TABLE IV

APPROXIMATE FRACTION OF MOLECULES HAVING VARIOUS INTERNAL CONFIGURATIONS AT 300°K.

Fraction at an angle ϕ (including those at $-\phi$)

ϕ	0°	30°	60°	90°	120°	150°	180°
Ethylene chloride	0.0	0.001	0.044	0.093	0.101	0.282	0.478
Ethylene chlorobromide	.0	.0	.018	.059	.099	.289	.535
Ethylene bromide	.0	.0	.015	.047	.105	.277	.556

tial function for ethylene chloride is shown in reference 2, Fig. 4, curve B. For the chlorobromide and the bromide these potential functions appear in Fig. 4, curve D, and Fig. 5, curve D, respectively. They follow the 5 kcal./mole curves quite closely and the electron scattering functions obtained from them are identical with those calculated assuming a potential barrier of 5 kcal./mole. We have therefore obtained potential functions that are compatible with the electron diffraction photographs of these substances.

In Fig. 1 both curves show a small maximum at positions corresponding to halogen–halogen separations due to a value of ϕ of about 80°. The shortcomings of the radial distribution method as applied at present prohibit the placing of any definite significance to these small peaks. In both radial distribution curves the distance between the large peaks is so great that it is not surprising that the curve is not flat throughout the whole region between them.

Ethylene chlorobromide has not been investigated previously by electron diffraction. Wierl,[11] from electron diffraction photographs showing only four maxima, concluded that ethylene bromide was a *trans* molecule rather than a *cis* or a

(11) Wierl, *Ann. Physik*, **13**, 453 (1932).

freely rotating molecule. He reported a bromine–bromine distance of 4.75 $\pm$ 0.15 Å.

From the final potential curves for the three molecules we have calculated the fractions of the molecules that possess any given configuration. These fractions are given in Table IV.

Summary

The electron diffraction investigation of the molecular structures of ethylene chlorobromide and ethylene bromide leads to the following results. For both molecules, if $V(\phi) = V_0/2$ (cos ϕ + 1), then 5 kcal./mole $\leqslant V_0 \leqslant \infty$. In ethylene bromide the carbon–bromine distance is 1.91 $\pm$ 0.02 Å. In ethylene chlorobromide the carbon–chlorine distance is 1.75 $\pm$ 0.02 Å. and the carbon–bromine distance is 1.90 $\pm$ 0.02 Å. The carbon–carbon distance was assumed to be 1.54 Å. and the carbon–hydrogen distance was assumed to be 1.09 Å. in both cases.

The observed potential barriers can be calculated by taking into account the electrostatic interactions and the exchange repulsions of the two ends of the molecules. The exchange repulsions, however, must be calculated by the method required for ethylene chloride in reference 2.

PRINCETON, N. J.   RECEIVED NOVEMBER 10, 1938

[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

The Thermodynamics of Bi-univalent Electrolytes. IV. Cadmium Bromide in Aqueous Solution

BY ROGER G. BATES[1]

Cadmium bromide, in common with the other cadmium halides, has been shown to display extreme deviations from normal behavior in aqueous solution as indicated by its low activity coefficient[2] and the formation of rather stable ion aggregates with alkali bromides.[3]

This investigation was undertaken with the two-fold purpose of obtaining accurate measurements of the thermodynamic behavior of this abnormal salt in solution over a wide range of concentration and of ascertaining, from studies of very dilute solutions, the extent to which the Debye–Hückel theory is applicable to an intermediate electrolyte of this type.

(1) Sterling Fellow.

(2) (a) Getman, *J. Phys. Chem.*, **32**, 91 (1928); (b) Lucasse, THIS JOURNAL, **51**, 2597 (1929).

(3) The stability of cadmium bromide complex ions has been determined by (a) cryoscopy, Cornec and Urbain, *Bull. soc. chim.*, **25**, 215, 218 (1919); (b) ebullioscopy, Rouyer, *Ann. chim.*, [10] **13**, 423 (1930), and Hun, *Compt. rend.*, **192** 355 (1931); (c) ultraviolet

absorption spectra, Job, *Ann. chim.*, **9**, 113 (1928); and (d) potentiometric studies of mixtures of cadmium salt and alkali bromide, Knobloch, *Lotos*, **78**, 110 (1930), and Riley and Gallafent, *J. Chem. Soc.*, 514 (1932).

Electromotive force measurements of the cell

$$Cd-Hg\ (2\text{-phase})/CdBr_2(m)/AgBr-Ag \qquad (1)$$

were made at 5° intervals from 5 to 40° and at molalities of cadmium bromide ranging from 0.0004 to 1.8. From these results the standard potentials of cell (1) and of the cadmium amalgam electrode have been evaluated, and calculations of the activity coefficients, relative partial molal heat content and relative partial molal specific heat of cadmium bromide have been made. The change of activity coefficient with concentration has been shown to approach the limiting slope of the Debye–Hückel theory above 0.001 m only when a correction for incomplete dissociation of the intermediate cation (or ion pair) is made.

