in order to obtain vapor pressure equilibration. All other chemicals, including those used in buffer preparation, were of reagent or C.P. grade and were used without further purification; they were "polarographically pure."

Apparatus.—A Sargent Model XXI Polarograph, a Leeds & Northrup Model E Electro-Chemograph and a Fisher Elecdropode were used; potentials were checked with a Leeds & Northrup Type K potentiometer. A thermostated, jacketed H-type polarographic cell[16] containing a saturated calomel reference electrode was used. When changing from one temperature to another (20, 25 or 30 ± 0.1°), at least 24 hr. was allowed for the S.C.E. to reach thermal equilibrium. Capillaries, prepared from Corning marine barometer tubing, had $m^{2/3}t^{1/6}$ values at open circuit in water at 25° at 68 cm. mercury head of (1) 2.06, (2) 2.17 and (3) 2.04 mg.$^{2/3}$ sec.$^{-1/2}$; one capillary used only in drop-time studies had $m^{2/3}t^{1/6} = 1.75$ at 81 cm.

The coulometric apparatus was a modification of that of Lingane,[17] employing a water-jacketed (25 ± 0.1°) electrolysis cell, a stirred massive mercury electrode, a large external silver anode and an oxygen–hydrogen coulometer. The cathode potential was measured against S.C.E. with the Type K potentiometer.

A Beckman Model G *p*H meter was used to measure *p*H; in the alkaline region a Type E electrode was employed.

Polarographic Procedure.—A weighed portion of the reducible compound was dissolved in oxygen-free water and then diluted to the desired concentration with a stock solution of background electrolyte which had also been purged with nitrogen. The polarographic cell was rinsed twice with the test solution and then filled; the capillary was introduced and a rapid stream of nitrogen passed through the cell for 2 to 3 min., during which time the initial potential was set at the desired value. Nitrogen was passed over the solution during the polarographic run. All test solutions contained from 0.01 to 0.02% gelatin as a maximum suppressor. Potentials are reported *vs.* S.C.E. and at 25° unless otherwise noted; cell *iR* drops were negligible.

Constant ionic strength MacIlvaine buffers (Table II) were used between *p*H 2 and 7.6. Buffers of ionic strength 0.2 and 0.3 for use between *p*H 7 and 12 were prepared by titrating a solution of 0.05 *M* H_3PO_4 with 0.1 *M* tetramethylammonium hydroxide to the desired *p*H; both the acid and hydroxide solutions were approximately 0.1 *M* in tetramethylammonium bromide.

Coulometric and Macroscale Electrolysis Procedures.—The background electrolyte was deoxygenated in the electrolysis cell with a rapid nitrogen stream which was maintained throughout the experiment. The cathode mercury was then added; the bridge from the reference S.C.E. was adjusted so that it just touched the vigorously stirred mercury surface; the gas coulometer, in which the solution had just been saturated with hydrogen and oxygen,[17] was connected in series with the cell. The potential of the mercury cathode was made several tenths of a volt more negative than that at which the run was to be made; electrolysis was continued until the last traces of reducible impurities had been removed as indicated by the decrease in current.

Without breaking the circuit, the applied potential was reduced until the cathode potential attained the desired value; the coulometer buret was read; the deoxygenated sample solution was added to the cell and the potential readjusted to the desired value which was maintained during electrolysis.

After electrolysis had proceeded for 2.0 to 2.5 hr., the circuit was opened, a sample of the cell solution withdrawn and the residual aromatic N-nitrosohydroxylamine concentration determined polarographically. From the decrease in concentration and the volume of gas evolved, the number of electrons involved in the electrode reaction was calculated after making the necessary corrections,[17] including, if required, those for the homogeneous decomposition of the cupferron. In addition, the main product of the electrolytic reduction was isolated and identified as follows.

In the case of an acidic solution, the solution was drained from the cell and 2 or 3 drops of benzaldehyde was added followed by sufficient ethanol to take the benzaldehyde into solution; the mixture was then set aside. In all cases a precipitate appeared within 15 or 20 min.; however, additional time was allowed for the reaction to proceed to completion. After about 2 hr., an equal volume of water was added and the mixture cooled to 0° in an ice-bath. The precipitate was isolated and recrystallized at least twice from ethanol–water mixture; after drying, its melting point was determined. The benzaldehyde adducts isolated from the solutions of the products formed by electrolysis in acidic solution had the following melting points (literature values in parentheses for the $RHN-NH_2$–benzaldehyde condensation products where R is phenyl, α-naphthyl or *p*-xenyl): cupferron, 156–158° (155–156°); neocupferron, 143–144° (144–145°); *p*-phenylcupferron, 151–152° (153°).

In alkaline solution, the reduction product precipitated from the electrolysis solution and could be isolated by filtration. The product precipitated from neocupferron solution melted at 78–79° (m.p. of naphthalene, 80.2°) and the product from *p*-phenylcupferron solution at 68–69° (m.p. of biphenyl, 69–70°).

Acknowledgment.—The authors wish to thank the Atomic Energy Commission which helped support the work described.

ANN ARBOR, MICHIGAN

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND LABORATORY FOR NUCLEAR SCIENCE OF THE MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

A Spectrophotometric Study of the Indium–Bromide Complex Ions[1]

BY EUGENE A. BURNS AND DAVID N. HUME

RECEIVED JULY 9, 1956

The aqueous bromide complexes of indium have been investigated by means of ultraviolet spectrophotometry. The spectra obtained can best be interpreted by terms of the mono-, di-, tri- and tetrabromoindium ions whose stepwise formation constants have been evaluated at an ionic strength of 4.00 *M*. Analysis of the data by five distinct methods gives average values for the stepwise formation of $InBr^{++}$, $InBr_2^+$, $InBr_3$ and $InBr_4^-$ of 120, 19, 4 and 7, respectively.

In the past three years, fourteen articles have appeared in the literature concerning the nature of indium(III) in halide media, twelve specifically dealing with the bromide system. Table I lists the values of the consecutive formation constants of the indium bromide system observed by these workers, together with the values obtained in this investigation. The considerable lack of agreement among previous workers prompted the present investigation using spectrophotometric methods which are not subject to some of the difficulties in other methods.

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[1] Abstracted from a thesis submitted by Eugene A. Burns in partial fulfillment of the requirements for the degree of Doctor of Philosophy at the Massachusetts Institute of Technology, May 4, 1956.

