for the limiting conductance and of 3.2×10^{-4} for the dissociation constant were obtained. Since the specific conductance of the solvent, which was subtracted, amounted to 5% of the total conductance in the most dilute solution, these numerical values may not be very accurate. However, the treatment did indicate that the salt was not completely dissociated in dilute solution. Furthermore, the product of limiting conductance and viscosity, 0.435, is substantially equal to the conductance–viscosity product of the pure salt, 0.452. Walden[3] has shown that this agreement is quite general, but this is the first demonstration of it where the dilute solution and the fused salt have been treated at the same temperature. Mead and Fuoss[6] report a value of 0.4508 for the limiting conductance–viscosity product of tetra-*n*-butylammonium picrate in ethylene chloride (*D* 10.23) at 25°.

The data appear to indicate that tetra-*n*-butylammonium picrate is a weak electrolyte when at low concentrations in butyl alcohol but that it becomes a strong electrolyte at high concentrations. Extension of the experiments, with variation of both components, is planned.

(6) D. J. Mead with R. M. Fuoss, THIS JOURNAL, **61**, 2051 (1939).

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF WISCONSIN]

Moving Boundary Systems Formed by Weak Electrolytes. Study of Cadmium Iodide Complexes[1]

BY ROBERT A. ALBERTY AND EDWARD L. KING

It has been shown that the moving boundary method may be used to study complex ion equilibria. The constituent mobility of cadmium has been determined at 0° over a range of iodide concentrations from 0.003 to 0.4 *N*. The constituent mobility of iodide in a solution containing 0.010 mole/liter of iodide has been determined over a range of cadmium concentration of 0.03 to 0.07 mole/liter. The equilibrium constants for the formation of the complexes CdI^+, CdI_2, CdI_3^- and $CdI_4^=$ have been calculated from these data.

Numerous types of experimental data indicate that cadmium iodide in aqueous solution is not a strong electrolyte. Studies of the transference number of cadmium in solutions of cadmium iodide carried out by both the Hittorf method[2] and the differential moving boundary method[3] indicate that the cation transference number of cadmium decreases with increasing concentration, becoming negative at a concentration of 0.25 mole/liter. The activity coefficient of this substance is very low, even in relatively dilute solution.[4] The existence in solutions of cadmium iodide of species with some covalent bond character is demonstrated by the Raman lines which are observed.[5] Various complex species of cadmium and iodide have been proposed to explain the observed phenomena; it appears likely that all of the species, Cd^{++}, CdI^+, CdI_2, CdI_3^- and $CdI_4^=$, are present in solutions containing cadmium ion and iodide ion.[6]

It appears worthwhile to study, by the moving boundary method, solutions containing cadmium and iodide ions. The data are mainly of interest in connection with recent studies of weak electrolyte moving boundary systems[7] and are also of value in the further elucidation of the complex ion equilibria which exist in solutions containing cadmium and iodide. Svensson, Benjaminsson and Brattsten[8] have shown that the ionization constants of amino acids may be determined from moving boundary experiments with solutions of different *p*H.

As pointed out by Longsworth[3] it is doubtful if the direct moving boundary method could be applied to solutions of cadmium iodide owing to the difficulty of finding sufficiently slow indicator ions. In the present study the mobility of the cadmium and iodide constituents have been determined by means of moving boundary systems similar to those used in the electrophoresis of proteins, *e. g.*, a cadmium salt is dissolved in an electrolyte which extends throughout the U-tube. This method has the advantage that it is unnecessary to find an indicator electrolyte and the ratio of iodide concentration to cadmium concentration may be varied over a wide range.

It will be assumed provisionally that all of the species Cd^{++}, CdI^+, CdI_2, CdI_3^-, $CdI_4^=$ exist. The equilibria which are established very rapidly in solution are

$$Cd^{++} + nI^- \rightleftharpoons CdI_n^{+2-n} \qquad n = 1, 2, 3, 4 \quad (1)$$

for which the corresponding concentration equilibrium constants are

$$K_n = (CdI_n^{+2-n})/(Cd^{++})(I^-)^n \qquad n = 1, 2, 3, 4 \quad (2)$$

The moving boundary experiments in which cadmium disappears across the boundary lead to a direct evaluation of the cadmium constituent mobility.[7] This is the average mobility of the cadmium in solution and is given by the equation

$$\bar{u}_{Cd} = \frac{(Cd^{++})u_0 + (CdI^+)u_1 + (CdI_2)u_2 + (CdI_3^-)u_3 + (CdI_4^=)u_4}{(Cd^{++}) + (CdI^+) + (CdI_2) + (CdI_3^-) + (CdI_4^=)} \quad (3)$$

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(1) Presented at the Chicago Meeting of the American Chemical Society, September, 1950.

(2) Redlich and Bukschnewski, *Z. physik. Chem.*, **37**, 673 (1901).

(3) Longsworth, THIS JOURNAL, **65**, 1755 (1943).

(4) Robinson and Wilson, *Trans. Faraday Soc.*, **36**, 738 (1940); Bates and Vosburgh, THIS JOURNAL, **59**, 1583 (1937).

(5) Delwaulle, Francois and Wiemann, *Compt. rend.*, **208**, 184 (1939).

(6) Leden, *Z. physik. Chem.*, **188A**, 160 (1941).

(7) Svensson, *Acta Chem. Scand.*, **2**, 855 (1948); Alberty and Nichol, THIS JOURNAL, **70**, 2297 (1948); Brattsten and Svensson, *Acta Chem. Scand.*, **3**, 359 (1949); Alberty, THIS JOURNAL, **72**, 2361 (1950); Nichol, *ibid.*, **72**, 2367 (1950).