Materials and Methods

Cadmium Bromide.—"Analytical reagent" cadmium bromide was purified by recrystallization from conductivity water and was dried rapidly *in vacuo*. Stock solutions were prepared from the pure salt and conductivity water which had been freed of dissolved gases. They were stored in Pyrex vessels under an atmosphere of hydrogen which had been purified by contact with hot copper and were expelled, as needed, by hydrogen pressure. The presence of a slight precipitate of hydrolytic product made filtration necessary.

The bromide content of the stock solutions was established by the Volhard method, using a gravimetrically standardized silver nitrate solution. Cadmium determinations were carried out electrolytically after the method of Beilstein and Jawein.[4] Weight burets were used for the titrations, and vacuum corrections were made on all weighings.

Cadmium Amalgam Electrodes.—A 10% amalgam was prepared from the best grade of Kahlbaum stick cadmium and thrice-distilled mercury. This product was kept under hydrogen in an amalgam pipet similar to the one described in an earlier communication.[5] As needed, it was melted and drawn into the evacuated cell vessel.

Amalgam electrodes were apparently quite reproducible over the entire concentration range. It was shown that the formation of a white deposit on the amalgam, as observed by Harned and Fitzgerald[6] with cadmium chloride solutions more concentrated than 0.1 M, could be obviated by the careful exclusion of air. According to Bijl,[7] an amalgam containing 10% by weight of cadmium is heterogeneous over the range of temperature studied.

Silver–Silver Bromide Electrodes.—The silver bromide electrodes were formed by heating a paste of 10% silver bromate and 90% silver oxide on small platinum spirals at 575° for ten minutes. Two samples of crystalline silver bromate were used. The first was prepared metathetically by the author and recrystallized once from hot conductivity water. The second was similarly prepared

by Dr. Foering in this Laboratory and was part of the same preparation used for the determination of the standard potentials of the thermal type of silver bromide electrode.[8] The two samples formed identical electrodes.

Preparation of the Cells.—The cell vessels have been described elsewhere.[9] In the preparation of the cells a vacuum-hydrogen technique was employed throughout. With the silver–silver bromide electrode in place, the vessel was evacuated and the amalgam drawn in. When the amalgam had cooled, the vacuum was broken with dry hydrogen. Both electrodes and the interior of the vessel were washed with two portions of cell solution from the saturator flask before the final electrolyte was admitted. The evacuation of the silver–silver bromide electrodes is thought to be of value in effecting rapid attainment of equilibrium, especially in dilute solutions.

Measurements.—The cadmium amalgam–silver bromide cell was found to be quite satisfactory for the study of both dilute and concentrated cadmium bromide solutions.

Cells were made in triplicate and were allowed to remain overnight at 25° to attain initial equilibrium, although experience showed that considerably less time than this was necessary for satisfactory constancy. Agreement of triplicate cells was of the order of 0.05 to 0.08 mv., although occasionally one cell was rejected as being unreliable on the basis of drifting electromotive force or abnormal temperature coefficient. Such a cell would, likewise, not resume its initial value at the end of the temperature run. Each group of three cells was measured at the eight temperatures over a period of about eight hours, the measurements being made in the order, 25, 30, 35, 40, 5, 10, 15, 20 and 25°. Temperatures were maintained within ±0.03°. The cells usually attained equilibrium upon temperature change within about thirty minutes, although longer periods of time were not infrequently required at 5 and 10°.

The absolute reproducibility of the experimental electromotive forces is probably of the order of 0.1 to 0.2 mv. above 0.002 M and 0.2 to 0.4 mv. below that concentration.

Results

The electromotive force data for cell (1) observed in the most satisfactory runs are recorded in Table I. A small correction has been made to all of the values to relate them to solutions containing equivalent molalities of cadmium and bromide ions. This correction was made necessary by the removal of precipitated basic salt in the preparation of the stock solutions and in no case amounted to more than 0.09 mv. A large scale plot of E_{25} against the logarithm of the molality was made and smoothed values of E_{25} at round molalities were obtained by interpolation.

The constants of the quadratic equation

$$E_t = E_{25} + a(t - 25) + b(t - 25)^2 \qquad (2)$$

were obtained from the straight first order differ-

(4) Beilstein and Jawein, *Ber.*, **12**, 446 (1879).
(5) Bates, THIS JOURNAL, **60**, 2983 (1938).
(6) Harned and Fitzgerald, *ibid.*, **58**, 2624 (1936).
(7) Bijl, *Z. physik. Chem.*, **41**, 641 (1902).
(8) Owen and Foering, THIS JOURNAL, **58**, 1575 (1936).
(9) Bates and Vosburgh, *ibid.*, **59**, 1583 (1937).

