1000 g. of water. To economize space, initial amounts of substances are not quoted. Inspection of them would show that at each temperature the equilibrium was approached from both sides.

In the experiments at 136°, benzoic acid alone was directly determined in the equilibrium solutions, the hippuric acid as well as the glycine finally present being calculated from the amounts of benzoic acid found and the known initial compositions of the solutions. On this account, less reliance is placed on the 136° values.

TABLE I

Temp., °C.	Equilibrium amounts in grams H$_2$O	B. A.	H. A.	Gl.	Loss	K
184	12.124	0.1172	0.0125	0.3116	0.0001	4.71
184	10.554	.1164	.0158	.3482	.0005	4.75
184	11.185	.1197	.0112	.2522	.0000	4.71
194	11.804	.1208	.0153	.3009	.0005	3.94
194	10.054	.1226	.0176	.3003	.0003	3.98
194	9.929	.1230	.0191	.2997	.0003	3.80
194	9.800	.1243	.0190	.3013	.0000	3.94
136	11.241	.1316	.0053	.3030		13.09
136	11.042	.1319	.0053	.3031		13.36

The average values of the constants at 184 and 194°, namely, 4.72 and 3.92, give the following value for the heat of the reaction in aqueous solution

$$C_6H_5CONHCH_2COOH + H_2O = C_6H_5COOH + CH_2NH_2COOH; \quad \Delta H = -7850 \text{ cal.}$$

The constant at 136° calculated from the values at 184 and 194° is 13.06 as against the directly determined average value of 13.23.

The free energies of benzoic acid and of glycine being known, as well as their solubilities, and that of hippuric acid, in water at 25°, it is possible to calculate the approximate value of the free energy of hippuric acid. This is not done here, in absence of heat capacities and activities needed for calculation of an accurate value.

Summary

The equilibrium in aqueous solution between benzoic acid, hippuric acid, glycine and water has been measured at 136, 184 and 194°.

BURLINGTON, VERMONT RECEIVED NOVEMBER 30, 1937

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF DUKE UNIVERSITY]

Equilibria in Cadmium Iodide Solutions[1]

BY ROGER G. BATES AND WARREN C. VOSBURGH

The equilibria in solutions of cadmium iodide have been investigated by McBain, Van Rysselberghe and Squance[2] and by Riley and Gallafent[3] with differing results. This investigation was undertaken to check the previous results by an electromotive force method that does not have the objection of liquid junction potentials. The electromotive force of the cell

$$Cd(Hg)/CdI_2(m)/CdI_2(m),\ Hg_2I_2/Hg \qquad (I)$$

was measured with varying amounts of either cadmium sulfate or potassium iodide added to the electrolyte, and with a cadmium iodide molality of 0.01 or 0.02. In cells in which the potassium iodide concentration was large, a cuprous iodide electrode was substituted for the mercurous iodide electrode. From the results, together with the stoichiometrical activity coefficients for cadmium iodide,[4] equilibrium constants were calculated for the following reactions

$$CdI_2 \rightleftarrows Cd^{++} + 2I^- \qquad (1)$$

$$CdI_2 \rightleftarrows CdI^+ + I^- \qquad (2)$$

$$CdI^+ \rightleftarrows Cd^{++} + I^- \qquad (3)$$

$$CdI_3^- \rightleftarrows Cd^{++} + 3I^- \qquad (4)$$

$$CdI^= \rightleftarrows Cd^{++} + 4I^- \qquad (5)$$

Experimental Methods

The apparatus, experimental methods and the preparation of most of the materials have been described in previous papers.[4,5] A cadmium sulfate solution about 0.8 *m* was prepared from thrice recrystallized cadmium sulfate and standardized by the evaporation to dryness of weighed samples and heating the residue at 500°. For the preparation of the cell electrolytes that contained cadmium sulfate, the calculated quantities of a carefully standardized cadmium iodide solution and the above cadmium sulfate solution were weighed and diluted by weight to the desired molality. The electrolytes that contained potassium iodide were made by dissolving weighed portions of recrystallized and carefully dried potassium iodide[5] in 0.01 or 0.02 *m* cadmium iodide solutions. A 1% copper amal-

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(1) Part of a thesis submitted by Roger G. Bates in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the Graduate School of Arts and Sciences of Duke University, June, 1937.

