# The Thermodynamics of Bi-univalent Electrolytes. VII. The Activity Coefficients of Lead Bromide from 5 to 40°

BY ROGER G. BATES[1]

Among the bivalent metal halides are found salts differing widely in behavior. In earlier papers of this series thermodynamic quantities were reported[2,3,4] for aqueous solutions of zinc iodide, a typical strong electrolyte, and of cadmium bromide and cadmium iodide, salts which display properties characteristic of weak electrolytes. It was shown that the stoichiometrical activity coefficients of zinc iodide could be represented by the Hückel[5] equation with an ion-size parameter, a_i, of 6.0 Å. With cadmium bromide, however, both the Hückel equation and the extended terms equation for unsymmetrical electrolytes of La Mer, Gronwall and Greiff[6] failed to represent the data above 0.001 M. The formation of stable ion pairs, CdBr$^+$, the dissociation of which could be expressed by an equilibrium constant. was postulated. With the use of the Debye–Hückel limiting law and the actual ion concentrations, the activity coefficient could be reproduced satisfactorily up to a concentration limit of about 0.01 M. With cadmium iodide this device was unsuccessful, and no function yielding an unambiguous extrapolation was found.

Lead bromide was chosen as an example of an electrolyte intermediate in behavior between the zinc and cadmium halides.

Electromotive force measurements of the cell

$$\text{Pb–Hg} \mid \text{PbBr}_2(m) \mid \text{AgBr–Ag} \qquad (1)$$
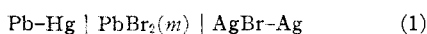
were made at 5° intervals from 5 to 40° with molalities of lead bromide varying from 0.0015 to 0.018. The standard potentials of the cell and activity coefficients of the solute have been determined. The extended terms equation with a constant a_i parameter of 1.55 Å. and an added term linear in molality was found to give an adequate representation of the activity coefficient from 5 to 40° in this range of solute concentration.

Experimental Procedure

Lead bromide was prepared metathetically by the drop-wise addition of a 0.4 M solution of reagent grade potassium bromide to a vigorously stirred 0.2 M solution of lead nitrate, previously acidified with nitric acid and heated to 60°. The salt was recrystallized from hot water to which a few drops of hydrobromic acid solution had been added to inhibit hydrolysis. The cell solutions were made by the weight dilution of three stock solutions with conductivity water. The stock solutions were prepared by shaking lead bromide in two liters of conductivity water containing a little hydrobromic acid. In recognition of the possibility of an acidity effect on the lead amalgam, an excess of acid was carefully avoided. The recrystallized salt contained some basic lead bromide; the amount of acid used in preparing the three stock solutions was sufficient to yield bromide/lead atomic ratios of 1.97, 1.99 and 2.04. Each stock solution was analyzed by gravimetric methods for both lead and bromide. The lead was converted to sulfate and the bromide to silver bromide. A correction for the solubility of lead sulfate was applied. It is believed that the molality of lead in each stock solution was established with an accuracy of 0.1% and that the bromide molality was accurate to 0.05%.

The **lead amalgam** used in all of the cells contained 10 to 12% by weight of lead. Phase investigations of the lead–mercury system[7] indicated the advisability of employing an amalgam more rich in lead than the 5% amalgam often used heretofore. The preparation of the electrodes, the method of filling the cells in the absence of air, and other experimental procedures were as described in detail in other communications.[2-4]

Three cells were made at each molality. During the period of measurement, usually about twenty-four hours, no irreversible changes were noticed. Reproducibility of the cells at molalities in excess of 0.005 was of the order of 0.08 mv. Below that molality, triplicate cells usually agreed within 0.15 mv.

Standard Potentials

The observed electromotive forces for cell (1) at the eight temperatures are given in Table I. The constants a and b of the equation

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

are also included in the table, and ΔE is the mean deviation of the observed electromotive forces from the calculated values. The molality, m^*, was calculated from the compositions of the cell solutions by the expression

$$m^* = (m_{\text{Pb}^+} + m_{\text{Br}^-}^2/4)^{1/3} \qquad (3)$$

The relation between the molality, the stoichiometrical activity coefficient of lead bromide, γ, and E, the electromotive force of cell (1) is given

(1) Sterling Fellow, Yale University, 1937–1939; present address: National Bureau of Standards, Washington, D. C.