TABLE I

COMPARISON OF REPORTED SUCCESSIVE FORMATION CONSTANTS OF THE INDIUM–BROMIDE SYSTEM

Investigator	Method	Ionic strength	k_1	k_2	k_3	k_4
Hepler and Hugus[2]	pH	Vary	159			
Schufle and Eiland[3]	Ion exchange	1.00	16	3.8	5.0	
DeSesa[4]	Potentiometric	Vary	65			
Sunden[5]	Potentiometric	2.00	95	3.8		
Sunden[6]	Extraction		85	4.7		
Cozzi and Vivarelli[7]	Polarography	2.00	6300	10		
Carleson and Irving[8]	Ion exchange	0.691	103	12.1	1.5	
Irving and Rossotti[9]	Extraction	1.00	114	19.1	2.3	0.2
This investigation	Spectrophotometric	4.00	120	19	4	7

Experimental

Metallic indium was obtained both from the Indium Corporation of America, Utica, N. Y. (99.97% pure) and from Fisher Scientific Company, N. Y. (99.9+% pure). The metal was dissolved in concentrated nitric acid and fumed down to near dryness with perchloric acid five times. The resulting solutions were tested for the presence of chloride and nitrate ions. It was observed that every attempt to dissolve indium metal in perchloric acid (which proceeded slowly) caused the reduction of some perchlorate to chloride. The dissolving of indium in 70% perchloric acid proceeded fairly rapidly if it was performed in a platinum dish, but still there was a detectable amount of chloride formed. The molarity of the indium was checked gravimetrically by precipitation with ammonium hydroxide followed by ignition at 1000°. The perchloric acid concentration was calculated by titration with standard sodium hydroxide to a phenolphthalein end-point and subtraction of the known equivalents of indium that were present.

Fisher C.P. sodium perchlorate (once recrystallized) and Mallinckrodt analytical reagent sodium bromide and perchloric acid were the chemicals employed.

All absorbance measurements were made using a Beckman model DU quartz photoelectric spectrophotometer with an ultraviolet attachment in a room whose temperature was controlled at 21.7 ± 0.6°. Matched silica cells of 0.100, 1.000 and 10.00 cm. lengths were employed. The corrections for scattered light were determined by observing the differences in absorbance of water when present in each of the cells and then applied to the appropriate observed absorbance in each cell.

Results

The solutions of indium perchlorate, and varying amounts of an excess of sodium bromide, gave spectra with maxima between 220 and 235 mμ, depending on the concentration of the two reactants. The initial studies showed that the absorption of the solutions changed with time, and on standing overnight the solutions became yellow in color. Chemical tests proved this to be due to free bromine being formed.

Several factors in the production of bromine were examined qualitatively. It became evident that: (1) indium was not necessary; (2) the solution had to be acidic, for concentrated solutions of sodium perchlorate and sodium bromide were relatively stable and (3) sodium perchlorate had to be present. Air was shown not to be the cause of the difficulty and the possibility of chlorate impurity in the sodium perchlorate was eliminated. Indium appeared to catalyze the oxidation, since when the spectra of indium solutions containing excess bromide at high ionic strength were examined with reference to identical solutions, not containing indium perchlorate, it was observed that the peak at 270–280 mμ grew as a function of time and in 90 minutes completely obliterated the peak at 235 mμ.

The addition of small amounts of sodium sulfite (to give about 5×10^{-4} M sulfurous acid) eliminated the bromine absorption peak, and the solutions remained colorless for 12 to 24 hours. No evidence for complex formation between sulfite and indium was found under these conditions: the weak absorption spectrum of sulfite was unaffected by the presence of indium.

The complexing of indium with sulfate that is formed as the sulfite is oxidized by the bromine was also considered. Assuming all of the sulfite (10^{-4} M in the experiments described below) to be converted to sulfate, and taking Sunden's[5,6] values for the formation constants of the indium sulfate and bromide complexes, it was found that the ratio of $InBr^{++}$ to $InSO_4^+$ was over 3000. Thus, since it was observed that indium in sulfate media does not absorb in the regions examined, the amount complexed as the sulfate is negligible and will not affect the spectra of indium in bromide media.

In the initial exploratory work it was observed that, as would be expected from the plus three oxidation state of indium, the ionic strength of the solutions examined was quite an important factor. This pronounced effect is illustrated in Fig. 1, which shows the effect of ionic strength on the absorption spectra of indium in the presence of a large excess of bromide.

Continuous Variations.—To get a general idea of what complexes might be seen by their absorption, continuous variations experiments were done over a range of concentration, wave length and ionic strength. The results are shown in Fig. 2. It is known[10,11] that the method of continuous variations may not be valid if more than one absorbing complex is present or if the complex being studied is not fairly stable in comparison with the others. Inasmuch as it was shown later that more than one complex showed absorption in this region, and that the formation constants were not greatly different from each other, the system is not ideally suited to study by this method. The work is, however, sug-

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(2) L. G. Hepler and Z. Z. Hugus, Jr., THIS JOURNAL, **74**, 6115 (1952).

(3) J. A. Schufle and H. M. Eiland, *ibid.*, **76**, 960 (1954).

(4) M. A. DeSesa, Ph.D. Thesis, Mass. Inst. of Tech., 1953.

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(9) H. Irving and F. J. C. Rossotti, *ibid.*, 1927, 1938, 1946 (1955).

(10) L. I. Katzin and E. Gebert, THIS JOURNAL, **72**, 5455 (1950).

(11) F. Woldbye, *Acta Chem. Scand.*, **9**, 299 (1955).