TABLE I

OBSERVED ELECTROMOTIVE FORCES OF THE CELL

Cd-Hg(2-phase)/CdBr$_2$(m)/AgBr-Ag

m	E_5	E_{10}	E_{15}	E_{20}	E_{25}	E_{30}	E_{35}	E_{40}
0.0003240	0.7021	0.7069	0.7110	0.7150	0.7190	0.7235	0.7276	0.7310
.0006795	.67872	.68238	.68582	.68925	.69302	.69635	.69990	.70306
.001539	.65927	.65662	.66012	.66337	.66653	.66963	.67240	.67500
.002841	.63558	.63825	.64118	.64406	.64680	.64923	.65177	.65419
.005505	.61678	.61952	.62210	.62456	.62686	.62905	.63131	.63322
.007702	.60892	.61146	.61390	.61628	.61849	.62054	.62252	.62444
.008559	.60617	.60870	.61108	.61335	.61564	.61771	.61965	.62144
.01577	.59154	.59382	.59597	.59797	.59999	.60180	.60357	.60515
.03720	.57201	.57386	.57559	.57716	.57876	.58019	.58160	.58288
.05820	.56282	.56452	.56614	.56758	.57892	.57033	.57158	.57275
.1029	.55191	.55334	.55471	.55600	.55723	.55832	.55942	.56045
.1555	.54469	.54600	.54719	.54832	.54941	.55046	.55146	.55237
.3344	.53259	.53360	.53455	.53543	.53625	.53711	.53791	.53866
.7046	.52201	.52271	.52336	.52398	.52459	.52519	.52580	.52639
1.897	.50605	.50632	.50654	.50678	.50700	.50727	.50753	.50778

ence plots by the method suggested by Harned and Nims.[10] These a and b values were smoothed by plotting them against log m and are listed in Table II with E_{25}. Average deviations of the experimental results from the quadratic equation were of the order of a few hundredths of a millivolt. Below 0.001 m, however, the mean deviation was larger than 0.1 mv.

TABLE II

CONSTANTS OF EQUATIONS (2) AND (9)

m	E_{25}	$a \times 10^5$	$b \times 10^6$
0.0005	0.70377	73.3	−4.08
.001	.68029	65.2	−3.70
.002	.65815	57.6	−3.36
.005	.63070	46.8	−2.99
.007	.62128	43.8	−2.71
.01	.61160	40.9	−2.53
.02	.59395	35.4	−2.18
.03	.58392	32.1	−1.97
.05	.57230	28.4	−1.72
.07	.56508	25.9	−1.54
.1	.55773	23.9	−1.36
.2	.54496	19.9	−1.00
.5	.52944	14.6	−0.55
.7	.52386	12.5	− .37
1.0	.51783	10.2	− .19
1.2	.51440	8.7	− .09
1.5	.51097	7.1	.02
1.8	.50793	5.5	.09

	E_{25}^0	$a_0 \times 10^5$	$b_0 \times 10^6$
E^0:	0.42267	−20.9	−4.57

Extrapolations. Standard Potentials

The electromotive force of cell (1) is related to the standard potential, E^0, by the equation

$$E - E^0 = -k \log 4m^3 - 3k \log \gamma_{\pm} \quad (3)$$

where $k = 2.3026\ RT/2F$, m is the molality and

(10) Harned and Nims, THIS JOURNAL, **54**, 423 (1932).

$\gamma_{\pm}$ is the stoichiometrical activity coefficient of cadmium bromide. To evaluate E^0, recourse must be had to extrapolation to the experimentally inaccessible limit of infinite dilution where the Debye–Hückel limiting law (with added linear term)

$$-\log \gamma_{\pm} = u'\sqrt{m} + Bm \quad (4)$$

or one of its modifications, may be expected to hold. The constant u' in equation (4) is the limiting slope of the Debye–Hückel theory, and B is an empirical constant.

When the data for cell (1) at 25° were used to calculate the apparent standard potential, $E^{0\prime}$ ($E^{0\prime} = E^0 + 3kBm$), by equations (3) and (4), the broken curve of Fig. 2 was obtained. The hump is characteristic of incomplete dissociation, and its height (17 mv. as compared with 11 mv. for cadmium chloride[6]) indicated somewhat less ionization than cadmium chloride at corresponding concentrations. This is in entire accord with expectation and with the experience of Getman.[2a] The almost asymptotic approach of the broken curve of Fig. 2 to the $E^{0\prime}$ axis emphasizes the futility of attempting to obtain E^0 accurately without (a), the use of an expression for log $\gamma_{\pm}$ that is more valid than equation (4), or (b), correcting for the presence of ion aggregates.

Application of the Extended Terms Equation of La Mer, Gronwall and Greiff.—Log $\gamma_{\pm}$ at 25° was computed by the La Mer, Gronwall and Greiff equation[11,12] for a number of values of

(11) La Mer, Gronwall and Greiff, J. Phys. Chem., **35**, 2245 (1931).