(2) McBain, Van Rysselberghe and Squance, *J. Phys. Chem.*, **35**, 1006 (1931).

(3) Riley and Gallafent, *J. Chem. Soc.*, 522 (1932).

(4) Bates and Vosburgh, THIS JOURNAL, **59**, 1585 (1937).

(5) Bates and Vosburgh, *ibid.*, **59**, 1188 (1937).

gam was made by the electrolysis of a solution of copper sulfate. It was filtered through a pin-hole in a filter paper. A portion was diluted with an equal weight of mercury and compared with the original in an amalgam concentration cell with a copper sulfate solution as the electrolyte. The identity of the two samples indicated that the amalgam as prepared was saturated.[6] Cuprous iodide was prepared by precipitation from solutions of recrystallized potassium iodide and cupric sulfate. In one preparation, 0.1 molar salts were employed at room temperature. In another, 0.4 molar potassium iodide solution was added to 0.2 molar cupric sulfate solution at about 100°, and sulfur dioxide was passed in to prevent the accumulation of iodine. The two preparations when digested under water at 85° for three to five days gave identical cuprous iodide electrodes.

The procedure in the construction of a cuprous iodide electrode was about the same as that followed in the construction of a mercurous iodide electrode. Cells with cuprous iodide electrodes did not agree well when the electrolyte was a cadmium iodide solution, but were quite reproducible in dilute potassium iodide solutions or when considerable potassium iodide had been added to the cadmium iodide solution. The mercurous iodide electrode is questionable with much potassium iodide present, because of the reaction of mercurous iodide with the potassium iodide.

Results

The effect of the addition of cadmium sulfate to the electrolyte of Cell I is shown in Table I. Each electromotive force is the average for two cells that agreed within 0.12 mv. or less. The cells were measured at 30° and the electromotive forces at 25° calculated by means of the relation between electromotive force and temperature found for similar cells without added cadmium sulfate.[4] Since the added cadmium sulfate has little effect on the electromotive force, its effect on the temperature coefficient is probably small also. The last column in Table I gives the activity, a_2, of cadmium iodide calculated in the manner described in the previous paper.[4]

TABLE I

CADMIUM–MERCUROUS IODIDE CELLS (TYPE I) CONTAINING CADMIUM SULFATE

CdI_2,[a] m	$CdSO_4$, m	E_{30}, v.	E_{25}(calcd.) v.	$a_2 \times 10^7$
0.01000	...	0.5123	0.5083	2.183
.01006	0.01006	.5123	.5083	2.183
.01008	.02016	.5131	.5091	2.052
.01014	.05071	.5165	.5124	1.587
.01025	.1025	.5208	.5166	1.144
.02015	...	.4969	.4932	7.057
.02019	.01010	.4970	.4933	7.006
.02023	.02023	.4975	.4938	6.737
.02036	.05091	.4997	.4960	5.675
.02058	.1029	.5035	.4997	4.257

[a] This molality is designated in the discussion as *M*.

The effect of the addition of potassium iodide to the electrolyte of Cell I is shown in Table II. For cells in which the potassium iodide concentration was large, a cuprous iodide electrode was substituted for the mercurous iodide electrode.

The relation between the mercurous iodide and cuprous iodide electrodes was determined by the cell

$$Cu(Hg)/CuI,\ KI(m)/KI(m),\ Hg_2I_2/Hg \qquad (II)$$

The best six cells (two of them with an electrolyte 0.02 molar with respect to both cadmium and potassium iodides) gave $E_{25} = 0.13308$ v. with an average deviation of ± 0.09 mv.[7] The value 0.1331 v. was therefore adopted, allowing the calculation of the electromotive force of Cell I from the corresponding cell with a cuprous iodide electrode. Such calculated values are given in the fifth column of Table II along with a number of similar electromotive forces that were observed directly.