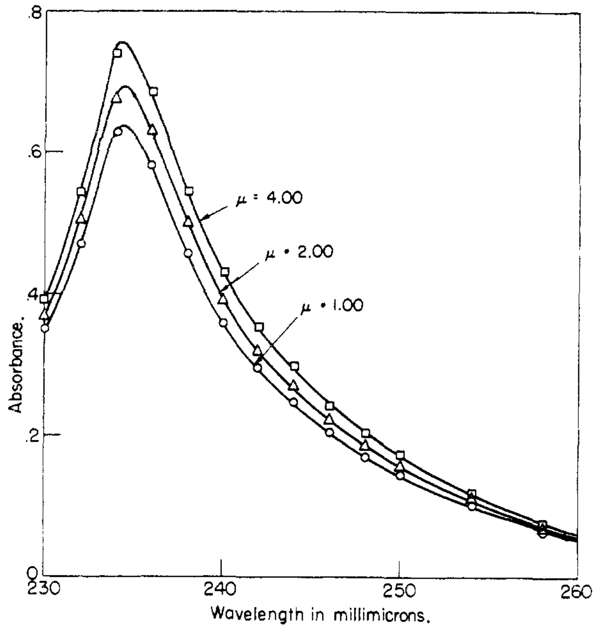

Fig. 1.—Spectra of indium in an excess of bromide as a function of ionic strength. Conditions: 2.50 × 10^{-4} *M* $\mathrm{In(ClO_4)_3}$, 0.500 *M* NaBr, 0.100 *M* $\mathrm{HClO_4}$, 1.00 × 10^{-4} *M* $\mathrm{Na_2SO_3}$, 1.000 cm. silica cells.

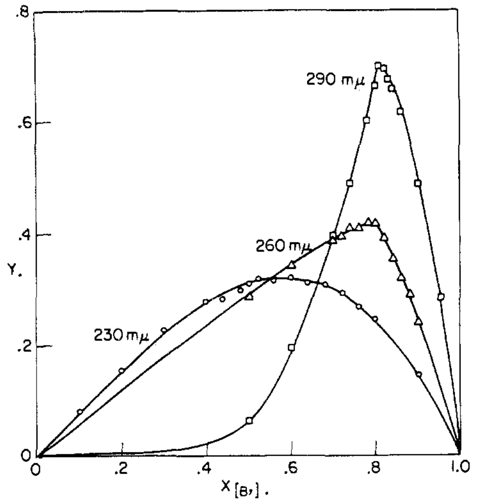

Fig. 2.—Typical continuous variations curves at varying concentrations, ionic strengths, acidities and wave lengths. 230 mμ: $(1 - x)(0.200)$ *M* $\mathrm{In(ClO_4)_3}$, $(x)(0.0200)$ *M* NaBr, 0.197 *M* $\mathrm{HClO_4}$, μ = 0.697 *M*, and 1.000 cm. silica cells. 260 mμ: $(1 - x)(0.100)$ *M* $\mathrm{In(ClO_4)_3}$, $(x)(0.100)$ *M* NaBr, 0.500 *M* $\mathrm{HClO_4}$, 5.00 × 10^{-4} $\mathrm{Na_2SO_3}$, μ = 2.100 *M*, and 10.00 cm. silica cells. 290 mμ: $(1 - x)(1.00)$ *M* $\mathrm{In(ClO_4)_3}$, $(x)(1.00)$ *M* NaBr, 0.796 *M* $\mathrm{HClO_4}$, 0.00100 *M* $\mathrm{Na_2SO_3}$, μ = 6.80 *M*, and 1.00 cm. silica cells.

gestive that the mono- and tetrabromo complexes, and possibly others, are formed in solutions containing both indium and bromide ions.

Spectra of Indium in Excess Bromide.—Using the results of the experiments in the previous sections as a guide, the determination of the successive formation constants of the indium bromide complexes at an ionic strength of 4.00 *M* was attempted. An ionic strength of 4.00 *M* was chosen, since it would therefore be possible to have a maximum bromide concentration of 3.90 *M*, (all solutions were 0.100 *M* in perchloric acid). Higher bromide concentrations had been observed to lead to no significant further increase in the absorbance of the 235 mμ peak. The concentration of indium perchlorate was 2.5 × 10^{-4} *M*; sodium sulfite, 1.0 × 10^{-4} *M*; perchloric acid, 0.100 *M*; and the ionic strength was maintained with sodium perchlorate. The location of the peak was constant at 235 ± 1 mμ for the range of bromide concentration of 0.200 to 3.900 *M*. Approximately 15 minutes were required to obtain the spectrum of one of these solutions, beginning at higher and moving toward lower wave lengths. Absorption by bromide ion places a lower limit on the wave length at which the spectra can be measured. The slit width, which was often as wide as 1.2 mm., was always kept constant in the region of the maximum.

In order to obtain better resolution at shorter wave lengths, the indium concentration was increased ten-fold in some experiments and 0.100 cm. cells used. Figure 3 shows how the resulting decrease in background bromide absorption allows the spectra to be taken to shorter wave lengths and a wider range of concentrations to be studied. Good agreement was found between molar absorptiv

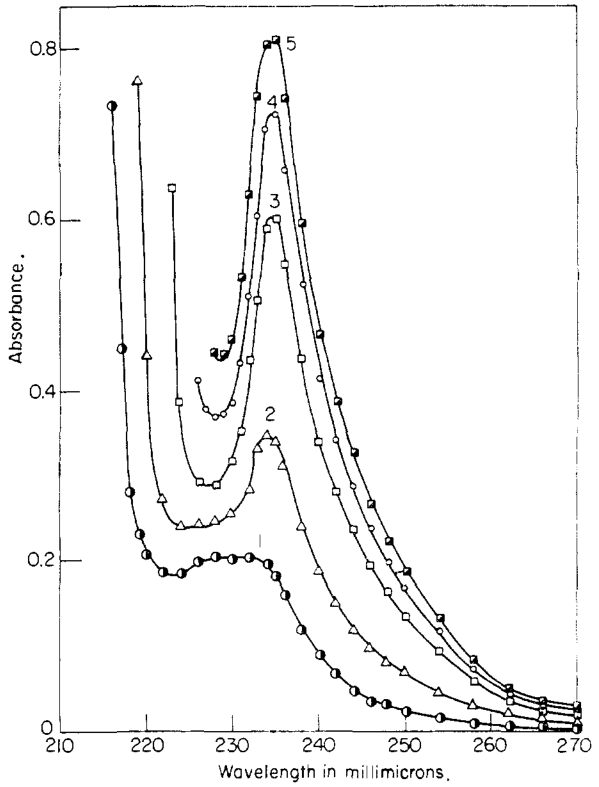

Fig. 3.—Spectra of indium in the presence of large excesses of bromide using 0.100 cm. silica cells. Conditions: 2.00 × 10^{-3} *M* $\mathrm{In(ClO_4)_3}$, 0.100 *M* $\mathrm{HClO_4}$, 5.00 × 10^{-4} *M* $\mathrm{Na_2SO_3}$, μ = 4.00 *M*. Curve 1, 0.100 *M* NaBr; curve 2, 0.200 *M* NaBr; curve 3, 0.500 *M* NaBr; curve 4, 1.000 *M* NaBr; curve 5, 3.90 *M* NaBr. When 1.00 cm. cells are used, the spectra have cutoffs between 225–234 mμ, depending on the concentration of bromide in the blank.

ities (extinction coefficients) measured under the two sets of conditions.

