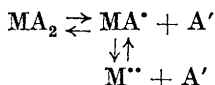


63. *A Potentiometric Investigation of Electrolytic Dissociation. Part I. Cadmium Halides.*

By HARRY LISTER RILEY and VICTOR GALLAFENT.

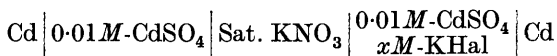
THE electrolytic behaviour of bi-univalent salts is complicated by the possibility of their dissociation occurring in two stages, *e.g.*,



When such salts contain kations which readily form complex ions, or anions which readily enter a co-ordinated complex, their behaviour is further complicated. Such a state of affairs exists in the case of the cadmium halides. A study has been made of aqueous solutions of cadmium chloride, bromide, and iodide (the fluoride could not be included owing to its sparing solubility) by a potentiometric method, and it has been found possible, not only to determine the concentration of free cadmium ions, but also to calculate the concentration of the halide ions, undissociated halide, and complex ions in solution. The method employed, although limited by hydrolysis and sparing solubility, is believed to be capable of extensive application and has been developed from the potentiometric studies already described (J., 1930, 1642; 1931, 2029).

EXPERIMENTAL.

Potentiometric titrations were carried out at room temperature in a manner essentially the same as that already described (*loc. cit.*), the following concentration cell being used:



(The symbol "Hal" is used throughout to represent Cl, Br, and I generally.) x varied from 0 to 1.8.

The cadmium electrodes were prepared by plating small pieces of sheet cadmium in a bath of the following composition: hydrated cadmium sulphate, 20 g.; water, 500 c.c.; concentrated sulphuric acid, 3 c.c.; ammonium sulphate, 5 g.; ethyl alcohol, 20 c.c.; a current density of app. 0.5 amp./100 cm.² was used. The three electrodes required for each titration were, after being plated, allowed to remain short-circuited in the bath over-night. Reproducible results were obtained with greater ease than with copper. It was unnecessary to boil out the water used, in a current of hydrogen, but it was found convenient to stir the solution in the right-hand half-element during the titration by bubbling a current of hydrogen

through it. Titrations were also carried out using sodium halides in place of potassium halides, and results in excellent agreement were obtained. "A.R." Salts were employed throughout.

The results recorded in Table I were obtained from two titrations in each case, the one using a dilute solution of the halide to determine

TABLE I.

Chloride.			Bromide.			Iodide.		
Conc.	P.D.	[Cd] × 10 ⁵ .	Conc.	P.D.	[Cd] × 10 ⁵ .	Conc.	P.D.	[Cd] × 10 ⁵ .
0.0149	6.4	367	0.0099	3.2	476	0.0050	6.6	364
0.0294	8.1	302	0.0196	6.2	376	0.0098	9.4	291
0.0437	14.7	184	0.0291	11.3	250	0.0183	15.3	182
0.0577	18.3	146	0.0385	17.3	156	0.0283	20.2	123
0.0714	19.1	135	0.0476	18.8	138	0.0370	23.6	94.3
0.0849	20.5	117	0.0566	21.6	111	0.0455	27.4	69.7
0.1111	24.8	85.7	0.0741	24.8	85.7	0.0614	34.2	40.6
0.1364	27.2	70.3	0.0909	28.2	64.5	0.0763	40.1	25.4
0.1607	29.0	58.6	0.1071	31.0	52.4	0.0968	47.6	14.0
0.2069	33.0	43.0	0.1379	35.9	35.5	0.1094	52.5	9.50
0.2500	36.4	32.8	0.1667	39.5	26.7	0.1212	56.9	6.70
0.2903	38.9	26.7	0.1935	42.7	20.7	0.1324	61.2	4.76
0.3636	44.1	18.0	0.2424	48.0	13.6	0.1429	64.6	3.64
0.4286	46.7	14.3	0.2857	52.1	9.81	0.1528	68.0	2.78
0.5000	50.5	11.0	0.3333	56.1	7.14	0.1667	72.6	1.93
0.5625	51.5	9.37	0.4286	60.2	5.16	0.2069	87.6	0.586
0.6176	54.4	7.97	0.5000	63.1	4.10	0.2500	97.3	0.271
0.6667	55.6	6.99	0.5625	67.7	2.84	0.2903	105.9	0.137
0.7500	58.6	5.29	0.6176	72.6	1.93	0.3636	117.1	0.0563
0.8571	64.8	3.58	0.6667	75.4	1.54	0.4286	124.0	0.0325
1.0000	69.0	2.56	0.7500	79.8	1.09	0.5000	133.5	0.0153
1.1250	72.7	1.91	0.8571	85.7	0.681	0.5625	138.6	0.0102
1.2353	76.3	1.44	1.0000	92.4	0.400	0.6176	143.3	0.00703
1.3333	78.4	1.21	1.1250	98.9	0.239	0.6667	150.0	0.00413
1.4211	80.6	1.02	1.2353	104.0	0.159	0.7500	158.0	0.00219
1.5000	82.8	0.857	1.3333	107.3	0.123	0.8571	162.5	0.00153
1.6364	85.7	0.681	1.4211	110.1	0.0958	1.0000	171.1	0.000773
1.8000	89.0	0.524	1.5000	113.8	0.0731	1.1250	176.5	0.000504
			1.6364	117.7	0.0564	1.2353	182.0	0.000325
			1.8000	122.4	0.0369	1.3333	185.4	0.000248
						1.4211	188.6	0.000193
						1.5000	191.8	0.000149
						1.6364	196.4	0.000104
						1.8000	201.3	0.0000703