TABLE II

CADMIUM–MERCUROUS IODIDE CELLS (TYPE I) AND CADMIUM–CUPROUS IODIDE CELLS CONTAINING POTASSIUM IODIDE

CdI_2,[a] m	KI, m	E_{25} (Hg_2I_2), v.	E_{25} (CuI), v.	E_{25} (obsd. and calcd.),[b] v.	$a_2 \times 10^7$
0.01032	...	0.5073	..	0.5073	2.353
.01023	...	.5076	..	.5076	2.299
.01032	0.00740	..	0.3715	.5046	2.913
.01023	.00824	.5025	..	.5025	3.430
.01032	.01615	..	.3669	.5000	4.201
.01023	.02079	..	.3653	.4984	4.721
.01023	.03228	.4975	..	.4975	5.062
.01032	.05293	..	.3641	.4972	5.182
.01023	.06253	..	.3643	.4974	5.101
.02020	...	..	..	.4931[c]	7.110
.02020	.00488	.4916	..	.4916	7.954
.02020	.01065	..	.3576	.4907	8.570
.02020	.01219	.4903	..	.4903	8.872
.02020	.01850	..	.3561	.4892	9.672
.02020	.04842	..	.3553	.4884	10.27

[a] See footnote to Table I. [b] The observed values are those for $E_{25}(Hg_2I_2)$; the calculated are $E_{25}(CuI) + 0.1331$ v. [c] Calculated for this molality from the data ref. 4.

Discussion

It is possible to check the compositions given by McBain, Van Rysselberghe and Squance[2] by the calculation of the stoichiometrical activity coefficients for cadmium iodide from their cadmium ion, iodide ion and total cadmium iodide concentrations and the activity coefficients of Kielland.[8]

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(6) Richards and Garrod-Thomas, *Carnegie Inst. Wash. Pub.*, No. 118, p. 50 (1909).

(7) With electrolytes of 0.1 *m* and saturated cadmium iodide solutions the electromotive force of Cell II was 0.1322 v. With 0.02 *m* cadmium iodide solution the results varied.

(8) Kielland, THIS JOURNAL, **59**, 1675 (1937).

The results of this calculation may be compared with the activity coefficients of Bates and Vosburgh.[4]

CdI_2, c	0.005	0.01	0.02	0.05	0.10	0.20
γ, calcd.	0.52	0.36	0.23	0.12	0.075	0.044
γ, obsd. B. and V.	0.49	0.38	0.28	0.17	0.11	0.069

The calculated coefficients agree fairly well with the observed in the more dilute solutions, but fall rather far below the observed in the more concentrated solutions.

In 0.01 m cadmium iodide solutions it is probable that the quantity of complex anions containing cadmium is small enough to neglect for a first approximation. This is in agreement with the results of Riley and Gallafent[3] and was assumed also by McBain, Van Rysselberghe and Squance.[2] Addition of cadmium sulfate increases the electromotive force of Cell I, indicating a smaller cadmium iodide activity. Since this must be mainly the result of a decrease in the iodide ion concentration, it follows that the complex anion concentration in the presence of cadmium sulfate is less than in the pure cadmium iodide solutions.

A preliminary calculation was made of the equilibrium constant of the reaction

$$CdI_2 \rightleftarrows Cd^{++} + 2I^- \qquad (1)$$

on the assumption that this equilibrium accounts for all of the difference between the activity of cadmium iodide and that of a typical bi-univalent salt. The equilibrium constant, K_1, was calculated from the equation

$$[CdI_2]K_1 = (Cd^{++})(I^-)^2 \qquad (5)$$

in which brackets indicate molality and parentheses activity. The right-hand term of the equation is the activity, a_2, as given in Table I. The molality of un-ionized cadmium iodide, $[CdI_2]$, in the solutions containing added cadmium sulfate was calculated by subtraction of half the iodide ion molality from the total cadmium iodide molality, M, as given in Table I. The iodide ion molality was calculated by an approximation method with the use of the equation

$$(Cd^{++})(I^-)^2 = [Cd^{++}][I^-]^2 f^3_{2-1} \qquad (6)$$

in which f_{2-1} is the mean activity coefficient of barium chloride[9] at the ionic strength of the cadmium iodide solution.