Determination of the First Stability Constant.—Modified McConnell–Davidson[12] techniques were employed to evaluate the first two stability constants. In order to determine the first formation constant, an excess of indium was added to ensure that only three absorbing species were present: *i.e.*, In^{+++}, $InBr^{++}$ and Br^-. Assuming that all three species absorb, and incorporating the mass-action expression, $k_1 = (InBr^{++})/(In^{+++})(Br^-)$, the resulting expression can be derived for a specific wave length

$$\frac{ab}{A_0 - A_a - A_b} = \frac{1}{(\epsilon_\alpha - \epsilon_a - \epsilon_b)k_1} + \frac{a}{(\epsilon_\alpha - \epsilon_a - \epsilon_b)} \qquad (1)$$

where ϵ_α, ϵ_a, and ϵ_b are the molar absorptivities of the complex, indic and bromide ions, respectively; a and b are the analytical concentrations of indic and bromide ions, respectively; A_0 is the observed absorbance of the solution containing the mixture of indium and bromide ions; and A_a and A_b are the absorbances of solution containing only a concentration of indium perchlorate and b concentration of sodium bromide, respectively. When $ab/(A_0 - A_a - A_b)$ is plotted *vs.* a, a straight line results, and the ratio of the slope to the intercept of the line is equal to the formation constant.

In the work performed in this section, each solution was 0.00200 *M* in sodium bromide, 0.100 *M* in perchloric acid, the concentration of indium perchlorate was varied from 0.006 to 0.100 *M*, and the ionic strength was maintained at 4.00 *M* by use of sodium perchlorate. The use of sodium sulfite was found to be unnecessary; bromide at these low concentrations was not appreciably oxidized Table II shows the results of the McConnell–Davidson plots, all of which gave good straight lines.

TABLE II

MCCONNELL–DAVIDSON DETERMINATION OF THE FIRST FORMATION CONSTANT

Wave length, mμ	ϵ_{InBr}^{++}	ϵ_{Br}^{-}	ϵ_{In}^{+++}	k_1
225.0	199.4	56.5	13.5	121
226.0	177.1	49.5	11.3	121
227.0	154.1	44.0	9.4	119
228.0	135.0	40.0	8.0	119
229.0	116.2	37.0	6.8	124
230.0	99.6	33.5	5.8	128
231.0	86.1	30.5	5.0	122
232.0	73.0	29.0	4.3	133

Av. $k_1 = 123$ Std. dev. = 4.9

Determination of the Second Stability Constant.—If the experimental conditions are altered slightly to give a small excess of bromide, the species $InBr_2^+$ will also be present. It is then possible to evaluate the second "stepwise" formation constant. If the second stepwise equilibrium is considered, the exact eq. 2 results

$$\frac{a}{D} = \frac{1}{(\epsilon_\beta - \epsilon_a - 2\epsilon_b)k_2} G + \frac{1}{(\epsilon_\beta - \epsilon_a - 2\epsilon_D)} \qquad (2)$$

where $D = A_0 - A_a - A_b$, $k_2 = (InBr_2^+/(InBr^{++})\cdot(Br^-)$, ϵ_β = molar absorptivity of the $InBr_2^+$ ion, and G is a function of the ligand concentration

$$G = \frac{1}{k_1X^2} + \frac{1}{X} + \frac{(\epsilon_\alpha - \epsilon_a - \epsilon_b)a}{DX}$$

where X represents the equilibrium concentration of bromide. All that is needed is to plot a/D *vs.* G and k_2 can be determined from the resulting curve, for k_2 is equal to the intercept divided by the slope.

The spectra for indium in the presence of a slight excess of bromide (with water as the reference solution), for wave lengths 226–240 mμ at an ionic strength of 4.00 *M* were determined. The concentration of indium perchlorate was 2.00 m*M*, perchloric acid concentration was 0.100 *M*, and the bromide was varied at concentrations of 5.00, 10.00, 15.00, 20.00, 25.00 and 30.00 m*M*. It is obvious that the equilibrium concentration of halide and thus the values of *G* must be estimated from the six different estimated values of *X*. It was found that after the third approximation of *X*, a 10% difference in the estimated k_2 gave rise to less than half of 1% change in *G*, and less than 0.3% difference in the value of *X*. The equilibrium concentrations of bromide under the above conditions were calculated to be 4.24, 8.74, 13.37, 18.12, 22.92 and 27.73 m*M*, respectively. The approximation was performed only at 230 mμ; and since the resulting values of k_2 all differed by less than 10%, the above values of *X* were used at all wave lengths considered to calculate the function *G*. The results of the good straight lines that were obtained using this interpretation for the wave lengths 226–240 mμ are shown in Table III. The values of the molar absorptivities of the first complex at these wave lengths found in the determination of the first stability constant were used.

TABLE III

MCCONNELL–DAVIDSON DETERMINATION OF THE SECOND FORMATION CONSTANT

Wave length, mμ	ϵ_{InBr}^{+2}	k_2
226.0[a]	1460	18.3
228.0[a]	1370	19.5
230.0	1310	18.6
232.0	1040	19.0
234.0	839	18.2
236.0	595	18.5
238.0	401	18.2
240.0	260	19.3

Av. $k_2 = 18.7$ $s = 0.51$

[a] Only 3 points determined this line.

Determination of Higher Complexes.—Further work was performed on solutions containing large excesses of bromide, in an effort to evaluate the stability constants of the higher complexes whose existence was suggested by the method of continuous variations. The data obtained were interpreted in a manner similar to that of Kingery and Hume[13]. At high halide concentrations, the stability constant for the highest complex can be determined on the basis of the reaction

$$InBr_j^{+3-j} + nBr^- = InBr_{j+n}^{+3-j-n} \qquad (4)$$

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[12] H. McConnell and N. Davidson, THIS JOURNAL, **72**, 3164 (1950).