the lower potentials, and the other, a more concentrated solution to obtain the higher potentials. The concentrations of the salts are given in mols. per litre, and the P.D.'s in millivolts.

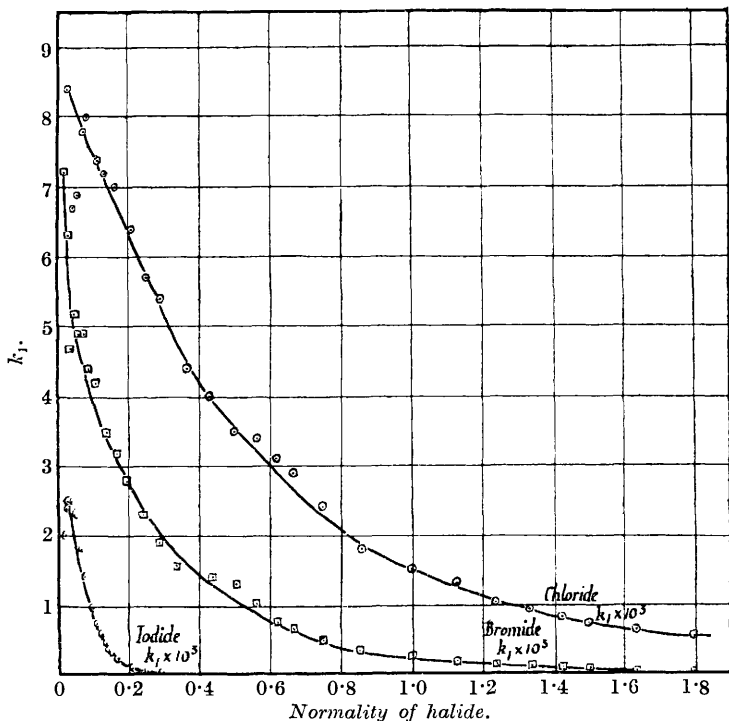
Analysis of Results.