(12) The constants of equation (3) of La Mer, Gronwall and Greiff were recalculated using 78.54 for the dielectric constant of water at 25°, the value given by Wyman, Phys. Rev., **35**, 623 (1930).

a, the mean distance of approach of the ions. By substitution in equation (3), apparent standard potentials were obtained for each value of a at 0.0005, 0.001, 0.002, 0.005 and 0.01 molal. Plots of these extrapolation functions are shown in Fig. 1 for six values of the mean distance of approach.
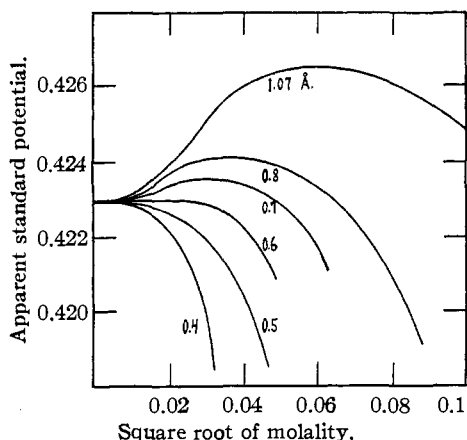

Fig. 1.—Extrapolation curves for cell (1) at 25°, calculated with the use of the extended equation of La Mer, Gronwall and Greiff.[11]

The a value of 0.6 Å. which best fits the data at low concentrations is physically improbable and yields constant E^0 values only below 0.001 m. The failure of the extended equation to describe the behavior of this electrolyte above 0.001 m suggests that in cadmium bromide solutions we have to deal with a situation not amenable to treatment on the basis of coulombic interactions alone.

Incomplete Dissociation.—By analogy with cadmium iodide,[13] it seems likely that, in dilute cadmium bromide solutions, the most significant ionic equilibrium is the reaction

$$CdBr^+ + Br^- \rightleftarrows Cd^{++} + 2Br^- \qquad (5)$$
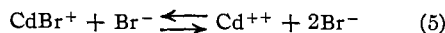
and that, as a first approximation, the quantities of other ion aggregates in these solutions safely may be neglected. The equilibrium constant, K, of reaction (5) is given by the equation

$$K = \frac{m'(m + m')}{m - m'} \frac{\gamma'_{Cd^{++}} \gamma'^2_{Br^-}}{\gamma'_{CdBr^+} \gamma'_{Br^-}} = \frac{m'(m + m')}{m - m'} \gamma'^2_{2-1} \qquad (6)$$

where m' and $(m + m')$ are the actual molalities of Cd^{++} and Br^-, respectively, γ'_i represents a real activity coefficient and γ'_{2-1} is the mean activity coefficient[14] of the ions of a normal (com-

(13) Bates and Vosburgh, THIS JOURNAL, **60**, 137 (1938).

(14) In dilute solutions, $\gamma'^2_{1-1} = \gamma'_{2-1}$. In equation (6), therefore, $\gamma'^2_{2-1}/\gamma'^2_{1-1} = \gamma'^2_{2-1}$.

pletely dissociated) bi-univalent electrolyte. In equation (6), ion interactions of the second and higher orders have been assumed to be negligible.

Equation (3) may be written, likewise, in terms of actual cadmium and bromide ion molalities and real activity coefficients as follows

$$E^0 = E + k \log m' + 2k \log (m + m') + 3k \log \gamma'_{-1} \qquad (7)$$

from which

$$E^0 + B'\mu = E^{0'} = E + k \log m' + 2k \log (m + m') - 3ku\sqrt{\mu} \qquad (7a)$$

In equation (7a), $B' = 3kB$, $u = u'/\sqrt{3}$ and μ, the ionic strength, equals $(5m' + m)/2$.

The evaluation of the standard potentials of cell (1) was made by plotting the right-hand side of equation (7a) against μ and extrapolating this function to $\mu = 0$, in which limit $E^{0'} = E^0$. The extrapolation curves are shown in Fig. 2.
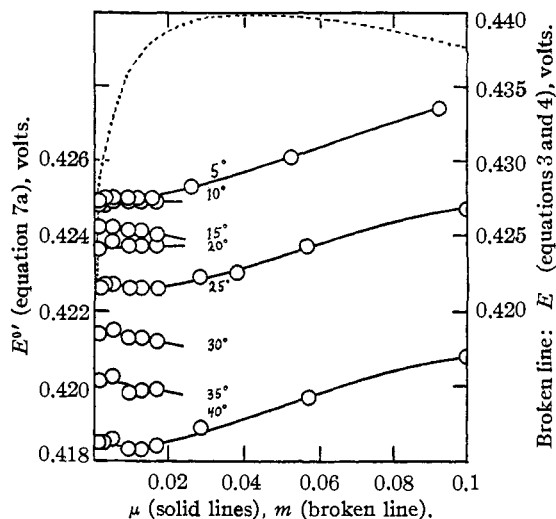

Fig. 2.—Extrapolation curves for cell (1). Circles represent $E^{0'}$ according to equation (7a). Broken line represents $E^{0'}$ from equations (3) and (4). Diameter of circles, 0.4 mv.

The cadmium ion molality, m', in each cadmium bromide solution was computed from equation (6) by the method of successive approximations, using the Debye–Hückel limiting law expression for the calculation of γ'_{2-1}. A comparison of the constants for the dissociation of the intermediate ions of cadmium iodide[3d,13] and cadmium chloride,[6,15] as well as the previous work on cadmium bromide equilibria,[3d] made it seem probable that K at 25° had a value lying between 0.006 and 0.008. Consequently, m' was evaluated and the extrapolation curves constructed for K values of 0.006, 0.0065, 0.007, 0.0075 and 0.008.