(8) Svensson, Benjaminsson and Brattsten, *Acta Chem. Scand.*, **3**, 307 (1949).

where the u_n's are the mobilities of the species in which n iodide ions are associated with one cadmium ion and the concentrations are in gram-formula-weights per liter. This may be converted to an equation

$$\bar{u}_{\text{Cd}} = \frac{u_0 + u_1K_1(\text{I}^-) + u_2K_2(\text{I}^-)^2 + u_3K_3(\text{I}^-)^3 + u_4K_4(\text{I}^-)^4}{1 + K_1(\text{I}^-) + K_2(\text{I}^-)^2 + K_3(\text{I}^-)^3 + K_4(\text{I}^-)^4} \tag{4}$$

It is seen that the constituent mobility depends upon the mobilities of the several species, the equilibrium constants for their formation and the concentration of iodide ion. The distribution of cadmium among the various species is dependent only on the concentration of iodide ion at a given temperature if the activity coefficients of the various complexes and iodide ion are assumed to be constant.[9]

The moving boundary experiments in which iodide disappears across the boundary lead to a direct evaluation of the iodide constituent mobility

$$\bar{u}_1 = \frac{(\text{I}^-)u_1 + (\text{CdI}^+)u_1 + 2(\text{CdI}_2)u_2 + 3(\text{CdI}_3^-)u_3 + 4(\text{CdI}_4^=)u_4}{(\text{I}^-) + (\text{CdI}^+) + 2(\text{CdI}_2) + 3(\text{CdI}_3^-) + 4(\text{CdI}_4^=)} \tag{5}$$

where u_{I} is the mobility of iodide ion. This equation becomes

$$\bar{u}_1 = \frac{u_{\text{I}} + u_1K_1(\text{Cd}^{++}) + 2u_2K_2(\text{Cd}^{++})(\text{I}^-) + 3u_3K_3(\text{I}^-)^2 + 4u_4K_4(\text{I}^-)^3}{1 + K_1(\text{Cd}^{++}) + 2K_2(\text{Cd}^{++})(\text{I}^-) + 3K_3(\text{Cd}^{++})(\text{I}^-)^2 + 4K_4(\text{Cd}^{++})(\text{I}^-)^3} \tag{6}$$

when the appropriate substitutions are made. Equation (6) lacks the simplicity of equation (4) since the concentrations of both cadmium ions and iodide ions are involved. The iodide constituent mobility depends only upon the cadmium ion concentration if the cadmium concentration is sufficiently high so that CdI^+ is the only complex ion of importance.

Experimental

The moving boundary experiments were carried out in a standard Tiselius cell of 3 × 25 mm. cross section, and the boundary velocities were determined with the aid of a schlieren camera utilizing a cylindrical lens.[10] The vertical magnification factor of the camera was 0.9610 ± 0.0004 over the region of the cell actually used in measurements.[11] Since the refractive index change across the moving boundaries was small ($\Delta n \sim 0.0002$), a diagonal knife edge angle of 40° was used. The magnification of the cylindrical lens system was such that the boundaries had areas of from one to two sq. in. after enlargement of the photographs by a factor of 6.68.

The exact cross sectional area of the cell was obtained by weighing the cell with one limb filled with mercury or water. The same limb of the cell was then used in all mobility determinations. In the water calibration it was necessary to grease the cell but the quantity of grease used was kept to a minimum. The volume determined with mercury was 0.09% higher than that determined with water, and the average was used in calculating the cross sectional area. It was necessary to correct the volume of the limb of the cell for the fact that the cross sectional area of the rectangular holes in the end-plates was greater than the cross sectional area of the channel. The cross sectional areas of the holes in the end-plates were calculated from a number of measurements made with a microscope comparator, and the thicknesses of the end-plates were determined with a micrometer. This end-plate correction amounted to 0.89% of the volume of the limb, and therefore is not negligible as has often been assumed. The average cross sectional area of the channel (0.7580 sq. cm.) was obtained by dividing the corrected volume of the limb by the outside length of the cell.

A modified top section with attached electrode vessels was used.[3,12] Gas formed by slow electrolysis of a dilute electrolyte in a vessel attached to the closed electrode vessel was used to bring the initial boundaries into view.[13] Due to the small volume (about 25 ml.) between the upper surface of the concentrated salt and the top of the test-tube, this type of apparatus is not adapted for the injection of any appreciable volume of solution into the closed side, as in counter-current electrolysis. The Ag–AgCl electrodes were mounted on 40/35 standard taper joints. It would have been preferable to have used Ag–AgI electrodes as some conversion of the silver chloride to silver iodide must occur as the electrode is introduced into the electrode vessel. It has been shown by the use of iodine tracer(I^{131}) that this metathesis during the time that the electrode is being inserted into the test-tube introduces a negligible amount of chloride into the solution.

The current through the cell was maintained constant within 0.02% by a galvanometer–phototube–d.c. amplifier arrangement constructed by the Rubicon Company.[14] The galvanometer is connected in series with a standard cell across a standard resistance which is in series with the moving boundary cell. If the potential drop across the standard resistance decreases as the result of an increase in the resistance of the moving boundary cell, the light beam reflected from the galvanometer mirror is shifted so as to illuminate a larger area of the phototube. As a result the output voltage of the d.c. amplifier which supplies current to the moving boundary cell is increased. Since the photo-cell is partially illuminated when the galvanometer is in its normal or zero position, the device is able to make either positive or negative corrections. The current was calculated from the potential drop across a known resistance.[15] The specific conductances of the leading solutions were measured at 0° using a Jones conductivity bridge.[16]

The schlieren photographs were taken on Eastman Tri-X Panchromatic plates using an exposure time of 10 seconds. The photographs were enlarged and traced by hand. In the case of unsymmetrical peaks the velocity of the centroidal ordinate was used.[3] The first photograph was taken as soon as the moving boundary had completely resolved from the concentration boundary. The schlieren patterns were then recorded at 10–20-minute intervals during the experiment so that the boundary displacements reported are averages of 5–10 measurements. The boundary velocities were determined with respect to an index on the plates produced by a fine wire stretched across the face of the limb of the cell.