The values of [Cd] obtained at various concentrations of halide can be analysed by the use of the following relationship :

$$\frac{[\text{Cd}][\{\overline{\text{H}\text{a}}\} - n(\overline{\text{C}\text{d}} - [\text{Cd}])\gamma]^n}{[\overline{\text{C}\text{d}} - [\text{Cd}]]} = k_n$$

where $[Cd]$ is the cadmium-ion concentration [calculated from the *P.D.* of the concentration cell by the use of the expression $E = RT/nF \cdot \log C_2/C_1$, $[Cd]$ in 0.01*M*-cadmium sulphate being taken as 0.00614 at 18° (Noyes and Falk, *J. Amer. Chem. Soc.*, 1912, **34**, 475)]; \overline{Cd} is the total cadmium and \overline{Hal} the total halide present in solution, γ an activity correction, n a positive integer, and k_n a "mass-action" relationship. Then $[\overline{Cd} - [Cd]] =$ concentration

FIG. 1.



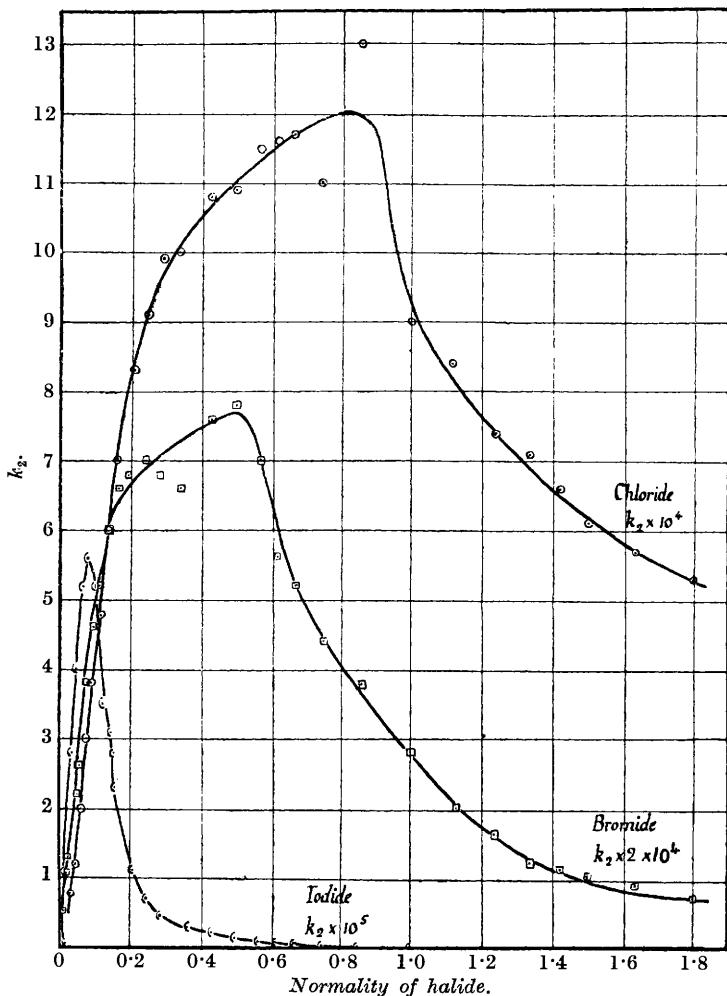
of the total undissociated cadmium halide and complex cadmium halide ions.

The concentration of the sulphate ions is neglected because this rapidly becomes negligible compared with that of the halide. The advantage of using sulphate in both half-elements of the cell lies in the fact that it is possible to check the condition of the electrodes before commencing the titration, a reading of zero potential across the cell indicating that they are in the same condition.

$[\{\overline{Hal} - n(\overline{Cd} - [Cd])\}\gamma]$ is equal to the concentration of the "free" halide ions. This expression can be evaluated by assuming some value for n . When \overline{Hal} is large compared with \overline{Cd} , any alteration in the

value of n from 1 to 2, 3, or 4 will cause only relatively small changes in the value of this expression. If, however, n is put equal to 1, then it is tacitly assumed that the only undissociated ionic species

FIG. 2.

