadmium iodide molecules,* these results must be regarded as clear proof of the existence of complexes in these solutions. On the other hand, if the effect is largely or wholly due to complexes, as is probably the case, the relative constancy of the values in the last column of Table IV is an indication that the complexes are present in considerable quantity even in the more dilute solutions. On account of the low solubility of iodine in water at 0° the depression due to the iodine which remains uncombined is so small† as not to affect the validity of this reasoning.

Owing to the presence of complexes it is of course impossible to get any accurate measure of the concentration of the iodine ion from the value of i , but in the present case the error so involved would not necessarily be very large. Of the various kinds of complex ions to be expected here the two simplest and most probable are CdI_3' and CdI_4'' , formed as products of the equilibria



In both of these cases the number of ions produced is the same as the number of CdI_2 molecules disappearing, so that the net result of the complex formation will be to diminish the freezing point depression by a small amount due to that part which remains in the form of non-ionized polymerized molecules, $(\text{CdI}_2)_2$ or $(\text{CdI}_2)_3$ as the case may be. Hence, if values for the concentrations of the iodine ion are calculated in the usual way from the freezing point lowerings the results will in general be low, but in sufficiently dilute solutions should not be very far from the truth.

In Table V the iodine ion concentrations, so calculated, are tabulated for comparison with those derived from the measurements of electromotive force. For the two lowest concentra-

* A rough calculation shows that to account for the results in the absence of complexes the ratio of these two degrees of ionization would have to be over 2 in the 0.01 molar solution, about 8 in the next, and about 25 in the strongest.

† Its maximum value is 0.0012°, which is reached only when the solution is saturated with iodine.

tions the agreement is fairly good, but in the 0.25 molar solution the difference is not in the expected direction, and in the strongest solution the discrepancy is surprisingly large, far exceeding the probable experimental error. For this result there is no evident explanation, but it is significant that it

TABLE V.

(CdI ₂)	(I') at 0° From freezing point	(I') at 25° From E. M. F.
500	74	30.4
250	36	31.2
125	24	27.5
10	9.6	10.5

coincides with a marked irregularity in the freezing point lowering. As was noted on page 463, the results of all cryoscopic measurements with cadmium iodide show that above about 0.3 molar the value of i apparently rises with the concentration, although the attendant decrease in ionization and increase in polymerization would both tend to lower it.

Nature and Concentration of the Complexes.—Thus far the question of the nature of the complex ions and molecules has been left open. Of the various complex ions which may be present in the solutions, CdI₃' as McBain* has shown, is apparently the most probable one. The high transport number of the anion, which approaches 1.25 in the most concentrated solutions, cannot be explained by assuming the predominance of CdI₄" without assigning to that ion an improbably high velocity. This objection, however, would not apply to such ions as Cd₂I₅' or Cd₃I₇", though there would be less reason to expect their presence than that of the less complex ones just mentioned.

McBain has calculated the approximate composition of a 0.1 molar solution of cadmium iodide upon the assumption that CdI₃' is the only complex ion present in appreciable amount. This calculation, which is based entirely upon freezing point, transference, and conductivity data, gives the values (CdI₃') = 0.0084 and (I') = 0.0126. This would make (Cd⁺⁺) = 0.0105, thus accounting for about 19 per cent of the total iodide. McBain concludes that the remaining four-fifths is present in the form of simple, non-ionized CdI₂ molecules, and that the proportion of complex molecules is negligible.

There are several serious objections to these figures: (a) If so large a part of the salt is in the form of simple CdI₂ molecules the power of the salt to combine with iodine should be but slightly lower than normal, while in reality the "active

* Loc. cit.

fraction" at this concentration is only about 20 per cent.* (b) The molecular conductivity of the solution as calculated for 18° from the above composition is 22.5,† or less than half the value actually measured, which is 46.7. (c) The value of (I') calculated by McBain is much lower than that given by the electromotive force method.

In a similar manner it is possible to calculate the approximate composition of cadmium iodide solutions from the experimental data furnished by our measurements of electromotive force, and by our previous study of the iodine-cadmium iodide equilibrium. These calculations will be confined to the 0.01 and 0.125 molar solutions, for which the data are presumably most accurate. It will be assumed that CdI_3' is the only complex ion present in significant amount, and that the degree of ionization of $(\text{CdI}_2)_3$ is of about the same order of magnitude as that of the average uni-bivalent electrolyte.

Allowing for the effect of the excess of Cd^{++} ions, which is much larger in the 0.01 molar than in the 0.125 molar solution, we may assume that the degree of ionization is 80 per cent in the former and 75 per cent in the latter. An error of a few per cent in the degree of ionization assumed will not greatly change the results. Using these degrees of ionization, the "active fractions" given on page 453 and the values of (I') from Table I, we obtain the results recorded in Table VI. That these values differ greatly from those of McBain is evi-

TABLE VI.

	(CdI_3')	(Cd^{++})	(I')	(CdI_2)	$(\text{CdI}_2)_3$
0.01 molar.....	2.4	6.45	10.5	0.25	0.3
0.125 molar.....	52.	39.7	27.5	7.2	8.6

dent. Interpolation of these results for 0.1 molar concentration gives, approximately, $(\text{CdI}_3') = 0.045$ and $(\text{I}') = 0.021$, figures which are respectively 5 and 1.7 times those of McBain.