(2) Paper III, ZnI$_2$, THIS JOURNAL, **60**, 2983 (1938)

(3) Paper IV, CdBr$_2$, ibid., **61**, 308 (1939).

(4) Paper VI, CdI$_2$, ibid., **63**, 399 (1941).

(5) Hückel, Physik. Z., **26**, 93 (1925).

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

(7) Puschin, Z. anorg. Chem., **36**, 213 (1903); Janecke, Z. physik. Chem., **60**, 399 (1907)

<div align="center">TABLE I</div>

<div align="center">ELECTROMOTIVE FORCES OF CELL (1). CONSTANTS OF EQUATION (2)</div>

t								
5	0.4187	0.39167	0.38112	0.37138	0.36651	0.36433	0.35723	0.34841
10	.4222	.39541	.38456	.37466	.36960	.36738	.36025	.35117
15	.4256	.39892	.38787	.37748	.37264	.37040	.36305	.35370
20	.4297	.40221	.39093	.38069	.37550	.37325	.36551	.35602
25	.4334	.40526	.39392	.38352	.37838	.37578	.36817	.35841
30	.4365	.40824	.39662	.38620	.38069	.37842	.37059	.36076
35	.4400	.41119	.39925	.38858	.38312	.38077	.37287	.36289
40	.4431	.41390	.40198	.39109	.38546	.38305	.37510	.36493
$m^* \times 10^3$	1.536	3.626	5.157	7.196	8.799	9.551	12.736	18.200
$a \times 10^5$		61.2	56.6	54.6	52.2	51.1	50.2	46.4
$b \times 10^6$		− 3.97	− 3.53	− 3.20	− 3.13	− 2.90	− 2.70	− 2.37
ΔE, mv.		0.08	0.03	0.14	0.11	0.08	0.08	0.06

at each temperature by the equation

$$(E/3k) + \log m^* + (\log 4)/3 = (E^0/3k) - \log \gamma \quad (4)$$

where E^0 is the standard potential of the cell and k is $2.3026RT/2F$.

The standard potential was derived at each temperature from the measured electromotive forces by extrapolation to infinite dilution with the aid of the extended terms equation of La Mer, Gronwall and Greiff[6] for electrolytes of the unsymmetrical valence type. Substitution of the extended equation for $\log \gamma$ in eq. (4) yields an expression for E^0 in terms of a_i, the ion-size parameter, natural constants and complex functions of the molality, the numerical values of which are tabulated in the papers of Gronwall, La Mer and Sandved[8] and of La Mer, Gronwall and Greiff:

$$(E^0/3k) = (E/3k) + \log m^* + (\log 4)/3 - Ax/(a_i - a_ix) - B(10^2\phi_1)/a_i^2 + C(10^3\phi_2)/a_i^3 + D(10^3\phi_3)/a_i^3 \quad (5)$$

where $x = 10^{-13}a_i(2.4\pi Nm^*p)^{1/2} = 0.21316a_i(m^*p)^{1/2}$;

$A = p/2.3026$;

$B = 2(10^{-2})p^2/2.3026$;

$C = 6(10^{-3})p^3/2.3026$;

$D = 3C$;

$p = 10^8\epsilon^2/(\mathbf{D}kT)$;

and ϕ_1 is $[{}^1\!/_2X_2(x) - Y_2(x)]$, ϕ_2 is $[{}^1\!/_2X_3^*(x) - 2Y_3^*(x)]$ and ϕ_3 is $[{}^1\!/_2X_3(x) - 2Y_3(x)]$ in the notation of the extended theory.

Values of p at 5° intervals from 5 to 40° were recalculated from recent values of ϵ, the electronic charge; $\mathbf{k}$, the Boltzmann constant; and $\mathbf{D}$, the dielectric constant of water.[9] The constants A, B, C and D are given in Table II.