[13] W. D. Kingery and D. N. Hume, *ibid.*, **71**, 2393 (1949).

and

$$k_{r+n} = \frac{(\mathrm{InBr}_{r+n}^{+3-r-n})}{(\mathrm{InBr}_r^{+3-r})(\mathrm{Br}^-)^n} \qquad (5)$$

If the higher complex is the only absorbing species, and the next lower complex is the only other species of indium present in appreciable amounts, an equation results

$$\log \frac{A_\mathrm{i}}{A_\mathrm{L} - A_\mathrm{i}} = n(\log X_\mathrm{i}) + \log k_{r+n} \qquad (6)$$

where A_i is the observed absorbance for a concentration X_i of bromide and A_L is the asymptotic limit of absorbance of A_i as X_i approaches infinity. By plotting $\log A_\mathrm{i}/(A_\mathrm{L} - A_\mathrm{i})$ *vs.* $\log X_\mathrm{i}$, it is seen that the slope reveals the value of n, and the intercept, when $\log X_\mathrm{i}$ is zero, is the formation constant, k_{r+n}. In this work, the bromide absorbs quite strongly due to its high concentration, and its absorbance was compensated for in the reference cell.

Figure 4 shows three typical curves in the determination of A_L. The plot of $\log A_\mathrm{i}/(A_\mathrm{L} - A_\mathrm{i})$ *vs.* $\log X_\mathrm{i}$ was linear for 20 wave lengths between 235 and 270 mμ. All of these data were obtained using 2.50×10^{-4} *M* indium perchlorate, 0.100 *M* perchloric acid, 1.00×10^{-4} *M* sodium sulfite, and the bromide concentration was varied at 1.00, 1.20, 1.60, 2.00, 2.40, 2.80, 3.20, 3.60 and 3.90 *M*. Ten-centimeter cells enabled readings to be taken at wave lengths from 260 to 270 mμ, where it is felt the lower complex would not be absorbing, and readings were taken between 235 and 250 mμ with one-centimeter cells. Since the ratio $A_\mathrm{i}/(A_\mathrm{L} - A_\mathrm{i})$ was relatively constant in the two ranges for a particular bromide concentration, it can be concluded that the lower complex is not absorbing in the 235–250 range.

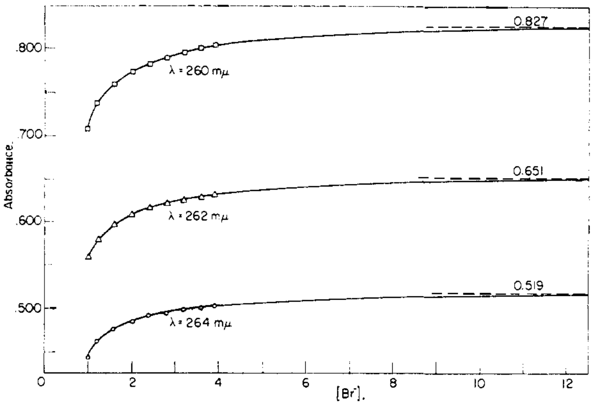

Fig. 4.—Typical determinations of the molar absorptivity. Conditions: 2.50×10^{-4} *M* $\mathrm{In(ClO_4)_3}$, 0.100 *M* $\mathrm{HClO_4}$, 1.00×10^{-4} *M* $\mathrm{Na_2SO_3}$, $\mu = 4.00$ *M*, and 10.00 cm. cells.

The formation constant for the addition of the last ligand was evaluated to be 6.1. The slope, 1.19, indicated that only one bromide was added.

The fact that the ratio $A_\mathrm{i}/(A_\mathrm{L} - A_\mathrm{i})$ at a particular value of X_i was relatively constant over the whole wave length range that was examined shows that the same species is absorbing throughout the range. The fact that the same method yielded a straight line shows that the method is valid, and hence the lower species does not absorb throughout the wave length range.

Since the continuous variation work suggested an $\mathrm{InBr_4^-}$ species, it is reasonable to interpret the preceding work on the assumption that $k_{r+n} = k_4$. If this is the case, since $n = 1$, the lower species—*i.e.*, $\mathrm{InBr_3}$—must exist in solution, and the third formation constant, k_3, can be determined by a difference technique. The fraction of the indium in the form of the fourth complex is

$$\frac{(\mathrm{InBr_4^-})}{(\Sigma\mathrm{In^{+++}})} = \frac{k_1k_2k_3k_4X^4}{1 + k_1X + k_1k_2X^2 + k_1k_2k_3X^3 + k_1k_2k_4X^4} \qquad (7)$$

If $\mathrm{InBr_4^-}$ is the only absorbing species, then the ratio $(\mathrm{InBr_4^-})/(\Sigma\mathrm{In^{+++}})$ will equal $A_\mathrm{i}/A_\mathrm{L}$, where A_i and A_L have the same meaning as before. If the equilibrium concentration of bromide is large with respect to the equilibrium concentrations of the complexed indium, then the equilibrium concentration approximates the analytical concentration of bromide.

Absorbance measurements were taken as previously, with an ionic strength of 4.00 *M*, 2.50×10^{-4} *M* indium perchlorate, 1.00×10^{-4} *M* sodium sulfite, 0.100 *M* perchloric acid, and varying the sodium bromide concentration at 0.050, 0.100, 0.150, 0.200, 0.300, 0.400, 0.500, 0.600, 0.700 and 1.000 *M*. At these concentrations it was felt that the missing complex could be detected using the 1.000 and 10.00 cm. silica cells in the wave length ranges 240–250 and 260–270 mμ, respectively. Utilizing the limiting absorbances that had been determined before, the ratio $A_\mathrm{i}/A_\mathrm{L}$ was determined for a particular bromide ion concentration as a function of wave length. With the exception of wave lengths below 244 mμ (particularly at low bromide concentrations), this ratio was constant.

Table IV lists the average values of the ratio $A_\mathrm{i}/A_\mathrm{L}$ over the wave length regions examined as a function of the bromide concentration and cells employed. Since the values are in reasonably good agreement, it can be concluded that only one species is present and absorbing in these regions. The fact that the data obtained with the 10.00 cm. cells show a lower standard deviation—and give lower values for each respective bromide ion concentration, indicates that lower complexes are absorbing in the 240–250 mμ range, although not enough to change the ratio appreciably.