Since the values in Table VI depend upon neither freezing point nor conductivity measurements, their correctness may properly be tested by calculating the van't Hoff coefficient i and the molecular conductivity for each solution. For i we obtain $0.0199 / 0.01 = 1.90$, and $0.135 / 0.125 = 1.08$ respectively, while the measured values (see Table V) are 1.96 and 1.19.

* This low power to unite with iodine cannot be explained by the low ionization of the CdI_2 molecules unless it is assumed that the degree of ionization of the cadmium tri-iodide is about nine times larger. This is obviously very improbable.

† For the method of calculation see p. 467. The ionic conductivities here used were those employed by McBain, namely, $\frac{1}{2}\text{Cd} = 51$, $\text{CdI}_3' = 41$, and $\text{I}' = 66.4$. If the values given on p. 467 be employed the result is 21.1 instead of 22.5.

To calculate the molecular conductivity we must obtain a value for the conductivity of CdI_3' . If we assume with McBain that the value 1.25, the limit which the observed (anion) transport number of a cadmium iodide solution tends to approach with increasing concentration, is that of the anion CdI_3' , then the relative velocity of this ion must be $\frac{1.25}{3} = 0.42$, that is, $\frac{42}{58}$ that of Cd^{++} . For the equivalent conductivity of the Cd^{++} ion we may use the value 47 for 18° , which corresponds to 56 at 25° . This gives, for CdI_3' , 34 at 18° and 40.5 at 25° . For iodine ion the values are 66.6 and 76.5 respectively. The molecular conductivity of the 0.01 molar solution at 25° should therefore be

$$\{ (0.00645)(112) + (0.0024)(40.5) + (0.0105)(76.5) \} \div 0.01 = 162.2,$$

and for the 0.125 molar solution, calculated in the same way, 69.2.

These calculated conductivities are much too high, the measured values being 120 and 57 respectively, a result which seems to be due to some fault in the assumptions made rather than to experimental errors. It is not clear, however, how this discrepancy can be eliminated without introducing some other one. The evidence at hand is in some respects conflicting and is obviously insufficient for an exact solution of the problem. In short, though some of the values in Table VI are probably nearly correct, the figures as a whole can represent, at best, no more than a rough approximation to the truth.

The Iodine-Cadmium Iodide Equilibrium at 0° .—Each of the starred values in Table V represents the solubility of iodine in the given solution at its freezing point, which, as an approximation, may be assumed to be the same as the solubility at 0° in the same medium. By subtracting the solubility of iodine in pure water at 0° (0.000638 mols/liter*) we obtain (ΣI_2) , the equivalent concentration of the tri-iodide formed, and can therefore calculate the approximate value of the equilibrium constant $K_1 = (\Sigma \text{I})(\text{I}_2)/(\Sigma \text{I}_3)$.

The results so obtained are given in Table VII, which compares the values of K_1 for cadmium iodide at 0° and 25° with those for potassium iodide at the same temperatures and concentrations. All of these figures refer to solutions saturated with iodine. The values for cadmium iodide at 25° were taken from our previous article; those for potassium iodide at 0° were calculated in the way just described from data given by Jones and Hartmann;† those for potassium iodide at 25° were taken from the article of Bray and MacKay.

* Jones and Hartmann, Jour. Am. Chem. Soc., xxxvii, 256, 1915.

† Loc. cit., p. 250.

TABLE VII.

Concentration. equiv./liter	Cadmium Iodide		Potassium Iodide	
	K_1 at 0° (approximate)	K_1 at 25°	K_1 at 0° Jones and Hartmann.	K_1 at 25° Bray and MacKay
1.0	0.0154	0.0234	0.00046
0.5	0.0090	0.0137	0.00088
0.25	0.0053	0.0082
0.10	0.000696	0.00131
0.02	0.0011	0.00247	0.000716	0.00137

These figures show that the value of K_1 for cadmium iodide at 0° is abnormal in the same way as at 25°, being larger throughout than for a normal iodide like potassium iodide, and increasing rapidly with the concentration. The effect upon K_1 of a change in temperature, however, is practically the same for the cadmium as for the potassium salt.

Summary.

1. Measurements have been made: (a) by the electromotive force method, of the iodine ion concentration in cadmium iodide solutions of 0.5, 0.25, 0.125, and 0.01 molar strength, containing various amounts of dissolved iodine; also (b) of the freezing point lowering of each of these cadmium iodide solutions, and of the further lowering produced by the addition of known amounts of iodine.

2. Values of (I') calculated in the ordinary way from the cryoscopic measurements should be slightly lower, if complexes are present, than those electrically measured. This was found to be the case in the 0.01 and 0.125 molar solutions, but not in the two stronger solutions.

3. The freezing point of a cadmium iodide solution was depressed by the addition of iodine in a nearly constant ratio, which in the stronger solutions was about 1.4° per mol, and only slightly smaller in the weakest solution. This indicates the presence of complexes in considerable quantity even in the 0.01 molar solution. Neither this result nor the abnormally low power of cadmium iodide to unite with iodine can be accounted for, in the absence of complexes, by the assumption that the degree of ionization of the cadmium iodide is very small, unless this low ionization is accompanied by high ionization of the cadmium tri-iodide, a state of affairs which is decidedly improbable.

4. A tentative calculation of the composition of the two more dilute cadmium iodide solutions, based upon the assumption that the ion CdI_3' and its parent molecule $(\text{CdI}_2)_2$ are the only complexes present, failed to give results in quantitative agreement with other experimental data.