The best value of a_i at 25° was ascertained by computing E^0 from the electromotive forces of

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

(9) D was taken from the paper of Wyman and Ingalls, THIS JOURNAL, 60, 1182 (1938). Values of ε, k and N, the Avogadro number, were from Wensel, J. Research Nat. Bur. Standards, 22, 375 (1939).

<div align="center">TABLE II</div>

<div align="center">CONSTANTS OF THE EXTENDED TERMS EQUATION</div>

	A	B	C	D
5	3.02684	0.42192	0.8822	2.6466
10	3.04299	.42643	.8964	2.6892
15	3.06002	.43122	.9115	2.7345
20	3.07782	.43625	.9275	2.7825
25	3.09646	.44155	.9445	2.8335
30	3.11587	.44710	.9624	2.8872
35	3.13598	.45289	.9811	2.9433
40	3.15660	.45887	1.0006	3.0018

each of the lead bromide solutions for several ion sizes somewhat less than 1.75 Å., the value which gives the closest representation of the activity coefficient of lead chloride.[10] Figure 1 shows the change of the "apparent standard potential" with change of molality, the intercept at zero molality giving the true standard potential. It is evident
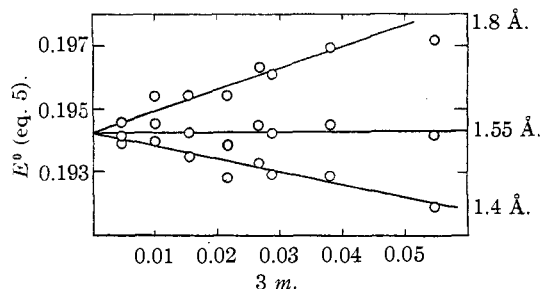

Fig. 1.—The apparent standard potential as a function of molality for three different values of a_i.

that the extended terms equation with a value of 1.55 Å. for a_i will reproduce γ_{PbBr_2} closely over the range of solute concentration studied. This value of a_i was employed for the computations at the other seven temperatures as well. It is known that the deviations in E^0 caused by differences in postulated a_i are linear in molality. Thus the ex-

(10) S. Mary Consilia Hannan, Dissertation, The Catholic University of America, 1936. The data of Carmody [THIS JOURNAL, 51, 2905 (1929)] have also been fitted to the extended equation at 25°, with the use of an ion-size parameter value of 1.75 Å. (ref. 6).

trapolation plots at the other temperatures were substantially straight, although their slopes were not zero. The true value of the standard potential was obtained in each instance from the equation

$$E^0_{(apparent)} = E^0 + \beta m^* \qquad (6)$$

The numerical values of the constants E^0 and β were derived at each temperature by the method of least squares and are given in Table III. The

TABLE III

CONSTANTS OF EQUATION 6. STANDARD POTENTIALS

t	β	E^0	E^0(eq. 7)
5	0.051	0.19542	0.19538
10	.055	.19520	.19521
15	.053	.19488	.19493
20	.008	.19480	.19453
25	.004	.19423	.19403
30	.002	.19345	.19341
35	−0.019	.19267	.19267
40	−0.032	.19178	.19183

E^0 values may be calculated from the equation

$$E^0_t = 0.19403 - 0.00113 (t - 25) - 0.00000227 (t - 25)^2 \qquad (7)$$

with a mean error at the eight temperatures of 0.08 mv.

Activity Coefficients

Large-scale graphs of E_{25}, a and b against m^* were constructed and values at round molalities were obtained by interpolation. These constants are given in Table IV, along with the activity coefficient of lead bromide at 25° calculated from eq. 4.

