The Journal of the American Chemical Society

VOL. 51 SEPTEMBER, 1929 No. 9

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

ACTIVITY COEFFICIENTS OF CADMIUM CHLORIDE AND BROMIDE

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RECEIVED NOVEMBER 6, 1928 PUBLISHED SEPTEMBER 5, 1929

When this investigation was started, the only recent electromotive force data from which the activity coefficients of the cadmium halides could be calculated were those of Horsch for cadmium chloride. His measurements,[1] using cadmium amalgam, led to values of the electromotive force for cells of the type

$$\text{Cd} \mid \text{CdCl}_2 \mid \text{AgCl} \mid \text{Ag}$$

and covered the range from very high dilution up to 0.0074 *M* with single points at 0.0995 and 6.62 *M*. In view of the peculiar properties of the cadmium halides, the low conductance ratios of their aqueous solutions, their tendency to form complex ions and other anomalous behaviors, it seemed well to study cells of this type somewhat more fully at higher concentrations and to extend the work to the other halides.

In the present paper are given results of measurements of cells of the type

$$\text{Hg, Cd} \mid \text{CdCl}_2 \mid \text{AgCl} \mid \text{Ag}$$

and

$$\text{Hg, Cd} \mid \text{CdBr}_2 \mid \text{AgBr} \mid \text{Ag}$$

from 0.01 *M* to 6 *M* and from 0.01 *M* to 3 *M*, respectively.

Recently Getman[2] has published values for the activity coefficients of the cadmium halides calculated, however, from measurements of cells using as the negative electrode mercury and the appropriate mercurous halide, except in the case of cadmium iodide where two series of determinations were made, one with silver–silver iodide electrodes and the other with lead amalgam–lead iodide electrodes.

Apparatus, Materials and Procedure.—The cell used was of the simplest type, being in the form of a straight tube about 2 cm. in diameter and 15 cm. in height. Connection

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[1] Horsch, THIS JOURNAL, **41**, 1787 (1919).

[2] Getman, *J. Phys. Chem.*, **32**, 91 (1928); **32**, 940 (1928).

with the amalgam in the bottom of the tube was made by means of a sealed-in platinum wire. The other electrode was supported in the upper part of the solution by means of a rubber stopper which served also to prevent evaporation.

The electrodes were made in the manner described by Noyes and Ellis,[3] the silver being formed from silver oxide as was done by Lewis.[4] The silver chloride or bromide was formed on the electrode by making it the anode in a 0.75 *M* hydrochloric or hydrobromic acid solution for about five hours with a current of 0.004 ampere. A number of different sets of electrodes were made up throughout the course of the investigation, replacement being necessary more frequently with the bromide than with the chloride electrodes. Before using, the electrodes were tested against each other in each case in order to make sure that no inconsistencies were introduced from this source.

The cadmium amalgam was made by electrolyzing a solution of cadmium sulfate over a mercury cathode. When the electrolysis was completed the amalgam was allowed to flow into a small evacuated flask which was then pumped out until the last traces of moisture had been removed. As soon as it had been sealed off the flask was inverted and set aside for several days so that any oxide might rise to the surface and thus be removed. Finally, the lower part of the amalgam was allowed to flow into a large evacuated flask containing such an amount of mercury as to bring its concentration to that used. Just before making a series of determinations a quantity of the amalgam was drawn into an evacuated tube so built that a stream of hydrogen could be passed over the amalgam as it was being transferred into the cell.

Standard solutions of cadmium chloride and bromide were prepared by dissolving the purified salts in conductivity water and the concentration was determined by gravimetric analysis. These standard solutions were then diluted quantitatively by weight with boiled, twice distilled water to give the solutions used in the measurements.

In making the electromotive force measurements, the solution was introduced into the empty cell and after placing the silver–silver halide electrode in position, the cell was suspended in the thermostat. It was allowed to remain thus for about four or five hours in order to come to temperature and so that the electrode might come to equilibrium with the solution. At the end of this time, the electrode was removed for an instant while a few cc. of the amalgam were introduced. A reading of the electromotive force was immediately taken, followed by others at about half-hour intervals for the next three hours. The first reading showed no definite trend of variation from the subsequent ones but frequently, due perhaps to the temperature change caused by introducing the amalgam, varied more widely from the later readings than they did among themselves. In such cases the first reading was disregarded. Otherwise a mean of all of the readings throughout this period was taken as the value of the cell. The variation of the accepted readings was always very slight, never more than five hundredths of a millivolt, and showed no particular trend. In several cases the cell was allowed to stand for twenty-four hours after taking these readings. It was usually found at the end of this time that the electromotive force had dropped slightly, never, however, more than half a millivolt. All measurements were made at 25 ± 0.01°.

Results

In Table IA are given the results obtained from the cells containing cadmium chloride. The first column gives the molality of the solution (moles of salt per 1000 g. of water) and the second the observed electromotive force. Plotting these values led to a smooth curve continuous

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[3] Noyes and Ellis, THIS JOURNAL, **39**, 2532 (1917).