All of the solutions were prepared using freshly boiled doubly distilled water. The final dilutions were made in a cold room at 1°. The concentrations reported are for this temperature. Reagent grade sodium iodide and cadmium iodide were used without further purification. Cadmium perchlorate solutions were prepared by treating reagent grade cadmium carbonate with an equivalent amount of perchloric acid. The concentrations of the solutions were determined by standard analytical procedures, and the pH values were between 5.3 and 7. The lithium iodide and lithium perchlorate were recrystallized from water several times. The mercury(II) iodide was N.F. VII grade and was used without further purification.

Moving Boundary Systems

$\text{LiI}, \text{LiClO}_4(\delta) \leftarrow \text{LiI}, \text{LiClO}_4(\gamma)::\text{LiI}, \text{LiClO}_4(\beta) \rightarrow 0.0050\ M\ \text{Cd(ClO}_4)_2, x\ N\ \text{LiClO}_4, y\ N$

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[9] This statement is not correct if species involving more than one cadmium are present at appreciable concentrations. Leden[5] has shown the cadmium iodide complexes to contain but one cadmium ion in the concentration range studied in the cadmium constituent boundary experiments.

(10) Longsworth, *Ind. Eng. Chem., Anal. Ed.*, **18**, 219 (1946).

(11) The authors are indebted to R. M. Bock for the focusing and testing of this optical system.

(12) Alberty, *J. Phys. Colloid Chem.*, **53**, 114 (1949); supplied by the Pyrocell Company, New York.

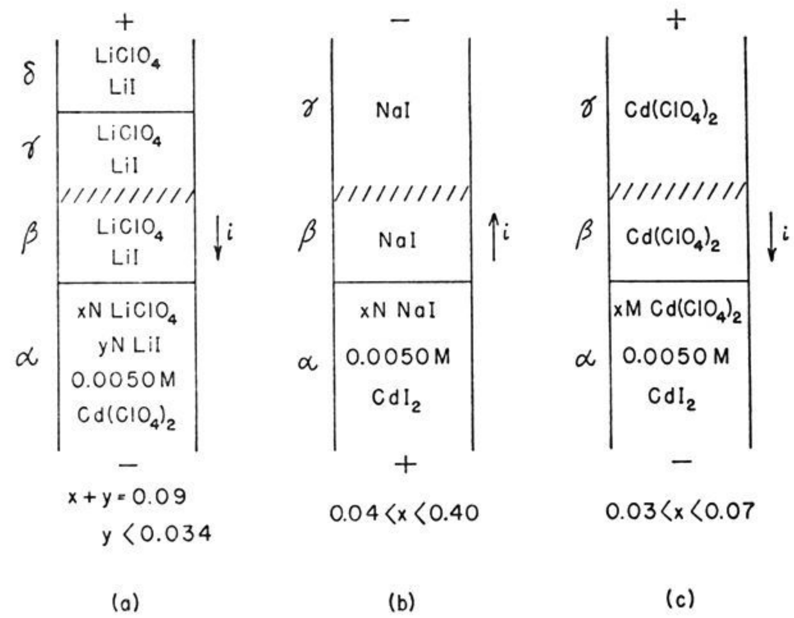
(13) Johnson and Shooter, *Science*, **109**, 39 (1949).

(14) Bonn, Marvin and Alberty, forthcoming publication.

(15) The authors are indebted to H. H. Marvin for the assembly current source and measuring circuits.

(16) Supplied by Leeds and Northrup Company.

LiI(α).[17]—This moving boundary system which is illustrated in Fig. 1a was used to determine the positive cadmium constituent mobilities. The total salt concentration of the α solution ($x + y + 0.010$) was 0.100 equiv./l. The ionic strength of these solutions is not constant but varies with the extent to which the reactions for complex formation occur. It is assumed that the variation in the mobilities and the equilibrium constants due to this variation in ionic strength is small. Lithium salts were used because it was found that sharper α,β boundaries were obtained by using lithium salts rather than sodium salts. The δ solution was made up to contain the salts in about the same ratio as the α solution and at about 40% of its concentration.



(a) (b) (c)

Fig. 1.—Moving boundary systems used to determine (a) positive cadmium constituent mobilities, (b) negative cadmium constituent mobilities, (c) positive iodide constituent mobilities. The concentration boundary near the initial boundary position is represented by /////.

Since the cadmium constituent disappears in the $\alpha\beta$ moving boundary, the weak electrolyte moving boundary equation for this constituent[7] reduces to

$$\bar{u}^{\alpha}_{\mathrm{Cd}} = v^{\alpha\beta}\kappa^{\alpha} \tag{7}$$

where $v^{\alpha\beta}$ is the displacement of the boundary in ml. per coulomb (after making the electrode correction to be discussed later), κ^{α} is the specific conductance of the α solution, and $\bar{u}^{\alpha}_{\mathrm{Cd}}$ is the average mobility of the cadmium constituent. A position sign is given to $v^{\alpha\beta}$ if the boundary moves with the current and a negative sign if it moves against the current. The data obtained with this moving boundary system are given in Table I and the constituent mobilities are plotted *versus* the logarithm of the total iodide concentration in Fig. 3a.