(15) Righellato and Davies, Trans. Faraday Soc., **26**, 592 (1930).

At 5°, a straight line of zero slope could be drawn through the $E^{0\prime}$ points below 0.01 m when $K = 0.006$. For 10, 15 and 20°, K is 0.0065, and at 25, 30, 35 and 40° it has a value of 0.007. It should be noted that K for cadmium bromide increases with temperature, whereas for cadmium chloride it has been found[6] to show an inverse variation. Riley and Gallafent found $K = 0.0068$ at 25°, a result which is in excellent accord with that found in this investigation. The agreement, however, is somewhat fortuitous, in view of the fact that Riley and Gallafent assumed the presence, simultaneously, of cadmium bromide ion aggregates of the type, $CdBr_n$, where n had all integral values from 1 to 4. On the other hand, the K of this calculation is a parameter accounting, as a first approximation, for all incomplete dissociation effects displayed by the solutions more dilute than 0.01 molal. The agreement, nevertheless, probably indicates that $CdBr^+$ is the only incompletely dissociated species present in appreciable quantity in these dilute solutions.

Several calculations of $E^{0\prime}$ at 25° were made with the use of the Debye–Hückel "first approximation" equation

$$-\log \gamma'_{\pm-1} = \frac{u\sqrt{\mu}}{1 + Xa\sqrt{\mu}} \qquad (8)$$

in which X is a quantity varying as $(DT)^{-1/2}$. Since K and a are parameters capable of independent variation, however, the limiting law ($a = 0$) was found to suffice. The cause of the curvature of the extrapolation plots above 0.01 m is possibly the rapid increase in the concentrations of $CdBr_2$ and of complex anions. Whereas the amount of $CdBr^+$ increases linearly with the bromide ion concentration, $CdBr_2$ and higher aggregates show a second and third power (or even higher) rate of increase.

In view of the very complex nature of the equilibria involved in the dissociation of a salt of the cadmium halide type, it is essential for an accurate determination of E^0 that measurements be extended to very dilute solutions. From a consideration of the broken line of Fig. 2 it is apparent that the assumption of complete ionization gives an $E^{0\prime}$ value over 3 mv. too high for a solution as dilute as 0.0005 m. The La Mer, Gronwall and Greiff equation (Fig. 1) gives a straight-line extrapolation only below 0.001 m. On the other hand, a correction for ion association of the first order yields substantially constant $E^{0\prime}$ values up to 0.01 m.

The standard potentials, E^0, of cell (1) are listed in Table III. They were found to fit the equation

$$E^0_t = E^0_{25} + a_0(t - 25) + b_0(t - 25)^2 \qquad (9)$$

with an average deviation at the eight temperatures of 0.02 mv. The constants of equation (9) are given at the bottom of Table II. The 25° value (0.4227 v.) is in agreement with the less certain value of 0.4229 v. resulting from the extrapolation with the use of the extended terms equation.

In the fourth and fifth columns of Table III are listed the standard potentials, $E^{0\prime\prime}$, of the saturated cadmium amalgam electrode from 5 to 40°. These values were obtained by subtracting the standard potentials of the hydrogen–silver bromide cell[8] from E^0 for cell (1) at corresponding temperatures. The accuracy of the silver–silver bromide electrode potentials is attested by the close agreement between the results given by Owen and Foering and those of Harned and Donelson.[16] Subtraction of the

TABLE III

STANDARD POTENTIALS

Cd-Hg/CdBr_2 (a = 1)/AgBr-Ag, E^0
Cd-Hg/Cd^{++} (a = 1), H$^+$ (a = 1)/H_2, $E^{0\prime\prime}$

t	E^0, obsd.	E^0 (Eq. 9)	$E^{0\prime\prime}$	$E^{0\prime\prime}$ (Eq. 11)	$E^{0\prime\prime}$ (H. and F.)
5	0.4250	0.42501	0.3451	0.34516	0.3465
10	.4248	.42477	.3468	.34678	.3477
15	.4243	.42430	.3483	.34834	.3491
20	.4236	.42360	.3499	.34987	.3503
25	.4227	.42267	.3514	.35133	.3515
30	.4215	.42152	.3528	.35275	.3526
35	.4201	.42012	.3541	.35412	.3539
40	.4185	.41851	.3554	.35544	.3553

equation of Owen and Foering

$$E^0_{HBr} = 0.07134 - 0.000498(t - 25) -$$
$$0.0000036(t - 25)^2 \qquad (10)$$

from equation (9) gives

$$E^{0\prime\prime} = 0.35133 + 0.000289(t - 25) - 0.00000097(t - 25)^2 \qquad (11)$$

Addition of the equation of Parks and La Mer[17] for the electromotive forces of the cell: Cd (metal)/ Cd^{++}/Cd-Hg(2-phase) to equation (11) gives for the cadmium metal electrode from 5 to 30°

$$E^0_{Cd} = 0.40178 + 8.9 \times 10^{-5}(t - 25) +$$
$$8.1 \times 10^{-7} (t - 25)^2 + 7.5 \times 10^{-8}(t - 25)^3 \qquad (12)$$

(16) Harned and Donelson, THIS JOURNAL, 59, 1280 (1937).