TABLE IV

FRACTION OF INDIUM COMPLEXED IN THE HIGHEST FORM

	1.000 cm. cells			10.00 cm. cells			
$\mathrm{Br^-}$	n	f	s	n	f	s	k_3
1.000	5	0.858	0.013	10	0.854	0.003	23.0
0.700	7	.791	.004	6	.789	.004	10.0
.600	7	.755	.008	6	.749	.005	7.9
.500	5	.703	.004	6	.699	.004	7.0
.400	5	.629	.006	6	.624	.003	6.0
.300	4	.520	.005	6	.512	.003	5.3
.200	4	.351	.003	6	.341	.002	4.7
.150	4	.245	.004	6	.230	.003	4.4
.100	4	.126	.006	6	.115	.002	4.3
.050	4	.039	.006	6	.025	.002	4.1
	Pooled std. dev.		= 0.007			= 0.003	

Knowing k_1, k_2, k_4 and $A_\mathrm{i}/A_\mathrm{L}$ as a function of the bromide concentration, it is possible to solve for k_3 in eq. 7. Table IV shows the resulting values of

k_3. The diminishing trend with decreasing bromide concentration is believed to be caused by (1) errors in the "known" (k_1, k_2 and k_4) formation constants, and (2) amplification of a small effect by taking the difference of two large numbers. To avoid the latter effect only the results in the range 0.05 to 0.4 M bromide were averaged to give the most probable value of 4.8 for k_3.

Alternative Treatments of the Data.—The data of this investigation have been treated by several alternative methods described in a recent publication by Rossotti and Rossotti,[14] in order to compare the efficacy of the various methods used and to establish the best possible values of formation constants from the experimental results at hand.

In the first of these, by defining f_c as the fraction of the metal complexed as MX_c, we have

$$f_c = \frac{MX_c}{\Sigma M} = \frac{K_cX^c}{1 + \Sigma KnX^n} \quad (8)$$

where K_n is the over-all formation constant $k_1 \cdot k_2k_3 \cdot \cdot \cdot k_n$. Taking logarithms, differentiating and substituting Bjerrum's $\bar{n}$ expression for the average number of ligands attached to the metal ion[15] we obtain

$$\frac{d(\log f_c)}{d(\log X)} = c - \bar{n} \quad (9)$$

The continuous variations experiments indicate that the maximum value of c is probably 4; however, it is seen that this method just described will in turn evaluate c when data obtained during the determination of the second formation constant are employed in conjunction with the data of Table IV. Log f_c was plotted *vs.* log Br^- for bromide concentrations 0.050–1.000 M, as is shown in Fig. 5, and the slopes were determined as a function of the bromide ion concentration. The values of $c - \bar{n}$ are given in Table V, together with values of $\bar{n}$ (calculated assuming c to be 3, 4 and 5).

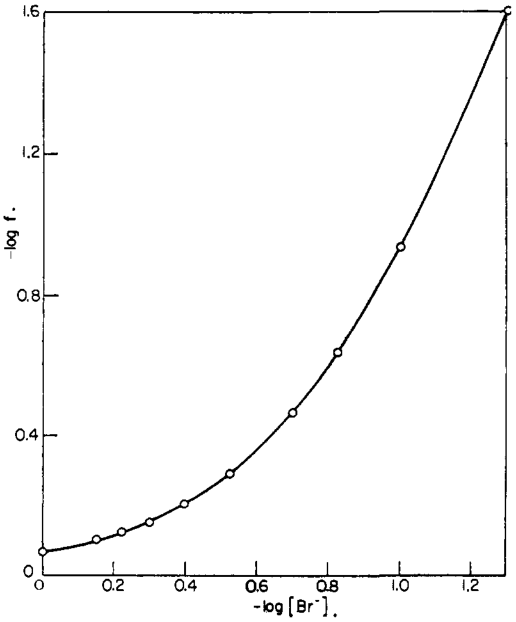

Fig. 5.—Graphical determination of the ligand number, n.

TABLE V

EVALUATION OF $\bar{n}$ VALUES

(Br^-)	$-\log f$	$-\log Br^-$	Slope	3-Slope	4-Slope	5-Slope
1.000	0.069	0.000	0.18	2.82	3.82	4.82
0.700	0.103	.155	.26	2.72	3.74	4.74
.600	.125	.222	.32	2.68	3.68	4.68
.500	.155	.301	.44	2.56	3.56	4.56
.400	.205	.398	.59	2.41	3.41	4.41
.300	.291	.523	.80	2.20	3.20	4.20
.200	.467	.699	1.24	1.76	2.76	3.76
.150	.638	.824	1.42	1.58	2.58	3.58
.100	.939	1.000	1.88	1.12	2.12	3.12
.050	1.602	1.301	2.34	0.66	1.66	2.66

$\bar{n}$ VALUES EVALUATED FROM DATA OBTAINED IN DETERMINATION OF SECOND CONSTANT

Total		Equilibrium bromide $\times 10^3$	$-\log Br^-$	$\bar{n}$
Indium $\times 10^3$	Bromide $\times 10^3$			
2.00	5.00	4.24	2.301	0.38
2.00	10.00	8.74	2.000	.63
2.00	15.00	13.37	1.824	.82
2.00	20.00	18.12	1.699	.94
2.00	25.00	22.92	1.602	1.05
2.00	30.00	27.73	1.523	1.14

Using the data obtained in the McConnell–Davidson determination of the second stability constant, $\bar{n}$ was calculated for a bromide range of 0.005–0.030 M.

Figure 6 shows the formation curve of indium in bromide medium: that is, $\bar{n}$ as a function of log Br^-

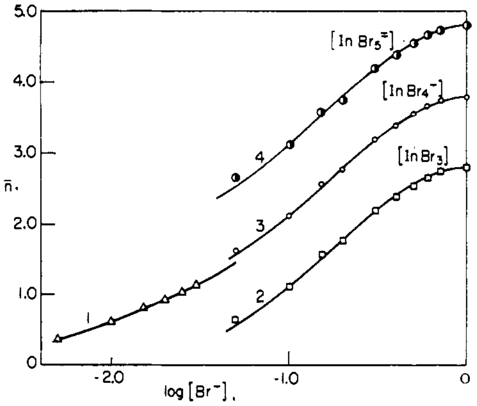

Fig. 6.—Formation curve of indium in a bromide medium. Curves 1, $\bar{n}$ calculated from data obtained in the determination of the second constant; 2, $\bar{n}$ calculated on the assumption that $InBr_3$ is absorbing species; 3, $\bar{n}$ calculated on the assumption that $InBr_4^-$ is absorbing species; 4, $\bar{n}$ calculated on the assumption that $InBr_5^=$ is absorbing species.