TABLE I

CADMIUM CONSTITUENT MOBILITIES ($\bar{u} > 0$)

$c^{\alpha} \times 10^3$ LiI (equiv./l.)	$c^{\alpha} \times 10^3$ LiClO$_4$ (equiv./l.)	$\kappa \times 10^3$ at 0° (ohm^{-1} cm.$^{-1}$)	$v_{\mathrm{b}}^{\alpha\beta} \times 10^4$ (ml./coul.)	$-\Delta v_0 \times 10^4$ (ml./coul.)	$\bar{u}^{\alpha}_{\mathrm{Cd}} \times 10^5$ (cm.^{2} volt^{-1} sec.$^{-1}$)
0	90.0	4.764	402.8	2.6	19.31
2.25	87.9	4.778	385.1	2.6	18.52
2.72	87.5	4.765	376.8	2.6	18.08
4.22	85.7	4.748	363.1	2.6	17.36
5.43	84.8	4.714	346.7	2.6	16.47
8.44	81.4	4.697	319.1	2.6	15.11
8.41	81.5	4.702	317.3	2.6	15.04
12.66	77.4	4.667	285.6	2.5	13.44
16.88	73.2	4.660	246.9	2.5	11.62
23.0	67.0	4.645	190.2	2.5	8.91
26.9	63.2	4.636	161.3	2.4	7.59
34.2	56.0	4.523	87.4	2.4	4.06

It was found that the composition of the δ solution had no effect on the velocity of the $\alpha\beta$ boundary over a wide range of values of the ratio (LiI)/(LiClO$_4$). The composition of the δ solution would, however, be expected to exert an influence on the sharpness of the moving boundary. The sharpness of the moving boundary depends upon the specific conductance of the β solution and upon the iodide ion concentration of the β solution. If the iodide concentration in the β solution is quite low, cadmium diffusing into the region immediately behind the moving boundary will have a higher constituent mobility than ahead of

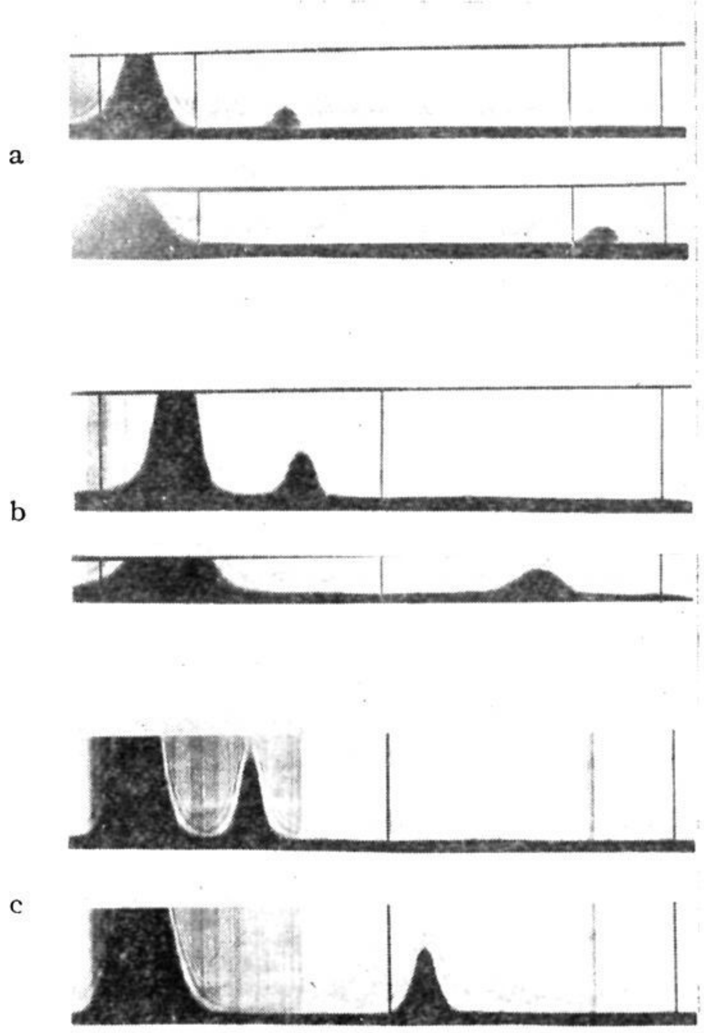


Fig. 2.—Schlieren patterns of the systems: (a) 0.0357 *N* LiClO$_4$(γ)::LiClO$_4$(β) → 0.0050 *M* Cd(ClO$_4$)$_2$, 0.090 *N* LiClO$_4$(α) at 31 and 93 minutes after the application of a current of 19.95 milliamperes; (b) 0.0357 *N* LiClO$_4$, 0.00096 *N* LiI(γ)::LiClO$_4$, LiI(β) → 0.0050 *M* Cd(ClO$_4$)$_2$, 0.0815 *N* LiClO$_4$, 0.00841 *N* LiI(α) at 45 and 105 minutes after application of a current of 19.96 milliamperes; (c) 0.0050 *M* CdI$_2$, 0.0895 *M* NaI(α) ← NaI(β)::0.032 *M* NaI(γ) at 37 and 76 minutes after the application of a current of 19.96 milliamperes. The vertical lines are produced by reference wires and the large boundary at the left in each case is the concentration boundary.

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[17] The moving boundary systems are represented by the notation of Longsworth, THIS JOURNAL, **67**, 1109 (1945).

the boundary and will tend to overtake the moving boundary. This sharpening effect is similar to the *p*H effect[18] observed in the case of proteins and weak acids and bases.[6] In experiment 6 of Table I the composition of the δ solution was (LiI) = 3.26×10^{-3}, ($LiClO_4$) = 3.56×10^{-2}, while in experiment 7 the concentrations were (LiI) = 0.96×10^{-3}, ($LiClO_4$) = 3.57×10^{-2}. The moving boundary in experiment 7 (shown in Fig. 2b) was somewhat sharper than in experiment 6 as would be expected.