$CdSO_4$, m	0.01	0.02	0.05	0.10
$K_1' \times 10^5$, $M = 0.01$	3.4	3.0	2.0	1.3

A similar calculation was made from the activities in dilute cadmium iodide solutions not containing cadmium sulfate.[4] For molalities of 0.001025, 0.002043, 0.005, 0.010 and 0.1023, the values of $K_1' \times 10^5$ were, respectively, 1.4, 1.7, 2.9, 4.2 and 4.4. It is to be concluded that Equation 1 does not represent the only equilibrium in a cadmium iodide solution. Furthermore, the assumption that the only other molecular or ionic species present is a complex anion leads to the prediction of decreasing values for K_1', when calculated as above for the pure cadmium iodide solutions.

A calculation was made from the results in Table I of the equilibrium constant K_3' of the reaction

$$CdI^+ + I^- \rightleftarrows Cd^{++} + 2I^- \qquad (3a)$$

with the assumption of the absence of molecular cadmium iodide, CdI_2, by means of the equation

$$[CdI^+][I^-]f^2_{1-1} K_3 = (Cd^{++})(I^-)^2 \qquad (7)$$

In this equation f_{1-1} is the activity coefficient for potassium chloride[10] at the ionic strength of the solution in question. The right-hand term is the activity from Table I, as before. The molality of the ion CdI^+ was assumed to be given by the relation

$$[CdI^+] = 2M - [I^-] \qquad (8)$$

in which M is the total molality of cadmium iodide and I^- was again calculated by an approximation method from Equation 6.

$CdSO_4$ (m)	0.01	0.02	0.05	0.10
$K_3' \times 10^3$, $M = 0.01$	3.4	3.7	4.2	4.5
$K_3' \times 10^3$, $M = 0.02$	3.1	3.3	3.9	4.2

Neither K_1' nor K_3' is of satisfactory constancy, but K_3' varies less than K_1'. This was taken to mean that both ions are present and a larger portion of the total cadmium is in the form of the ion CdI^+ than in the form of molecular cadmium iodide. Therefore, K_1 and K_3 were calculated on the assumption of the presence in the solution of both the ion CdI^+ and the compound cadmium iodide.

A plot of K_3' against the molality of cadmium sulfate suggested that a maximum was being approached as the molality increased. If the increase in K_3' was the result of a decrease in the quantity of molecular cadmium iodide present, as more and more cadmium sulfate was added, the maximum value of K_3' should be the true value of K_3. Accordingly, some values higher than 4.5

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(9) Tippetts and Newton, THIS JOURNAL, **56**, 1675 (1934).

(10) Harned, *ibid.*, **51**, 416 (1929).

$\times$ 10^{-3} were assumed for K_3 and corresponding values for K_1 calculated from the data in Table I. The value of K_3 that led to constant values for K_1 was taken as the correct value.

It was assumed for the first approximation that the iodine in each solution was entirely in the form of the ion CdI^+. The molality of the cadmium ion, $[Cd^{++}]$, was accordingly m'-M in which m' was the molality of cadmium sulfate as given in Table I. Substitution of m'-M for $[Cd^{++}]$ in Equation 6 gave a first value for $[I^-]$. The graphical solution of the simultaneous equations

$$m' + M - [CdI^+] - [Cd^{++}] = [CdI_2] \qquad (9)$$
$$2M - [CdI^+] - [I^-] = 2[CdI_2] \qquad (10)$$
$$[CdI^+][I^-]f^2_{1-1}\,K_3 = (Cd^{++})(I^-)^2 \qquad (7)$$

gave values of $[CdI^+]$ and $[CdI_2]$ and a corrected value of $[Cd^{++}]$ which, substituted in Equation 6 with an appropriate change of activity coefficient to correspond with the new ionic strength, enabled a second, more accurate, value of $[I^-]$ to be obtained. The simultaneous equations were solved again with this new value of $[I^-]$ and the process repeated until two successive approximations gave like values for the quantities involved. Then K_1 was calculated by Equation 5.