It is seen from this figure that assuming the absorbing species to be $InBr_3$ or $InBr_5^=$ leads to inconsistent results. A smooth curve can be drawn connecting the two sets of data only if $InBr_4^-$ is the species absorbing.

Using the values of $\bar{n}$ as a function of the bromide concentration, it is also possible to evaluate

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[14] F. J. C. Rossotti and H. S. Rossotti, *Acta Chem. Scand.*, **9**, 1166 (1955).

[15] J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.

the formation constants by a graphical method outlined by Rossotti and Rossotti.[14]

$$J_1(X) = K_1 + \left(\frac{2 - \bar{n}}{1 - \bar{n}}\right) K_2X + \left(\frac{3 - \bar{n}}{1 - \bar{n}}\right) K_3X^2 + \left(\frac{4 - \bar{n}}{1 - \bar{n}}\right) K_4X^3 \ldots \quad (10)$$

The value of $J_1(X)$ when extrapolated to $X = 0$ is equal to k_1. In a similar manner, defining

$$J_2(X) = [J_1(X) - K_1] \left(\frac{1 - \bar{n}}{2 - \bar{n}}\right) \frac{1}{X}$$

it is seen that the value of $J_2(X)$ when extrapolated to $X = 0$ is equal to K_2, and so on for higher orders of $J(X)$.

Table VI lists the values of the $J(X)$ functions. When $J_3(X)$ was plotted *vs.* X, a very low value for K_3 was obtained which was felt to be in error. Only the values of $J_3(X)$ at low bromide concentrations were used in evaluating the intercept, at which concentrations very little $InBr_3$ exists, and they had twice been differentiated graphically. To obviate this problem, it was seen that all the values of $J_3(X)$ could be used if $J_3(X)$ were plotted *vs.* $[(4 - \bar{n})/(3 - \bar{n})](Br^-)$, and therefore the intercept would still equal K_3; but now K_4 could be evaluated, since it was equal to the slope of the resulting straight line. The fact that a relatively good straight line was obtained substantiates the fact that $InBr_4^-$ is the highest species existing in this system. The stepwise constants for the first four complexes were calculated to be 120, 19.0, 2.9 and 8.5, respectively.

The data obtained showing the fraction of indium complexed as $InBr_4^-$ can be used to evaluate the formation constants in yet a different manner. Rossotti and Rossotti[14] have derived the expression

$$H_0(X) = \frac{X^4}{f} = \frac{1}{K_4} + \frac{K_1}{K_4} X + \frac{K_2}{K_4} X^2 + \frac{K_3}{K_4} X^3 + X^4 \quad (11)$$

from which the parameters K_1, K_2, K_3 and K_4 may be evaluated by graphical differentiation with respect to X.

In Table VII experimentally determined f values are given, together with the calculated values of $H_J(X)$. The values obtained for the "stepwise" formation constants by this treatment of the data are ~110, ~18, 3.7, 7.4. The method turns out to be not very good for k_1 or k_2 since the intercepts of $H_0(X)$ and $H_1(X)$ are very small and not very accurately known.

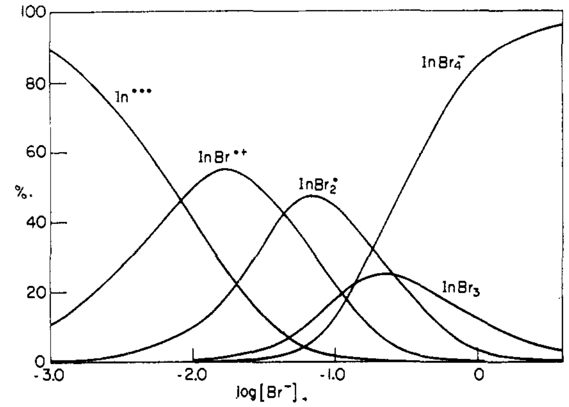

Fig. 7.—Percentage of indium in its various forms as a function of the free bromide concentration at $\mu = 4.00$.

TABLE VI

ANALYSIS OF SPECTROPHOTOMETRIC DATA USING $\bar{n}$ VALUES BY ROSSOTTI–ROSSOTTI $J(X)$ FUNCTIONS

Br^-	$\bar{n}$	$J_1(X)$	$J_2(X) \times 10^{-1}$	$J_3(X) \times 10^{-1}$	$\frac{4 - \bar{n}}{3 - \bar{n}}(Br^-)$
(0.00000)	(0.00)	(120)	(2.30)		
0.00424	0.38	+144	+2.21	(6.7)	
.00874	.63	+194	+2.31	0.6	+0.0124
.01337	.82	+340	+2.51	+ 8.5	+ .0195
.0181	.94	+869	+2.34	+ 1.1	+ .0269
.0229	1.05	−917	+2.38	+ 1.7	+ .0347
.0277	1.14	−293	+2.43	+ 1.7	+ .0426
.0496	1.50	− 60.4	+3.64	+ 9.0	+ .0827
.0995	2.12	− 19.0	−13.05	+21 0	+ 2127
.1494	2.58	− 10.9	−2.39	+43.3	+ .506
.200	2.76	− 7.8	−1.48	+59.7	+1.033
.300	3.20	− 4.8	−0.763	−61.2	−0.200
.400	3.41	− 3.5	− .528	−24.3	− .576
.500	3.56	− 2.8	− .403	−15.1	− .393
.600	3.68	− 2.3	− .325	−10.7	− .282
.700	3.74	− 1.9	− .274	− 8.6	− .246
1.000	3.82	− 1.4	− .188	− 5.5	− .220