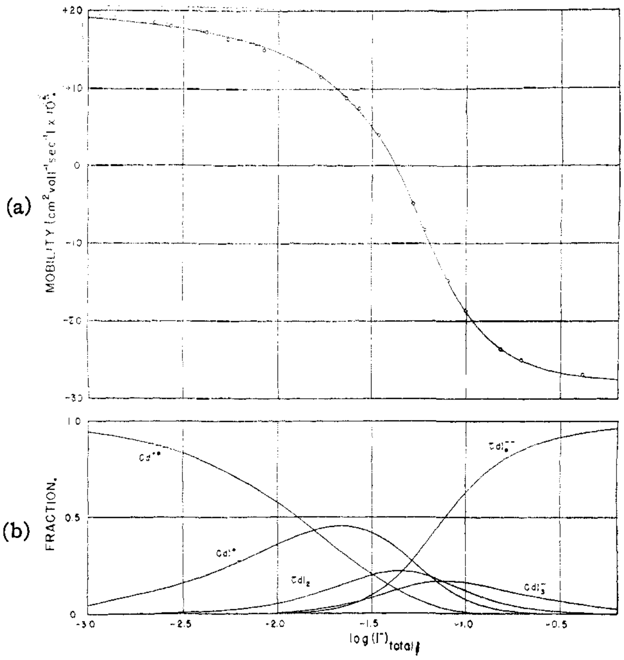

Fig. 3.—(a) Cadmium constituent mobility as a function of the logarithm of total iodide concentration. The solid curve was calculated by using the first set of equilibrium constants in Table V. (b) These curves give the fractions of the various species present as a function of the logarithm of total iodide concentration.

The αβ boundary spread slowly during the experiments except in the case in which lithium iodide was omitted entirely. As the cadmium constituent mobility decreased, this spreading became more serious and the refractive index change across the moving boundary became smaller so that it was not possible to make experiments very close to the isoelectric point.

0.0050 *M* CdI_2, *x* *N* NaI(α) ← NaI(β)::NaI(γ).—This moving boundary system which is illustrated in Fig. 1b was used to determine the negative cadmium constituent mobilities. Schlieren patterns for the system in which $x = 0.09$ are shown in Fig. 2c. It would have been desirable to add sodium perchlorate to keep the ionic strength nearly constant as in system (a). It was found, however, that at iodide concentrations at which cadmium has a negative constituent mobility such experiments were unsuccessful. This was caused by a boundary which moved more rapidly than the cadmium constituent boundary and was of the type across which no ion or constituent disappeared. Svensson[19] pointed out that such boundaries may be expected to develop if more than two ion species are present in both original solutions. In type (a) experiments the γδ boundary across which no constituent disappears moves in the opposite direction to the boundary which is being studied, and, therefore, does not interfere.

The data obtained with this moving boundary system are given in Table II and the corrected constituent mobilities are plotted *versus* the logarithm of the total iodide concentration in Fig. 3a.

0.0050 *M* HgI_2, *x* *N* NaI(α) ← NaI(β)::NaI(γ).—This moving boundary system differs from that illustrated in Fig. 1b only in that mercury(II) iodide has been substituted for cadmium iodide. This system was studied in order to determine the variation in the mobility of an ion of the type $MI_4^=$ with ionic strength. The equilibrium constants[20] at 25° for the formation of mercury(II) iodide complexes indicate that $HgI_4^=$ is the predominant ionic species above 0.1 *N* iodide. As shown in Table III the mercury(II) constituent mobility decreases as the sodium iodide concentration is increased. This is to be expected if $HgI_4^=$ is the predominant species present because of the decrease in ionic mobility with ionic strength. In the cadmium system, on the other hand, the constituent mobility continues to increase with increasing sodium iodide concentration to the highest concentration studied, 0.4 *N*. This is a result of the fact that the increase in the constituent mobility caused by the increase in the fraction of cadmium in the $CdI_4^=$ form offsets the decrease in the mobilities of CdI_3^- and $CdI_4^=$ caused by the higher ionic strength of the solution. In order to correct the cadmium constituent mobilities for the ionic strength effect, it is assumed that the fractional change in the cadmium constituent mobility and in the mobility of $HgI_4^=$ with ionic

TABLE II

CADMIUM CONSTITUENT MOBILITIES ($\bar{u} < 0$)[a]

$(I^-)^\alpha_T \times 10^3$ (equiv./l.)	$\kappa^\alpha \times 10^3$ at 0° (ohm⁻¹ cm.⁻¹)	$v^{\alpha\beta} \times 10^4$ (ml./coul.)	$\bar{u}^\alpha_{Cd} \times 10^5$ (cm.² volt⁻¹ sec.⁻¹) Exptl.	Adjusted
51.8	2.604	−188	− 4.96	− 4.81
60.2	3.058	−272	− 8.39	− 8.18
80.2	4.146	−358	−14.93	−14.76
99.7	5.249	−353	−18.64	−18.64
153	8.024	−284	−22.96	−23.6
197	10.580	−224	−23.93	−25.0
410	21.907	−110.5	−24.69	−26.9

[a] $\Delta v_e = 2.2 \times 10^{-4}$ ml./coul. in all expts.

TABLE III

MERCURY(II) CONSTITUENT MOBILITIES ($\bar{u} < 0$)[a]

$(I^-)^\alpha_T \times 10^3$ (equiv./l.)	$\kappa^\alpha \times 10^3$ at 0° (ohm⁻¹ cm.⁻¹)	$v^{\alpha\beta} \times 10^4$ (ml./coul.)	$\bar{u}^\alpha_{Hg} \times 10^5$ (cm.² volt⁻¹ sec.⁻¹)
100	5.229	−519.9	−27.30
205	11.059	−234	−26.15
400	21.345	−115.0	−25.02

[a] $\Delta v_e = 2.2 \times 10^{-4}$ ml./coul. in all expts.

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[18] Longsworth, *J. Phys. Colloid Chem.*, **51**, 171 (1947).

[19] Svensson, *Arkiv. Kemi, Mineral. Geol.*, **21B**, No. 5 (1945); **22A**, No. 10 (1946).