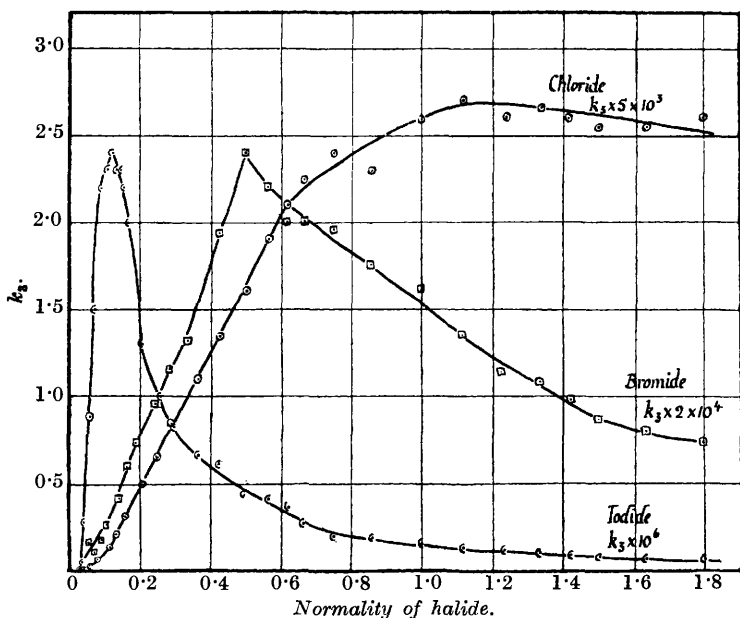


in solution is CdHal^* , i.e., $[\overline{\text{Cd}} - [\text{Cd}]] = [\text{CdHal}]$. Now as the concentration of the halide increases, those of CdHal_2 , CdHal_3 , etc., increase, and therefore the value of $[\overline{\text{Cd}} - [\text{Cd}]]$ becomes progressively greater than $[\text{CdHal}]$: consequently the value of k_1 will show a continuous decrease. This is shown in Fig. 1, where k_1 has been

plotted against the concentration of the total halide. It is interesting to note that the slope of the iodide curve is greater than that of the bromide, which is itself greater than that of the chloride. The slopes of these curves illustrate graphically the varying co-ordinating tendencies or deformabilities of the halide ions.

The curves obtained when $n = 2$ are shown in Fig. 2, and can be interpreted as follows. The assumption that $n = 2$ means that $[\overline{\text{Cd}}-\text{Cd}] = [\text{CdHal}_2]$. In the earlier part of the titration a considerable quantity of the lower halide CdHal' exists in solution, and therefore $[\overline{\text{Cd}}-\text{Cd}] > [\text{CdHal}_2]$. As the concen-

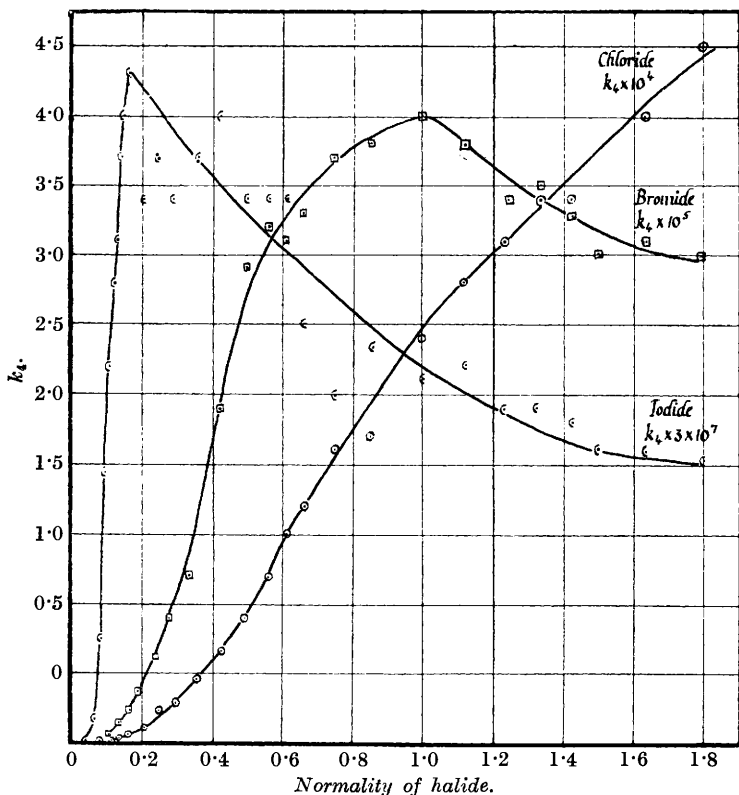
FIG. 3.