(17) Parks and La Mer, ibid., 56, 90 (1934). The value at 25° (0.05045 v.) is in excellent agreement with the earlier work of Hulett, Trans. Am. Electrochem. Soc., 7, 333 (1905), who found 0.0505 v., and of Getman, THIS JOURNAL, 39, 1806 (1917), who found 0.05047 v.

It is probable that this equation expresses the standard potential of that modification designated by Cohen[18] as γ-cadmium.

The standard potentials found by Harned and Fitzgerald for the electrode Cd–Hg(2-phase)/Cd^{++} are given in the last column of Table III. The agreement with the results of this investigation is quite satisfactory at 25, 30, 35 and 40°. Between 25 and 5°, however, the deviations become increasingly larger. A recalculation of the standard potential of the cadmium amalgam–silver chloride cell by equations (6) and (7a) from the electromotive forces of Harned and Fitzgerald at 0° (on which their E^0 values at 5, 10, 15 and 20° were partially dependent) failed to indicate the cause of the lack of agreement.

The disagreement among recorded estimates of the standard potential of the cadmium amalgam electrode (and, hence, that of the cadmium metal electrode) seems to be uniformly larger than can be attributed to arbitrary differences in method of extrapolation. Quintin[19] computed the standard potential of the cadmium amalgam–silver chloride cell by the use of equation (3), log $\gamma_\pm$ for cadmium chloride being evaluated with the use of the extended equation of La Mer, Gronwall and Greiff.[11] Subtraction of the normal potential of the silver–silver chloride electrode[20] from E^0 gives 0.3521 v. for the standard potential of the cadmium amalgam electrode at 25°, a value in fair accord with 0.3515 v. found by Harned and Fitzgerald and with 0.3514 v. obtained in this investigation.

Likewise, Shrawder, Cowperthwaite and La Mer[21] calculated 0.3519 v. from the standard potentials of the cadmium amalgam–lead sulfate cell[22] and of the lead amalgam–lead sulfate electrode. A further study[23] of the same cell at several temperatures, however, led to a high value of 0.3542 v. at 25°. The extrapolations of Parks and La Mer were carried out with the use of the Gronwall, La Mer and Sandved[24] equation for log γ_{CdSO_4}. Harned and Fitzgerald corrected for incomplete secondary dissociation of cadmium

chloride[25] and extrapolated with the use of the limiting law.

Quintin recently has reported[26] electromotive force measurements of liquid-junction cells containing cadmium benzenesulfonate solutions. Extensive hydrolysis was assumed to take place in the dilute solutions, and the molalities were corrected accordingly. It seems likely that the value of 0.3436 v. is considerably too low.

In Fig. 3 are plotted the electromotive forces of the hypothetical cell: Cd–Hg/Cd^{++} ($a = 1$), H$^+$ ($a = 1$)/H$_2$ as a function of temperature.
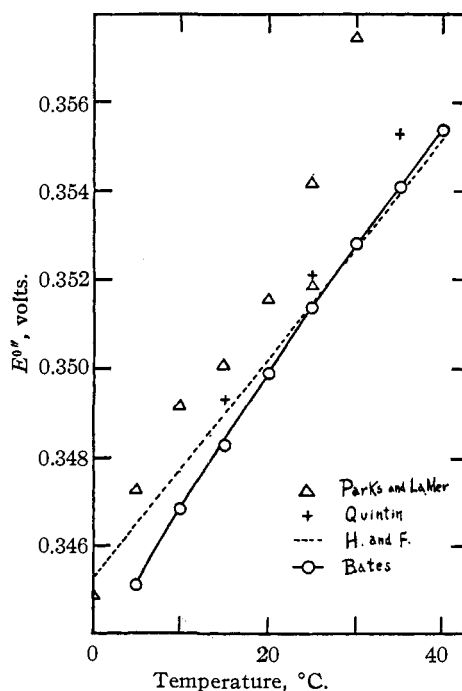

Fig. 3.—The standard potential, $E^{0''}$, of the saturated cadmium amalgam electrode as a function of temperature.

Activity Coefficients

The stoichiometrical activity coefficients have been calculated by equation (3) and are listed in Table IV. Table V gives a comparison of the activity coefficient from this investigation with the values of Getman[2a] and of Lucasse.[2b] The fifth column lists γ as calculated from freezing point measurements.[27]

(18) Cohen, "Physico-chemical Metamorphosis," McGraw-Hill Book Co., Inc., New York, N. Y., 1926.

(19) Quintin, Compt. rend., 200, 1754 (1935); J. chim. phys., 33, 111 (1936).

(20) Harned and Ehlers, THIS JOURNAL, 55, 2179 (1933).

(21) Shrawder, Cowperthwaite and La Mer, ibid., 56, 2348 (1934).