[20] $K_3 = 4.0 \times 10^{27}$, $K_4 = 6.8 \times 10^{29}$, Qvartfort and Sillen, *Acta Chem. Scand.*, **3**, 505-519 (1949).

strength is the same above a salt concentration of 0.1 *N*. Therefore, the cadmium constituent mobilities above 0.1 *N* were multiplied by a factor calculated from the mercury(II) constituent mobilities, to obtain the mobility which would have been obtained if the salt concentration could have been held at 0.1 *N*. It is realized that this approximation may be an under-correction if the mercury is not all in the form of $HgI_4^=$ and also that it undoubtedly over-corrects the contribution of CdI_3^- to the constituent mobility because the ionic strength effect on the mobility of an ion of single charge is slightly less than on an ion of double charge.

The cadmium constituent mobilities below 0.1 *N* total iodide were corrected to give the values which would have been obtained at a normality of 0.1 by use of chloride ion mobility data from 0.01 to 0.1 ionic strength at 0°.[21] This correction, which is quite small as indicated by Table II, was made by assuming that the fractional change in the cadmium constituent mobility and chloride ion with ionic strength are the same.

0.005 *M* CdI_2, *x* *M* $Cd(ClO_4)_2(\alpha) \leftarrow Cd(ClO_4)_2(\beta)::Cd(ClO_4)_2(\gamma)$.—This moving boundary system which is illustrated in Fig. 1c was used to determine positive iodide constituent mobilities. The data obtained with this moving boundary system are given in Table IV. Any interpretation of the data obtained in the study of boundaries of this type is rendered difficult by the variation of the ionic strength and the fact that the principle salt present is a 2–1 electrolyte.

TABLE IV

IODIDE CONSTITUENT MOBILITIES ($\bar{u} > 0$)[a]

$(Cd^{++})_T^\alpha \times 10^2$ (moles/l.)	$\kappa^\alpha \times 10^3$ at 0° (ohm^{-1} cm.$^{-1}$)	$v^{\alpha\beta} \times 10^4$ (ml./coul.)	$\bar{u}_I^\alpha \times 10^5$ (cm.^{2} volt^{-1} sec.$^{-1}$)
3.25[b]	2.873	47.6	1.29
3.87[b]	3.470	73.6	2.46
5.76[c]	5.228	85.5	4.33
6.81[c]	6.180	79.6	5.09

[a] $\Delta v_e = 2.8 \times 10^{-4}$ ml./coul. in all experiments except the last experiment in which the sign is reversed. [b] 0.0051 *M* CdI_2. [c] 0.0050 *M* CdI_2.

Electrode Volume Change Correction.—The displacement of the boundary $v_b^{\alpha\beta}$, in ml. per coulomb, was observed with respect to the cell, whereas the displacement required, $v^{\alpha\beta}$, is that with respect to the solvent. The electrode corrections Δv_e, defined by the equation: $v^{\alpha\beta} = v_b^{\alpha\beta} - \Delta v_e$, were calculated ignoring the cadmium complexes which carry only a small fraction of the current. The electrode corrections were calculated in the usual way[22] for the case in which the closed electrode vessel is attached to the top of the channel in which the boundary descends. The corrections for the systems illustrated in Fig. 1a, b and c are, respectively

$$\Delta v_e = (V_{Ag} - V_{AgCl} - T_{I^-}^\alpha \bar{V}_{LiI} - T_{ClO_4^-}^\alpha \bar{V}_{LiClO_4} + \bar{V}_{LiCl})/F \quad (8)$$

$$\Delta v_e = (V_{AgCl} - V_{Ag} - T_{Na^+}^\alpha \bar{V}_{NaI} + \bar{V}_{KI} - \bar{V}_{KCl})/F \quad (9)$$

$$\Delta v_e = (V_{AgCl} - V_{Ag} - T_{Cd^{++}}^\alpha \bar{V}_{Cd(ClO_4)_2}/2 - \bar{V}_{LiCl} + \bar{V}_{LiClO_4})/F \quad (10)$$

Partial molal volumes in ml. are represented by $\bar{V}$, molar volumes by V, the faraday by F, and ion transference numbers in the α solution (ignoring cadmium complexes) by T^α. The transference numbers were estimated from mobility determinations made in this Laboratory, and the partial molal volumes were measured or obtained from the literature.[3]

Estimation of Mobilities of Various Complexes.—In the absence of any evidence for the existence of perchlorate complexes of cadmium, the assumption is made that in solutions containing no iodide the cadmium is present as the hydrated ion. The first experiment of Table I, therefore, yields the cadmium ion mobility $u_0 = 19.3 \times 10^{-5}$ cm.^{2} volt^{-1} sec.$^{-1}$. The mobilities u_n of the other species $(CdI_n{}^{2-n})$ must be obtained indirectly. The mobility of the uncharged species, u_2, is taken as zero. The mobility u_4 would be obtained in the limit as the iodide concentration is increased; since no experiments were made above 0.4 *N* iodide and the concentration of the CdI_3^- was still appreciable at this concentration, u_4 was obtained by the following method. At a sufficiently high iodide concentration so that CdI_3^- and $CdI_4^=$ are the only complexes present at appreciable concentrations, equation 4 may be rearranged to yield

$$u_4 = \frac{\bar{u}(1 + R(I^-))}{r + R(I^-)} \quad (11)$$

where $R = K_4/K_3$ and $r = u_3/u_4$. Assuming tentatively that $r = 0.5$ and using values of R obtained by approximation methods, it is possible to calculate u_4 from the constituent mobilities in this region. The best value was found to be $u_4 = -28.2 \times 10^{-5}$ cm.^{2} volt^{-1} sec.$^{-1}$.