TABLE IV

THE ACTIVITY COEFFICIENT OF LEAD BROMIDE. CONSTANTS OF EQUATION 9

m^*	E_{25}	$a \times 10^5$	$b \times 10^6$	$-\log \gamma_{25}$	γ_{25}
0.002	0.42457				0.794
.004	.40215	59.9	−3.84	0.1487	.710
.005	.39483	57.9	−3.58	.1631	.687
.007	.38430	54.8	−3.21	.1905	.645
.01	.37458	51.5	−2.86	.2358	.581
.015	.36365	47.9	−2.51	.2887	.515
.018	.35865	46.2	−2.38	.3116	.488

For the other temperatures between 5 and 40° $-\log \gamma_t$ is expressed in terms of $-\log \gamma_{25}$, the change of $3k$ with temperature

$$(3k)_t = 0.08871 + 0.000299(t - 25) \qquad (8)$$

and the constants of eqs. 2 and 7 by the relation

$$-\log \gamma_t = -\log \gamma_{25} + \frac{(t - 25)}{0.08871 + 0.000299(t - 25)} [0.000767 - 0.00337E_{25} + a + (b + 0.00000227)(t - 25)] \qquad (9)$$

The activity coefficients listed in Table IV and those calculated from eq. 9 are thought to be correct to about ± 0.003, corresponding to an error in $E - E^0$ of about 0.3 mv. at a molality of 0.01.

The Lead Amalgam Electrode

Subtraction of 0.0713, the standard potential of the silver–silver bromide electrode at 25°,[11] from the standard potential of cell (1) gives 0.1229 for the potential of the 11% lead amalgam electrode, a value considerably higher than 0.1211 found for the 5% lead amalgam electrode by the extrapolation of electromotive force measurements of lead chloride solutions.[10]

The results of a recalculation of the potential of the electrode containing 5% of lead from literature data on the solubilities of the lead halides, together with the potentials of the lead halide–lead amalgam (5%) electrode, by means of the relation

$$E^0_{Pb \cdot Hg} = E^0_{PbX_2} + k \log K_{sp} \qquad (10)$$

where K_{sp} is the activity solubility product constant, are given in Table V. The activity coefficients were calculated from the extended terms equation. An estimated a_i value of 1.4 Å. for lead iodide was employed. It is evident that measurements of the electromotive forces of the saturated lead halide electrodes likewise indicate a lower potential for the 5% amalgam electrode than was found for the electrode formed of 11% amalgam.

TABLE V

CALCULATION OF THE POTENTIAL OF THE 5% LEAD AMALGAM ELECTRODE AT 25° FROM E. M. F. AND SOLUBILITY DATA

X	mPbX$_2$ (satd. soln.)	a_i	$-\log K_{sp}$	$E^0_{PbX_2}$	$E^0_{Pb \cdot Hg}$
Cl	0.03937[12,13]	1.75	4.801	0.2620[14,15]	0.1200
Br	.02666[12]	1.55	5.241	.2753[14]	.1203
I	.00165[12]	1.4	8.020	.3580[16]	.1208
	.00164[17]		8.026		.1206

Ag-AgCl, Cl⁻; $E^0 = 0.2224$
Hg-Hg$_2$Cl$_2$, Cl⁻; $E^0 = .2679$
Ag-AgBr, Br⁻; $E^0 = .0713$

Summary

Electromotive force measurements of the cell Pb—Hg (11%) | PbBr$_2$ (m) | AgBr–Ag have

(11) Owen and Foering, THIS JOURNAL, **58**, 1575 (1936).
(12) Burrage, J. Chem. Soc., **129**, 1703 (1926).
(13) Herz and Hellebrant, Z. anorg. allgem. Chem., **130**, 188 (1923).
(14) Jahn-Held and Jellinek, Z. Elektrochem., **42**, 401 (1936).
(15) Priepke and Vosburgh, THIS JOURNAL, **52**, 4831 (1930).
(16) Bates and Vosburgh. ibid., **59**, 1188 (1937).
(17) Lanford and Kiehl, ibid., **63**, 667 (1941).

·been made at intervals of 5° over the temperature range, 5 to 40°. The molality of lead bromide was varied from 0.0015 to 0.018. The standard potentials of the cell were evaluated with the use of the La Mer, Gronwall and Greiff extension of the Debye–Hückel equation. Activity coefficients were calculated.