tration of the halide increases, more and more higher halide ions are formed at the expense of the lower, and so $[\text{CdHal}_2]$ becomes more and more nearly equal to $[\overline{\text{Cd}}-\text{Cd}]$ as the titration progresses, until a point is reached where the concentration of CdHal_2 is a maximum and any further addition of halide causes a reduction owing to the formation of complex ions. The k_3 ($n = 3$) and k_4 ($n = 4$) curves are shown in Figs. 3 and 4 respectively, and can be interpreted in a similar manner to the k_2 curves. The presence of a maximum in a k curve does not necessarily prove the existence of a particular ionic species in solution when that value of n is not a final one. When this maximum occurs and the value

of n corresponds to some complex ion already isolated in a salt, there can be little doubt that the particular ion does exist in solution and that the maximum indicates the concentration of halide at which its concentration is greatest. Complex halides of cadmium containing 3, 4, 5, and 6 halogen atoms have been described (Mellor, "Comprehensive Treatise, etc.," IV, 550—584). Values of n up to 4 only have been studied in the present paper as its object is the

FIG. 4.



comparison of the three halides. A study of the greatest value of n to give a maximum in the case of the iodide is discussed later. The relative positions of the maxima in various curves illustrate how the co-ordinating tendency of these ions increases with increasing ionic radius. The positions of the maxima also make it possible to determine the most advantageous concentrations of the various constituents of a solution from which it is desired to crystallise a particular double salt.

Determination of Dissociation Constants.

It has been found possible, by the method of trial and error, to estimate, with a reasonable degree of accuracy, the true dissociation constants (K_n) of the various cadmium halide ions. It is obvious from the k curves that the values of the dissociation constants must be greater than the highest recorded values of k_n . By assuming a suitable value for K_1 (determined by trial) a little greater than the maximum value k_1 , the value of $[\overline{\text{Cd}}-\text{[Cd]}]$ employed to calculate K_2 can be corrected for the presence of CdHal' , and the criterion of a correct choice of K_1 is that the new value of K_2 shall be reasonably constant over a range of halide concentration where the concentration

TABLE II.

Chloride.

$K_1 = 0.01.$		$K_2 = 2.5 \times 10^{-3}.$		$K_3 = 2.0 \times 10^{-3}.$	
Conc.	$K_2 \times 10^3.$	Conc.	$K_3 \times 10^3.$	Conc.	$K_4 \times 10^3.$
0.0714	1.9	0.2500	3.5	0.7500	3.1
0.0849	2.2	0.2903	3.0	0.8571	1.2
0.1111	2.0	0.3636	1.7	1.0000	1.2
0.1364	2.4	0.4286	1.9	1.1250	1.4
0.1607	2.5	0.5000	1.7	1.2353	1.1
0.2069	2.5	0.5625	2.0	1.3333	1.1
0.2500	2.2	0.6176	2.0	1.4211	1.1
0.2903	2.2	0.6667	2.0	1.5000	1.0
0.3636	1.9	0.7500	2.0	1.6364	1.0
				1.8000	1.1

Bromide.

$K_1 = 6.8 \times 10^{-3}.$		$K_2 = 8.0 \times 10^{-4}.$		$K_3 = 4.0 \times 10^{-4}.$	
Conc.	$K_2 \times 10^4.$	Conc.	$K_3 \times 10^4.$	Conc.	$K_4 \times 10^4.$
0.0385	3.3	0.1379	3.6	0.6176	1.4
0.0476	6.6	0.1667	3.9	0.6667	1.2
0.0566	6.1	0.1935	3.3	0.7500	1.1
0.0741	8.4	0.2424	2.5	0.8571	0.87
0.0909	7.5	0.2857	2.2	1.0000	0.80
0.1071	7.5	0.3333	2.1	1.1250	0.65
0.1379	6.7	0.4286	3.4		
0.1667	6.1	0.5000	4.2		
		0.5625	2.9		

Iodide.