It is interesting to observe that the complex $CdI_4^=$ has a greater mobility than the hydrated Cd^{++} and thus the frictional coefficient of the ion with iodide in the coördination positions is lower than that of the ion with water molecules in these positions. In order to estimate the mobilities of CdI^+ and CdI_3^-, it is assumed that in the series of complex ions $Cd(H_2O)_iI_n{}^{+2-n}$ ($n = 0, 1, \ldots, 4$; $i + n = 4$ or 6), the ionic mobility is directly proportional to the charge on the ion and inversely proportional to a frictional coefficient. This frictional coefficient is taken to be a summation of contributions from the groups which surround the central cadmium ion. For $Cd(H_2O)_4^{++}$, $+19.2 \times 10^{-5} = 2/4k$, and for $CdI_4^=$, $-28.2 \times 10^{-5} = -2/4k'$. Thus k and k' may be evaluated and used to calculate the mobilities of $Cd(H_2O)_3I^+$ and $Cd(H_2O)I_3^-$ which are $u_1 = 1/(3k + k') = +10.5 \times 10^{-5}$ and $u_3 = -1/(k + 3k') = -12.7 \times 10^{-5}$. The mobilities obtained by assuming the complexes are $Cd(H_2O)_5I^+$ and $Cd(H_2O)_3\,I_3^-$ are not appreciably different from these values. The calculations in the next section were carried out using these mobilities, and to indicate the sensitivity of the equilibrium constants to these mobilities the calculations were repeated with $u_1 = +11.0 \times 10^{-5}$ and $u_3 = -13.2 \times 10^{-5}$.

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(21) E. A. Anderson, Ph.D. Dissertation, University of Wisconsin, 1949.

(22) MacInnes and Longsworth, *Chem. Revs.*, **11**, 171 (1932).

In principle it should be possible to calculate the mobility of CdI^+ from the iodide constituent mobilities at high cadmium concentrations. It is necessary to use rather high cadmium concentrations, resulting in high ionic strengths in order to make the concentration of CdI_2 negligible. Because the principal salt present is a 2–1 electrolyte, correction of these data to an ionic strength of 0.1 for comparison is uncertain.

The Determination of the Equilibrium Constants.—The concentration equilibrium constants defined in equation (2) are constant only if the activity coefficients of the various species are the same in all of the solutions studied. In those solutions in which the constituent mobility of the cadmium is positive, the ionic strength is maintained approximately constant and the assumption that the activity coefficients are constant should be reasonably valid. In solutions in which the constituent mobility of the cadmium is negative, however, the ionic strengths of the solutions vary. Any assumed activity coefficients for the several species in the solutions studied would be about as uncertain as is the assumption that the concentration equilibrium constants will not vary by too great a factor in these solutions. The measured mobilities in solutions in which the cadmium constituent mobility is negative have been corrected for the variation in the ionic strength, but no attempt was made to consider the change in the activity coefficients.

Although the total cadmium concentration in the solutions described in Tables I and II is only 0.0050 *M*, from 5 to 25% of the total iodide present is in the form of complex ions. In equation 4 the cadmium constituent mobility is expressed as a function of the concentration of iodide ion. It is possible to convert this to an equation $\bar{u} = f\cdot(u_i, K_i, (I^-)_{total})$, but such an equation would be extremely unwieldy. It has been possible to estimate (I^-) from $(I^-)_{total}$ by using approximate values of the equilibrium constants obtained by considering in a given calculation only a limited iodide concentration range and determining by successive approximations the equilibrium constants which are important in this concentration range.

In making these calculations the possibility that the data are consistent with the existence of less than the entire set of species provisionally assumed was investigated. The deviations between observed mobilities and those calculated on such a basis were too great to lead to a serious consideration of these more limited sets of species as representing the actual composition of the solution.

After the preliminary calculations had yielded $(I^-)_{total}$ as $f(I^-)$, four points on a smooth curve drawn through the experimental data were selected and the four equilibrium constants were calculated by solving the four equations (eqn. 4) simultaneously. It was then possible to recheck the assumed values of the total iodide concentration as a function of the true iodide concentration. Such a calculation was carried out by using two different sets of values for u_1 and u_3. The equilibrium constants calculated in this way are presented in Table V where the corresponding constants obtained by Leden[6] at 25° in media of ionic strength 3.0 by electromotive force studies are also given. The solid curve in Fig. 3a has been calculated using the first set of equilibrium constants given in Table IV. In Fig. 3b is shown the distribution of the cadmium among the various species calculated using this first set of equilibrium constants and a total cadmium concentration of 0.0050 *M*.

TABLE V

SUMMARY OF EQUILIBRIUM CONSTANTS

This work[a]	K_1	K_2	K_3	$K_4 \times 10^{-6}$
$u_1 = +10.5 \times 10^{-5}$ $u_3 = -12.7 \times 10^{-5}$	83	1600	2.6×10^4	1.20
$u_1 = +11.0 \times 10^{-5}$ $u_3 = -13.2 \times 10^{-5}$	95	1550	3.2×10^4	1.26
Leden[b]	120	500	10^5	3.1

[a] Approximately 1° and an approximate ionic strength of 0.1. [b] 25° and an ionic strength of 3.

Discussion.—It is of interest to find that the mobility data, like the electromotive force data of Leden,[5] require the existence of all of the complex species: CdI^+, CdI_2, CdI_3^- and $CdI_4^=$. A direct comparison of the equilibrium constants calculated in this work and those calculated by Leden is difficult because of the difference in temperature and ionic strength in the two studies. Comparison of Fig. 3b with a corresponding plot constructed by using Leden's data reveals that in both cases the most important species are Cd^{++}, CdI^+ and $CdI_4^=$. The constants reported here do not correspond to as important a contribution from CdI_3^- as do Leden's constants while the reverse is true for CdI_2.