In this manner, K_1 and K_3 were found to be 1.2 $\times$ 10^{-4} and 0.0052, respectively. Riley and Gallafent[3] found 4.0 $\times$ 10^{-4} and 0.0038. The values found for K_1 when K_3 is taken equal to 0.0052 are shown in Table III.

TABLE III

VALUES OF K_1 WHEN K_3 = 0.0052

CdI_2, $m(M)$	0.01	0.01	0.01	0.01	0.02	0.02	0.02	0.02
$CsSO_4$, m (m')	0.01	0.02	0.05	0.10	0.01	0.02	0.05	0.10
$K_1 \times 10^4$	1.10	1.17	1.24	1.04	1.79	1.35	1.46	1.34

When potassium iodide is added to 0.01 M cadmium iodide solution, the formation of a complex anion can be expected. McBain, Van Rysselberghe and Squance[2] have assumed that the ion CdI_3^- is present in cadmium iodide solutions. Riley and Gallafent[3] concluded that both CdI_3^- and $CdI_4^=$ are present, the latter, however, in much smaller concentration than the former. On the other hand, Cornec and Urbain[11] by a cryoscopic method, Job[12] by a spectrophotometric method and Bourion and Rouyer[13] and Rouyer[14] by a boiling point method obtained no evidence for the existence of the ion CdI_3^- in solution, finding only the ion $CdI_4^=$.

The data in Table II taken alone do not serve to distinguish between the two possible anions. They may be interpreted equally satisfactorily with either assumption, as shown in Table IV.

The instability constant, K_4, for the ion CdI_3^- was calculated by means of the equation

$$[CdI_3^-]K_4 = [Cd^{++}][I^-]^3f^3_{2-1} \qquad (11)$$

The molalities were calculated by means of the equations

$$2M - 2[CdI_2] + m'' - [CdI^+] - 3[CdI_3^-] = [I^-] \qquad (12)$$
$$M - [CdI_2] - [CdI^+] - [CdI_3^-] = [Cd^{++}] \qquad (13)$$

and Equations 5, 6 and 7, with the use of the values of a_2 in Table II. In Equation 12, m'' is the molality of potassium iodide. The assumption is thus made that the ion CdI_3^- was the only complex ion present. The equations were solved by a graphical method, and an approximation method was used for the calculation of the ionic strength. A similar calculation was made of the constant K_5 of the equation

$$[CdI_4^=]K_5 = [Cd^{++}]\ [I^-]^4f^4_{1-1}$$

with the assumption that $CdI_4^=$ was the only complex anion present. The quantity of complex anion in the solutions containing only a little potassium iodide was so small that errors of calculation were large, and the results for these solutions are not included in Table IV.

TABLE IV

INSTABILITY CONSTANTS K_4 AND K_5

CdI_2, $m \times 10^3$	10.23	10.23	10.23	10.23	20.20	20.20	20.20
KI, $m \times 10^3$	20.79	32.28	52.93	62.53	12.19	18.50	48.42
$K_4 \times 10^5$	2.6	1.2	1.0	1.0	2.3	2.1	1.0
$K_5 \times 10^7$	4.9	6.7	7.7	7.7	9.6	10.4	7.7

In the last column of Table IV it is shown that K_5 is somewhat more nearly constant than K_4, but it is probable that the difference is not significant. The accuracy of the data and calculations is probably not sufficient for making a decision between the two complex ions, or for showing whether or not both ions may be assumed present. The most probable values of the constants, K_4 = 1 $\times$ 10^{-5} and K_5 = 8 $\times$ 10^{-7}, agree with the corresponding constants of Riley and Gallafent, 1 $\times$ 10^{-5} and 7.0 $\times$ 10^{-7}, respectively, in spite of the fact that their constants were determined on the assumption of the simultaneous presence of the two complex ions. The value for K_5 is in fairly good agreement with the constant 4.3 $\times$ 10^{-7} found by Knobloch.[15]

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(11) Cornec and Urbain, *Bull. soc. chim.* **25**, 137 (1919).