$K_1 = 3.8 \times 10^{-3}.$		$K_2 = 4.0 \times 10^{-4}.$		$K_3 = 10 \times 10^{-6}.$	
Conc.	$K_2 \times 10^4.$	Conc.	$K_3 \times 10^6.$	Conc.	$K_4 \times 10^7.$
0.0283	0.80	0.0370	3.5	0.0455	2.4
0.0370	1.4	0.0455	4.9	0.0614	3.2
0.0455	1.4	0.0614	5.1	0.0763	3.7
0.0614	1.2	0.0763	4.9	0.0968	4.1
0.0763	0.96	0.0968	4.6	0.1094	3.7
		0.1094	4.0	0.1212	3.5
		0.1212	4.0	0.1324	3.1
				0.1429	3.1

of the higher halides CdHal_3' and CdHal_4'' is small, *i.e.*, over the initial rising part of the k_2 curve. In a similar manner, K_1 and K_2 being known, it is possible to correct the value of $[\overline{\text{Cd}}-\text{[Cd]}]$ for the presence of CdHal' and CdHal_2 when calculating K_3 , and similarly the calculation of K_4 can be corrected with a knowledge of K_1 , K_2 , and K_3 . The corrected dissociation constants are shown in Table II (concentrations, as before, being in mols. per litre). Owing to the very rapid formation of the higher iodides, as the concentration of the iodide ion increases, K , as obtained by the above method, can only be expected to be constant in this case over a very small range. It was necessary to increase the values of the corrected K_2 and K_3 in order to obtain a reasonably constant K_4 . The nature of the results renders it possible only to form these relatively rough estimates of the dissociation constants of the cadmium iodides. A summary of the dissociation constants is given in Table III.

TABLE III.

	K_1 .	K_2 .	K_3 .	K_4 .
Chloride	10×10^{-3}	2.5×10^{-3}	2.0×10^{-3}	1.0×10^{-3}
Bromide	6.8×10^{-3}	8.0×10^{-4}	4.0×10^{-4}	1.0×10^{-4}
Iodide	3.8×10^{-3}	4.0×10^{-4}	1.0×10^{-5}	7.0×10^{-7}

Calculation of the Concentration of the Various Ions in Aqueous Solutions of Cadmium Halides.

By employing the above dissociation constants it is possible to calculate the concentrations in aqueous solution of molarity M of the species: Cd'' (x), Hal' (y), CdHal' (α), CdHal_2 (β), CdHal_3' (γ), and CdHal_4'' (δ). It is assumed that the above are the only ionic species in solution. The concentrations of higher halide ions must be very small, and neglect of these will introduce only small errors into the results. The possibility of the existence of appreciable quantities of ions of the type Cd_nHal has also been considered. The shape of the k_1 curves indicates that the concentration of any such ions must be negligible. It appears highly improbable, on theoretical grounds also, that a highly deformable halide ion will possess the property of forming linkages with more than one positive ion at a time, except, of course, in the solid state or in very concentrated solutions. It is a most serious criticism of the Onsager-Debye-Hückel theory of "ionic atmospheres" that no account is taken of the above fact, for every negative ion must be relatively much more deformable than a positive one, and it is very doubtful whether a negative ion with a positive-ion atmosphere exists for any appreciable space of time in a dilute solution.