[4] Lewis, *ibid.*, **28**, 166 (1906).

TABLE IA

THE ACTIVITY COEFFICIENTS OF CADMIUM CHLORIDE

m	E'	E	γ (Obs.)	γ (Calcd.)
(0.01)	(0.7409)	(0.5837)	0.503	0.503
.01010	.74058	.58338	.503	.502
.02015	.72212	.56492	.407	.413
.03030	.71183	.55463	.353	.358
.05056	.69953	.54233	.291	.293
.06968	.69227	.53507	.255	.255
.08145	.68881	.53161	.239	.236
.1000	.68431	.52711	.219	.214
.2014	.67003	.51283	.157	.147
.3027	.66241	.50521	.128	.118
.5101	.65338	.49618	.096	.090
.6908	.64849	.49129	.080	.078
.7962	.64629	.48909	.074	.075
.9999	.64235	.48515	.065	.071
2.045	.63165	.47445	.042	.085
4.227	.61899	.46179	.028	..
5.133	.61481	.45761	.026	..
6.146	.61050	.45330	.024	..

TABLE IB

$m \times 10^4$	1.527	2.144	3.363	3.659	4.79	9.24	25.81
γ (L. and R.)	0.930	0.923	0.905	0.901	0.872	0.809	0.697
γ	.954	.935	.901	.895	.882	.809	.696

with one obtained from the results of Horsch (E_2, Table II, of his paper) save for a displacement of 0.0686 volt. This displacement represented largely the difference in electromotive force of the cell with pure cadmium and with the amalgam of the concentration used but was due in part also to the differences in the potentials of the silver–silver chloride electrodes used. The electrodes used by Horsch were made by electrolytic deposition and when measured against hydrogen in 0.01 M hydrochloric acid led, upon taking 0.00924 as the value of the activity of H^+ and Cl^-, to the value -0.2258 for the standard silver–silver chloride potential. Electrodes made in the manner indicated above have been carefully studied and found to lead to a value of -0.2233. Taking into account this difference in the electromotive force[3,5] contributed by the silver–silver chloride electrodes in the two series, the correction to convert the electromotive force of the cell measured to what would be obtained with pure cadmium electrodes amounts to 0.0661 volt.

The activity coefficient of the electrolyte may be calculated from the electromotive force of a cell of the type used by means of the equation

$$E = E_0 - \frac{RT}{nF} \ln (4m^3\gamma^3) \qquad (1)$$

This equation upon introducing the numerical values, including that of

[5] See also Gerke, *Chemical Reviews*, 1, 377 (1925).

the standard electrode potential of cadmium as calculated by Lewis and Randall[1,6] (0.3976), becomes for calculating the activity coefficient

$$\log \gamma = 4.28026 - \log m - 11.27\,E \tag{2}$$

To the values of the measured electromotive force as given in the second column, 0.0661 volt was added as indicated above and from the result there was subtracted the value of the standard potential of the silver–silver chloride electrode (0.2233). In this manner were obtained the values of E given in Col. 3, from which the values of the activity coefficients in Col. 4 were calculated by means of Equation 2.

In Table IB are given values of the activity coefficient at certain concentrations calculated from the data of Horsch. In the first row are given the concentrations (molality × 10^4) and in the second the values of the activity coefficients at the corresponding concentrations as calculated by Lewis and Randall[7] on the assumption that at very high dilutions the values are the same as for barium chloride. In the third row are given values calculated in the same manner as those in Part A using, however, the value for the silver–silver chloride potential found by Horsch. The points determined by Horsch at the four lowest concentrations have been omitted because of the experimental uncertainty in this region. Both calculations lead to identical results at the concentrations higher than those given in IB (*i. e.*, at 0.003519, 0.0074, 0.0995 and 6.62 *M*). Due to a difference in interpolation between 0.0074 and 6.62 *M*, the values given by Lewis and Randall at round concentrations between 0.01 and 0.1 *M* vary considerably, especially at the lower concentrations, from those here given.

Above 0.05 *M* the values given in Table IA agree satisfactorily with those of Getman. Below this point, however, there is a marked difference in the form of the two curves, the values determined by Getman rising much more rapidly with increasing dilution. In Table II are given the results from cells containing cadmium bromide. The column headings have the same significance as in Table IA and the method of calculation was the same. The value of the standard potential of the silver–silver bromide electrode[8] was taken as 0.0734 and after correcting in the same manner as above to the value of the electromotive force with pure cadmium as electrode the calculation was made from the values in Col. 3 by means of Equation 2.

Above 0.02 *M* the agreement between these values of the activity coefficient and those given by Getman is satisfactory. Below this concentration there is again a sharper rise in his values than would be indicated by the points given here.

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[6] Lewis and Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., New York, **1923**, p. 419.