As indicated in the introduction the transference number of cadmium in solutions of cadmium iodide as determined by the Hittorf method or the differential moving boundary method decreases markedly with increasing concentration. Redlich[2] found the transference number of cadmium iodide at 18° to change sign just below 0.25 mole/l., and Longsworth's[3] measurements by the differential moving boundary method at 0° extrapolate smoothly to Redlich's value at 0.25 mole/l. It is of interest to calculate, using the equilibrium constants and mobilities determined in this work, the concentration of cadmium iodide in which the cadmium constituent mobility is zero. Using the first set of constants presented in Table V one calculates that the concentration of iodide ion in a solution in which $\bar{u}_{Cd}$ is zero is 0.0322 equivalent/liter. In such a solution the fractions of the cadmium present as Cd^{++}, CdI^+, CdI_2, CdI_3^- and $CdI_4^=$ are 0.133, 0.357, 0.222, 0.116 and 0.172, respectively. These data may be used in the equation

$$2C_{CdI_2} = (I^-) + (CdI^+) + 2(CdI_2) + 3(CdI_3) + 4(CdI_4^=) \quad (12)$$

or

$$C_{CdI_2} = \frac{(I^-)}{2 - f_1 - 2f_2 - 3f_3 - 4f_4}$$

where C_{CdI_2} is the molar concentration of cadmium iodide and f_n is the fraction of the total cadmium in the form CdI_n^{2-n}. The concentration of cadmium iodide at which the transference number would be zero calculated in this way is 0.20 mole/l. A concentration of 0.21 mole/l. is obtained if the second set of constants is used. These values are in as satisfactory agreement with the results of Redlich and Longsworth as could be expected in view of the difference in ionic strength.

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Elementary Processes in Radiation Chemistry. II. Negative Ion Formation by Electron Capture in Neutral Molecules[1,2,3]

BY JOHN L. MAGEE AND MILTON BURTON

Ionization processes characteristic of radiation chemistry yield energetic electrons which are ultimately degraded to thermal energies in ionization and collision processes. Although negative ions can be produced without positive-ion formation by impact of energetic electrons on molecules, the yield of such processes is so small that they make practically no contribution to the over-all picture. Thermal electrons can yield negative ions either in simple capture or in dissociative capture processes. When conditions for negative ion formation are satisfactory, low energy electrons ($< 1/3$ ev. in gases, $1/4$ ev. in liquids) disappear almost exclusively in formation of negative ions rather than in neutralization of positive ions. At usual irradiation intensities, common substances which give negative ions by thermal electron capture include oxygen, liquid water, alcohols, alkyl halides and, in general, all compounds in states in which they have low-lying vacant orbitals. For capture of thermal electrons in a dissociative process, the electron affinity of the ion produced must exceed the strength of the bond ruptured. In general, such processes tend to increase ion-pair yield, but certain clearly described exceptions exist.

Radiation chemical syntheses of ozone and of hydrogen peroxide show behavior characteristic of reactions in which the principal neutralization process involves negative oxygen ions. When a negative-ion source (*e.g.*, oxygen or water) is present as impurity in a substance of low ionization potential (*e.g.*, benzene), the principal neutralization reaction in a radiation-chemical process involves interaction of the negative ion of the former and of the positive ion of the latter. Resultant characteristic reactions may mask the normal radiation-chemical reaction of the uncontaminated principal constituent.

Water vapor captures thermal electrons without dissociation but solvation of the negative ion in liquid water confers large electron affinity and produces a situation conducive to capture accompanied by dissociation. Resultant anisotropic distribution and high concentration of positive and negative ions may have special consequences, particularly in biological systems.

1. Introduction

Free electrons and positive ions are produced when high-energy charged particles pass through matter. The kinds of positive ions and the energy distribution of the free electrons depend primarily upon the nature of the substance and to a lesser extent on the incident particle (*i. e.*, its charge, mass and energy).[4] The complete radiation-chemical mechanism, which describes in detail all the chemical reactions resulting from the irradiation, depends upon all ions and radicals produced.[5] One small, but important, possible step in that mechanism is electron capture in the neutral molecule of the irradiated material. If capture is possible, large numbers of negative ions will form in the system, and neutralization will occur principally by positive–negative ion reaction. If capture is not possible in the neutral molecules, the free electrons will be thermalized and eventually recaptured in the positive ions which exist in the system.

In this paper we are considering in a general way negative ion formation by the electron capture mechanism only. We find it convenient to divide the discussion into four parts: (a) electronic states of negative ions; (b) cross section for electron capture as a function of electron energy; (c) energy distribution of free electrons in irradiated systems; (d) probability for capture of such free electrons. These topics are treated in the required detail. A discussion of capture possibilities in real systems with possible radiation chemical effects follows thereafter.

In this paper we are not concerned with formation of negative ions in the primary radiation chemical act, *e. g.*

$$RX \rightsquigarrow R^+ + X^-$$

either by the action of the primary charged particle or by action of fast secondary electrons. Our concern is exclusively with negative ion formation by electron capture and the consequences of such a possible process.

2. Electronic States of Molecular Negative Ions

2.1. Negative Ions of Singly Bonded Diatomic Molecules.—Most atoms are able to form negative ions because they have an electron affinity *i. e.*, the reaction

$$A + e \longrightarrow A^-$$

is exothermic. A few, of course, have zero or negligible affinity. Molecules are more complicated systems. Most of them have stable negative ion forms[6]; thus, dissociation from the lowest energy state of such ions is always endothermic. It is an important fact that the stable form is not necessarily attainable directly by electron capture (see the case of hydrogen[3]). Whether or not such attainment is possible depends upon the nature of the potential curves for the negative ion. The purpose of this section is the examination

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[2] A contribution from the Radiation Chemistry Project, operated by the University of Notre Dame under Atomic Energy Commission contract No. AT(11-1)-38.

[3] Paper I of this series: THIS JOURNAL, **72**, 1965 (1950).

[4] H. A. Bethe, "Handbuch der Physik," Vol. 24, pt. 1, Julius Springer, Berlin, 1933.

[5] M. Burton, *Ann. Rev. Phys. Chem.*, **1**, 113 (1950).

[6] H. S. W. Massey, "Negative Ions," Cambridge University Press, 1938.