TABLE VII

ANALYSIS OF SPECTROPHOTOMETRIC DATA OF FRACTION OF $InBr_4^-$ BY ROSSOTTI–ROSSOTTI $H(X)$ FUNCTIONS

Br^-	f	$H_0(X)$	$H_1(X)$	$H_2(X)$	$H_3(X)$	$H_4(X)$
0.0000		(0.000020)	(0.0022)	(0.037)	(0.0135)	1.00
.0496	0.025	.000242	.00448	.0460	.182	0.95
.0995	.115	.00852	.00837	.0620	.251	1.17
.1494	.230	.00216	.0143	.0810	.294	1.06
.200	.341	.00469	.0234	.106	.345	1.05
.300	.512	.01573	.0524	.167	.434	1.00
.400	.624	.0410	.1025	.251	.535	1.00
.500	.699	.0890	.178	.352	.630	0.99
.600	.749	.173	.288	.477	.733	1.00
.700	.789	.304	.434	.617	.829	0.99
1.000	.854	1.171	1.171	1.169	1.132	1.00

Table VIII lists the values of the stability constants obtained by the different treatments of the spectrophotometric data. The values chosen as the "best" values of the successive formation constants are 120, 19, 4 and 7 for the mono-, di-, tri- and tetrabromo complexes at an ionic strength of 4.00 *M*. Figure 7 shows the percentage of indium complexed in the various species as a function of the free bromide concentration using the above formation constants.

TABLE VIII

COMPARISON OF FORMATION CONSTANTS OBTAINED BY DIFFERENT SPECTROPHOTOMETRIC METHODS

Method	k_1	k_2	k_3	k_4
McConnell–Davidson	123	18.7	..	..
$\log A_i/(A_L - A_i)$	..	..	..	6.1
Difference	..	..	4.8	..
$J(X)$	120	19.2	2.9	8.5
$H(X)$	~110	~18	3.7	7.4
Best value	120	19	4	7

Discussion

From the spectrophotometric study, it is definite that four species, $InBr^{++}$, $InBr_2^+$, $InBr_3$ and $InBr_4^-$ are present in aqueous solutions under the conditions examined: *i.e.*, ionic strength of 4.00 *M*, 0.100 *M* perchloric acid, and 5×10^{-4} *M* sodium sulfite. The fact that the fourth complex is present in appreciable amounts is contrary to the findings of Irving and Rosotti[9] who were the only other workers to observe the existence of the fourth complex. In all previous studies, any small error in the determination of the equilibrium concentration of indium and/or a graphically determined quantity might be amplified on successive graphical treatment with the result that the information on the highest complexes would be least accurate. The spectrophotometric method, however, is unique in that a direct measure of the fourth complex in aqueous solution is possible. The formation constants for the first three complexes obtained in this investigation agree reasonably well with those of previous authors.

The evidence was so clear-cut for the four monomeric species that it was not necessary to consider the possibility of dimerization. The dimeric species observed by Irving and Rossotti were found only for "macro" amounts of indium in high hydrobromic acid concentrations, conditions not strictly comparable to ours.

The fact that Woodward and Bill,[16] from a study of the Raman spectra of indium salts in the presence of a large excess of bromide, concluded no tetrahedral $InBr_4^-$ ion to be present in aqueous solution, does not necessarily contradict the present findings. Indium frequently shows hexacoördination, and one would expect to find $[In(H_2O)_2Br_4]^-$ ions in solutions such as ours. The case of iron is a pertinent analogy. It is extracted from hydrochloric acid solutions by ether and other solvents in the form of $HFeCl_4$, which is described as tetracoördination,[17] although some water is also extracted. The stoichiometric solubility of KCl in anhydrous ethyl acetate solutions of $FeCl_3$ to form the compound $KFeCl_4$ appears to be a clean-cut example of tetracoördination of iron[18]; yet in aqueous media, the octahedral character of ferric complexes is beyond question.[19]

Acknowledgment.—This work was supported in part by the United States Atomic Energy Commission.

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Electrode Potential Studies of Liquid–Solid Equilibrium in Zn–Cd and Zn–In Alloys

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RECEIVED DECEMBER 14, 1956

Thermodynamic properties of liquid alloys were determined in binary Zn–Cd and Zn–In alloys by the measurement of electrode potentials of galvanic cells of the type: Zn(liq)/$ZnCl_2$(in KCl–LiCl liq)/Zn(in liq soln.). Measurements were carried out over a range of temperatures from 420 to 530°. Liquid–solid phase equilibrium was calculated by finding the temperature at which activities of zinc in the solid state and in liquid alloys were equal. The activity of zinc in the solid was calculated from heat of fusion and heat capacity data for pure zinc. The e.m.f. data were used in turn to calculate the heat of fusion of pure zinc, based on published values of liquidus point. Values thus determined showed much less scatter than published values based on calorimetric techniques. The properties of the liquid alloys were examined with regard to solution theory, and Zn–Cd alloys were shown to closely approach regular behavior, while Zn–In alloys showed some deviation from this behavior. Both systems showed positive deviations from Raoult's Law, and positive heats of solution over the entire composition range.

Introduction

Electrode potential studies have long been used to evaluate thermodynamic properties of solutions, but this technique has seldom been applied to the study of phase equilibrium in metal systems. Early applications of electrode potential studies to metal systems by Lindeck[2] and Richards[3] were limited to the study of thermodynamic properties of amalgams. Later, Taylor[4] and Hildebrand[5] used the principles of e.m.f. measurements in studying the thermodynamics of liquid metal solutions. Seltz and his co-workers[6] were among the first to apply the technique to the problem of phase equilibrium in binary metal systems. An excellent review of recent experimental results, techniques, and methods of calculation in this field is given by Dunkerley and Mills.[7]

In this investigation, accurate and precise e.m.f. measurements were made on galvanic cells of liquid alloys of the binary systems Zn–Cd and Zn–In, and the data used to calculate the thermodynamic properties of the liquid alloys and determine the liquid–solid equilibrium. The cells were of the type

$$\text{Zn(liq)}/\text{Zn}^{++}/\text{Zn(in liq soln.)} \qquad (1)$$

If the cell reaction, Zn(liq) → Zn(in liq soln.), is reversible and unique, and only Zn^{++} ions carry the current, the following relation applies to the reaction

$$\Delta \bar{F}_{Zn} = -2E\mathfrak{F} \qquad (2)$$

where $\mathfrak{F}$ is the Faraday constant and E is the e.m.f. in volts. If pure liquid zinc is taken as the standard state, the activity of Zn, the more electropositive component of the cell, can be calculated

(1) Abstracted from a thesis submitted to the Graduate College of the University of Illinois, June, 1956, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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