(22) Parks and La Mer, ibid., 53, 2040 (1931).

(23) Parks and La Mer, ibid., 55, 4343 (1933).

(24) Gronwall, La Mer and Sandved, Physik. Z., 29, 358 (1928).

(25) In Table II of Harned and Fitzgerald, E^0 at 25° should read "0.57390." $E^{0'}$ should read "0.3503" at 20° and "0.3526" at 30°. On page 2625, the second and third lines preceding equation (4) should read "replacing log $\gamma_\pm$ by $(-u\sqrt{\mu} + B'm)$ where u is, etc." On page 2626, column 1, fifth line, the term "$-3ku\sqrt{m}$" should be "$-3ku\sqrt{\mu}$"; k has been omitted from the second term on the right of equation (11).

(26) Quintin, Compt. rend., 206, 1564 (1938).

(27) Getman, J. Phys. Chem., 33, 1781 (1929).

TABLE IV
STOICHIOMETRICAL ACTIVITY COEFFICIENTS OF CADMIUM BROMIDE

m	γ_5	γ_{10}	γ_{15}	γ_{20}	γ_{25}	γ_{30}	γ_{35}	γ_{40}
0.0005	0.850	0.852	0.854	0.855	0.855	0.855	0.855	0.853
.001	.777	.781	.784	.786	.787	.787	.786	.784
.002	.688	.692	.696	.698	.699	.699	.698	.696
.005	.553	.559	.564	.568	.570	.571	.571	.569
.007	.504	.510	.514	.518	.520	.521	.520	.518
.01	.453	.459	.463	.466	.468	.468	.467	.465
.02	.358	.363	.366	.369	.370	.370	.369	.367
.03	.309	.313	.317	.319	.320	.320	.319	.317
.05	.250	.254	.257	.259	.259	.259	.258	.256
.07	.215	.218	.221	.223	.223	.223	.222	.221
.1	.182	.185	.187	.189	.189	.189	.188	.186
.2	.127	.129	.130	.131	.132	.132	.131	.129
.5	.0753	.0768	.0779	.0786	.0789	.0787	.0781	.0772
.7	.0619	.0633	.0643	.0649	.0651	.0650	.0645	.0638
1	.0505	.0517	.0526	.0531	.0533	.0532	.0528	.0522
1.2	.0449	.0459	.0467	.0471	.0475	.0473	.0471	.0465
1.5	.0400	.0410	.0418	.0422	.0425	.0424	.0422	.0417
1.8	.0359	.0369	.0376	.0381	.0383	.0383	.0381	.0376

TABLE V
COMPARISON OF ACTIVITY COEFFICIENTS

m	γ_{25} (Getman)	γ_{25} (Lucasse)	γ_{25} (Bates)	γ (f. p.)
0.005	0.65		0.570	0.527
.01	.50	0.476	.468	.432
.02	.36	.375	.370	.354
.05	.23	.264	.259	.249
.1	.17	.191	.189	.179
.2	.12	.134	.132	.127
1.0	.06	.053		.0533

Agreement with the results of Lucasse is good. When the activity coefficient is recalculated from
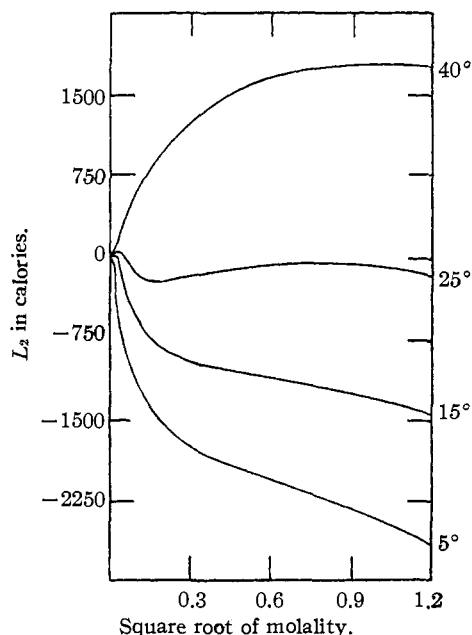

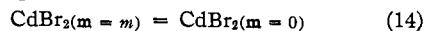Fig. 4.—The relative partial molal heat content, $\bar{L}_2$, as a function of the square root of the molality.

the electromotive forces of Lucasse and a recent value[8] for the standard potential of the silver–silver bromide electrode, however, the results show a larger deviation than do those in Table V. Since the newer E^0 values relate to the thermal type of electrode, rather than the electrolytic type used by Lucasse, such a recalculation is perhaps unjustified.

Relative Partial Molal Heat Content and Relative Partial Molal Specific Heat

The relative partial molal heat content, $\bar{L}_2$, is given by the equation[5,28]

$$\bar{L}_2 = \alpha + \beta T^2 \qquad (13)$$

where α is $-46148(A - A_0)$, β is $46148(C - C_0)$ and $\bar{L}_2$ represents the heat content change in the transfer process

$$CdBr_2(m = m) = CdBr_2(m = 0) \qquad (14)$$

in calories per mole of cadmium bromide.