Structures of Complex Fluorides.[1] Potassium Oxyhexafluocolumbate, K₃CbOF₆

BY M. B. WILLIAMS AND J. L. HOARD

Hampson and Pauling[2] have reported X-ray data which indicate that $ZrF_7^=$ ions with the point group symmetry of C_{3v}–$3m$ exist within cubic crystals of potassium and ammonium heptafluozirconates. Cubic crystals of potassium oxyfluocolumbate, K_3CbOF_6, might be expected to have a structure like that of potassium heptafluozirconate and to contain $CbOF_6^=$ ions of symmetry C_{3v}. The fact that two compounds of similar formulas both crystallize in the cubic system is, however, by no means conclusive evidence that they belong to the same structural type (compare, for example, potassium and cesium chlorides). It has seemed of particular interest to investigate the structure of K_3CbOF_6 in detail since monoclinic crystals of potassium heptafluocolumbate, K_2CbF_7, have been shown[1b] to contain discrete $CbF_7^=$ ions with the point-group symmetry of C_{2v}–mm, entirely different from that found for $ZrF_7^=$. There are, moreover, certain features of the structure proposed by Hampson and Pauling[2] for the heptafluozirconates of potassium and ammonium which make it desirable to investigate other compounds that are presumably of a similar type. We find actually that crystals of K_3CbOF_6 and K_3ZrF_7 give rise to closely similar X-ray diffraction data.

Crystalline potassium oxyfluocolumbate, K_3CbOF_6, has been prepared in the form of small shining cubes by several investigators.[3] Marignac[3a] reported that his crystals were doubly refracting; Balke and Smith[3b] observed only a faint double refraction along the edges of their specimens, and Baker[3c] concluded that his preparation was perfectly inactive in polarized light. The specimens of K_3CbOF_6 used in our work were small brilliant cubes which seemed to be perfectly isotropic under the polarizing microscope and entirely stable in air. They resulted from the isothermal evaporation of an aqueous solution prepared from freshly recrystallized $K_2CbOF_5·H_2O$ and KF taken in the mole ratio one to four. It may be noted by way of comparison that crystals of K_3ZrF_7 commonly assume an octahedral habit.

Accurately oriented Laue and oscillation photographs from K_3CbOF_6 show no deviation from the point-group symmetry of O_h–$m3m$; the probable space-group of the crystal is thus limited to O_h, O, or T_d. The lattice constant a is 8.87 Å. as given by back reflection data, and the corresponding unit cell contains four stoichiometric molecules. The absence of reflections from planes with mixed indices points to a face-centered lattice.

Excepting that $a = 8.95$ Å. (instead of 8.87 Å.) all statements of the preceding paragraph apply equally well to K_3ZrF_7.[2] Indeed a further detailed comparison between the observed intensities of X-ray powder lines for K_3CbOF_6 (Table I) and the data reported[2] for K_3ZrF_7 makes it quite certain that the two substances crystallize with similar structures. Except for a few lines at large angles of scattering, the description of the intensity patterns is nearly identical for the two compounds. Such minor differences as appear are readily understood in terms of the small difference in lattice constant, the substitution of columbium for zirconium and of oxygen for fluorine, and possible variations in the effects of thermal vibrations on the scattering of X-rays by the crystals.

To establish the exact character of the structural type in which K_3CbOF_6 and K_3ZrF_7 (also

(1) For earlier papers in this series see (a), THIS JOURNAL, 57, 1985 (1935); (b), ibid., 61, 1252 (1939); (c), 61, 2849 (1939); (d), 62, 3126 (1940); (e), 63, 11 (1941); (f), 64, 633 (1942).

(2) G. C. Hampson and L. Pauling, ibid., 60, 2702 (1938).

(3) See (a) Ch. de Marignac, Bibl. univ., Arch. sc. phys. nat. Genève, 23, 259 (1865); (b) C. W. Balke and E. F. Smith, THIS JOURNAL, 30, 1637 (1908); (c) H. Baker, J. Chem. Soc., 35, 760 (1879).