If it be assumed that the law of mass action applies to the

solutions under consideration, the following relationships must exist:

$$xy = K_1\alpha \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$xy^2 = K_2\beta \quad . \quad . \quad . \quad . \quad . \quad (2)$$

$$xy^3 = K_3\gamma \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$xy^4 = K_4\delta \quad . \quad . \quad . \quad . \quad . \quad (4)$$

$$x + \alpha + \beta + \gamma + \delta = M \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$y + \alpha + 2\beta + 3\gamma + 4\delta = 2M \quad . \quad . \quad . \quad . \quad . \quad (6)$$

Substituting the values of α , β , γ , and δ from equations (1), (2), (3), and (4) into equations (5) and (6), we get the following equations in x and y , which can be solved graphically.

$$x = \frac{M}{1 + \left[\frac{y}{K_1} + \frac{y^2}{K_2} + \frac{y^3}{K_3} + \frac{y^4}{K_4} \right]}$$

$$x = \frac{\frac{2M}{y}}{\left[\frac{1}{K_1} + \frac{2y}{K_2} + \frac{3y^2}{K_3} + \frac{4y^3}{K_4} \right]}$$

The results obtained when $M = 0.01$ are shown in Table IV, and have been used to calculate the molecular depression of the freezing point of water in 0.01M-solutions of the cadmium halides. The values obtained are compared with the experimental ones.

TABLE IV.
Percentage Ionic Concentrations.

0.01M-Cadmium halide solutions.

	CdCl ₂ .	CdBr ₂ .	CdI ₂ .
[Cd ⁺⁺]	41.0	32.8	23.1
[X ⁻]	137.3	125.7	109.3
[CdX ⁺]	56.3	60.6	66.4
[CdX ₂]	3.09	6.48	6.90
[CdX ₃]	0.0531	0.163	3.02
[CdX ₄]	0.00147	0.00409	0.471
Depression of f. p. calc. from above	4.41°	4.20°	3.85°
Exptl. values	4.71	4.47	3.86

The Maximum Value of n.—Titrations were carried out, employing very concentrated solutions of potassium iodide, in an attempt to determine the maximum value of n . The results at these high concentrations became somewhat uncertain, but fairly definitely indicated that 6 was the maximum value as the k_6 curve showed no tendency to form a maximum over a range of iodide concentration of 0.25—4.00M.

Discussion.

The above represents a new method of attack on the problem of the electrolytic dissociation of salts similar to the cadmium halides. It is interesting to note that the value of K_1 for cadmium chloride, *viz.*, 0.01, is in excellent agreement with the value 0.0101 obtained by Righellato and Davies (*Trans. Faraday Soc.*, 1930, **26**, 592) by the interpretation of conductivity data. A series of measurements on the dissociation of mercuric halides has been carried out by Morse (*Z. physikal. Chem.*, 1902, **41**, 709) by a partition method. The values of K_1 and K_2 only are given. No obvious parallelism exists between them and the above results, other than that the order is the same, *i.e.*, $K_1 > K_2$ and $\text{Cl} > \text{Br} > \text{I}$ in each case. The method employed by Morse is open to the serious criticism that no allowance can be made for complex-ion formation, and this undoubtedly discounts the results to a considerable extent.

It has been assumed that the value of n employed in the above calculations is an integer. This, of course, is probably not so, and the values obtained should be looked upon as "mean" values. It is possible also that the values of the dissociation constants obtained are not true dissociation constants but constants that have appeared in the mathematical analysis of the potential curves. The authors are inclined to the view that the values obtained are "mean" dissociation constants. If this be so, one is faced with the fact that the manner in which a simple salt such as cadmium chloride dissociates must be fundamentally the same as that in which a complex ion like CdCl_4^{2-} dissociates, for there is no marked difference, in the change in the value of the constant as we pass from K_1 to K_2 , compared with the change from K_2 to K_3 or K_3 to K_4 . This indicates that the fundamental mode of linkage in an "electrovalency" is identical with that in a "covalency."

The actual magnitude of the various dissociation constants is probably dependent on two main factors, *viz.*, the degree of localisation of the positive charge on the surface of the kation and the deformability of the anion. It is proposed to extend these studies to other bi-univalent electrolytes with a view to throw more light on the above factors.

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