The α- and β-constants were smoothed by plotting them against log m and are tabulated, with values of $\bar{L}_2$ calculated from equation (13), in Table VI. The relative partial molal heat content of cadmium bromide at 5, 15, 25 and 40° from 0 to 1.5 molal is plotted as a function of $m^{1/2}$ in Fig. 4.

The partial molal specific heat, $\bar{C}_p - \bar{C}_p^0$, relative to the infinitely dilute solution of the salt was computed from β by the equation

$$\bar{C}_p - \bar{C}_p^0 = 2\beta T \qquad (15)$$

The last column of Table VI gives values of the relative partial molal specific heat at 25° in calories.

(28) Harned and Thomas, THIS JOURNAL, 58, 761 (1936).

TABLE VI

RELATIVE PARTIAL MOLAL HEAT CONTENT AND RELATIVE PARTIAL MOLAL SPECIFIC HEAT OF CADMIUM BROMIDE

m	$-\alpha$	β	$(\bar{L}_2)_{298.1}$	$(\bar{C}_p - \bar{C}_p^0)_{298.1}$
0.0005	1840	0.0226	169	13
.001	3612	.0402	− 44	24
.002	5060	.0558	− 98	33
.005	7020	.0775	−133	46
.007	7775	.0858	−147	51
.01	8583	.0941	−217	56
.02	9961	.1103	−160	66
.03	10813	.1200	−151	72
.05	11811	.1315	−124	78
.07	12560	.1398	−134	83
.1	13233	.1481	− 69	88
.2	14671	.1648	− 31	98
.5	16529	.1855	− 44	111
.7	17299	.1938	− 75	116
1.0	18075	.2021	−113	121
1.2	18533	.2067	−161	123
1.5	19046	.2118	−223	126
1.8	19413	.2151	−303	128

The author is pleased to acknowledge the kind assistance of Professor Herbert S. Harned.

Summary

1. Electromotive force measurements of the cell

Cd–Hg(2-phase)/CdBr₂(m)/AgBr–Ag
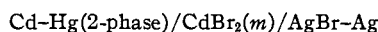
have been made at eight temperatures ranging from 5 to 40°. The molality of cadmium bromide was varied from 0.0004 to 1.8.

2. The standard potential of the cell has been evaluated on the assumption that $CdBr^+$ is the only ion aggregate present in appreciable quantities below 0.01 m. The constant for the dissociation of this intermediate ion appeared to have the following values: 0.006 ± 0.0003 at 5°, 0.0065 ± 0.0003 at 10, 15 and 20° and 0.007 ± 0.0003 at 25, 30, 35 and 40°.

3. The standard potential of the cadmium amalgam electrode from 5 to 40° has been determined, and a critical comparison with previous results has been made.

4. The stoichiometrical activity coefficients, relative partial molal heat content and relative partial molal specific heat of cadmium bromide in aqueous solution have been computed.

5. When incomplete dissociation effects are not taken into consideration, the La Mer, Gronwall and Greiff extension of the Debye–Hückel equation is inapplicable to cadmium bromide solutions more concentrated than 0.001 M.

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[CONTRIBUTION FROM THE BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

The Solubility in Water of Carbon Dioxide at 50, 75 and 100°, at Pressures to 700 Atmospheres

BY R. WIEBE AND V. L. GADDY

The work presented here is a continuation of high pressure investigations of the properties of gases that are of importance to the fertilizer industry.[1] Sander[2] was the first to make an extended determination of the solubility of carbon dioxide in water under pressure. His results are valuable only in a qualitative sense, since his two sets differ from each other in many cases by more than 10%. Recently Zelvinskii[3] measured the solubility at several temperatures and in some cases to about 90 atm. We will discuss his work later in relation to our own.

Apparatus and Procedure.—The apparatus is shown in Fig. 1. Carbon dioxide from a tank was introduced into cylinder B through valve a.

This valve was then closed and the carbon dioxide compressed into C, D and E through valve b by means of hydraulic pressure on the mercury in A. Cylinders A and B were kept at 0° to facilitate compression. During runs, B was kept at a slightly higher pressure, serving as gas reservoir. D and E were enclosed in a thermostat, accurately controlled. The solubility bomb contained a closely-fitting, thin glass test-tube and had in the center a silver tube leading through the head. Both the head and surrounding valve parts were made of stainless steel. Samples of saturated water taken from E were expanded into buret system F where the water and gas were measured at barometric pressure and 25°.[4] Between the solubility apparatus and the gage a mercury–oil system was interposed to keep carbon dioxide from reaching the gage, as shown in the upper left-hand corner of

(1) For references to past work see Wiebe and Gaddy, THIS JOURNAL, **57**, 1487 (1935); **59**, 1984 (1937); **60**, 2300 (1938).

(2) Sander, Z. physik. Chem., **78**, 513 (1912).

(3) Zelvinskii, J. Chem. Ind. (U. S. S. R.), **14**, 1250 (1937); C. A., **32**, 852 (1938).

(4) Wiebe and Gaddy, THIS JOURNAL, **55**, 947 (1933).