(12) Job, *Ann. chim.*, **9**, 135 (1928).

(13) Bourion and Rouyer, *ibid.*, **10**, 254 (1928).

(14) Rouyer, *ibid.*, **13**, 477 (1930).

(15) Knobloch, *Lotos*, **78**, 110 (1930).

While the evidence from freezing and boiling points and absorption spectra favors the assumption of the presence of the ion $CdI_4^=$ in cadmium iodide solutions and the absence of CdI_3^-, this assumption does not seem to be compatible with transport data. The transport experiments of Hittorf[16] and Redlich and Bukschnewski[17] showed[2] that in a cadmium iodide solution containing about 0.23 mole per liter the cadmium does not migrate in either direction, and that in more concentrated solutions it migrates to the anode. Calculation of the composition of various cadmium iodide solutions with the use of the above values of K_1, K_3 and K_5 gives calculated quantities of the complex anion $CdI_4^=$ that are too small in comparison with the quantities of the cations Cd^{++} and CdI^+ to account for the transport results in solutions of the order of 0.2 *M* or more. On the other hand, assumption of the ion CdI_3^- and calculation from the constants K_1, K_3 and K_4 gives results in better agreement with the transport data. Table V shows the results of such a calculation, the concentrations of the various ions being given in terms of the percentage of the total molality in the first column.

TABLE V

COMPOSITION OF CADMIUM IODIDE SOLUTIONS ON THE ASSUMPTION THAT CdI_3^- IS THE ONLY COMPLEX ANION PRESENT

CdI_3, *m*	I^-, %	Cd^{++}, %	CdI^+, %	CdI_2, %	CdI_3^-, %
0.001025	179	77.1	21	1.5	..
.002043	160	66.0	30	3.7	..
.00500	132	49.0	41	9.7	..
.01000	111	34.0	45	18	3
.02000	84.4	23.2	43	29	5
.0500	55.5	14.6	37	39	10
.1000	38.0	10.7	32	42	15
.2500	20.7	7.8	27	44	22
.500	12.5	6.9	23	46	24

It was of interest to extrapolate the electromotive force data presented in a previous paper[4] with the aid of the data in this paper on the composition of cadmium iodide solutions. The method of **Hitchcock**[18] was used, the equation being

$$E^{0''} = E + k \log [Cd^{++}][I^-]^3 - 3k\,(1.012\,\mu^{1/2})$$

in which $k = 2.303\ RT/2F$ and μ is the ionic strength. The concentrations of cadmium and iodide ions were those calculated for Table V. The results are shown in Fig. 1, in which the curve is drawn to give $E^0 = 0.3113$ v., the value calculated[4] by the addition of the two normal electrode potentials.

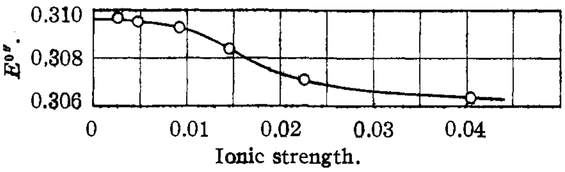

Fig. 1.—Extrapolation of electromotive force data for Cell I to zero ionic strength. The curve is drawn to pass through $E^{0''} = 0.3113$ v. at zero ionic strength.

Summary

The effect of the addition of cadmium sulfate and of potassium iodide to the electrolyte of the cell $Cd(Hg)/CdI_2(m)/CdI_2(m)$, Hg_2I_2/Hg was determined.

The results have been interpreted on the assumption of the simultaneous presence of unionized cadmium iodide, the ion CdI^+, and a complex anion, in addition to the simple ions, and corresponding equilibrium constants have been calculated. The results of this investigation alone do not serve to distinguish between the two complex anions CdI_3^- and $CdI_4^=$.

DURHAM, N. C. RECEIVED JULY 28, 1937

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(16) Hittorf, *Ann. Physik*, **106**, 543 (1859).

(17) Redlich and Bukschnewski, *Z. physik. Chem.*, **37**, 700 (1901).

(18) Hitchcock, THIS JOURNAL, **50**, 2076 (1928).