[7] Lewis and Randall, ref. 6, pp. 361–362.

[8] Lewis and Storch, THIS JOURNAL, 39, 2544 (1917); see also Livingston, *ibid.*, **48**, 45 (1926).

TABLE II

THE ACTIVITY COEFFICIENTS OF CADMIUM BROMIDE

m	E'	E	γ (Obs.)	γ (Calcd.)
0.01000	0.59319	0.58589	0.476	0.440
.01386	.58459	.57729	.429	.425
.01993	.57563	.56833	.376	.364
.02801	.56734	.56004	.332	.326
.03997	.55914	.55184	.288	.288
.05629	.55147	.54417	.249	.252
.08114	.54357	.53627	.212	.216
.1000	.53952	.53222	.191	.196
.1378	.53337	.52607	.163	.168
.2026	.52640	.51910	.133	.137
.2724	.52140	.51410	.113	.116
.4069	.51486	.50756	.089	.091
.5444	.51011	.50281	.075	.076
.8056	.50404	.49674	.060	.060
.9996	.50054	.49324	.053	.053
1.314	.49577	.48847	.045	.045
1.896	.48878	.48148	.038	.037
3.0815	.47773	.47043	.031	.034

Discussion

The above method of computing .the activity coefficient, because of using their value of the standard electrode potential of cadmium, is essentially accepting the extrapolation of Lewis and Randall[9] as a basis and was resorted to after attempts had failed to fit the data satisfactorily to the functions of Hückel and Brönsted.[10] This was due, very probably, to the presence of complex ions[11] whose equilibria would have to be taken into account in order to work out such a solution. It is possible also that the introduction of the higher terms[12] of the Debye-Hückel theory might lead to a more satisfactory expression of the results.

However, the deviations from the limiting law, unless very large errors have been made in the above assumptions, take place in an unusual manner and become apparent at very low concentrations. This can be seen from Table III, in which are given the values of the activity coefficient at very high dilutions. In the first column is given the molality and in the second the corresponding value of the activity coefficient of a bi-univalent electrolyte as calculated by the equation

$$\log \gamma = -1.749 \sqrt{m}$$

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[9] The calculation of the activity coefficients of cadmium chloride would have been considerably simplified by accepting their value at some one concentration but, considering also the cadmium bromide, the method used seemed preferable.

[10] Hückel, *Physik. Z.*, **26**, 93 (1925); Brönsted, THIS JOURNAL, **44**, 938 (1922).

[11] McBain and Van Rysselberge, *ibid.*, **50**, 3009 (1928).

[12] Gronwall, La Mer and Sandved, *Physik. Z.*, **29**, 358 (1928). So far this has been applied only to symmetrical types.

TABLE III

THE ACTIVITY COEFFICIENTS OF BI-UNIVALENT ELECTROLYTES AT HIGH DILUTIONS

$m \times 10^4$	γ, lim. func.	γ, $BaCl_2$	% diff.	γ, $CdCl_2$	% diff.
1.029	0.960	0.961	0.1	1.000	4.1
1.087	.959	.960	.1	1.042	8.7
1.137	.958	.959	.1	1.028	7.3
1.269	.956	.957	.1	1.004	5.0
1.527	.951	.953	.2	0.954	0.3
2.144	.943	.945	.2	.935	−0.8
3.363	.929	.932	.3	.901	−3.0
3.659	.926	.929	.3	.895	−3.3
4.79	.916	.920	.4	.882	−3.7
9.24	.885	.893	.9	.809	−8.6
25.81	.815	.834	2.3	.696	−14.6
35.19	.788	.812	3.0	.652	−17.3
74.0	.707	.751	6.2	.568	−19.7

a form to which the limiting function of Debye and Hückel may be reduced.[13] In the third column are given the values of the activity coefficient of barium chloride as calculated from the equation of Hückel using the constants obtained by Harned.[14] The equation agrees very well with the experimental data and we have assumed that it holds likewise at low concentrations. The percentage difference between the two values is given in the following column and indicates the magnitude of the deviation from the limiting law which might be expected in the case of a bi-univalent electrolyte. The fifth column gives the values of the activity coefficient of cadmium chloride as calculated above from the data of Horsch. The relatively large deviations given in the last column between these values and those calculated by the limiting law indicate the marked difference in the behavior of cadmium chloride from that of the more typical bi-univalent electrolytes.

The relation between the values of the activity coefficients of cadmium chloride and bromide given above and the molality can be expressed with a fair degree of accuracy over a considerable concentration range by the equation of Harned[15]

$$\log \gamma = \alpha m - \beta m^{\alpha'}$$

The constants α, β and α' were found to have the values 0.6, 1.75 and 0.38 for cadmium chloride and 0.2, 1.48 and 0.308 for the bromide. The activity coefficients calculated by these equations are given in the last columns of Tables I and II. By changing the constants somewhat closer agreement with the experimental values over shorter or over different

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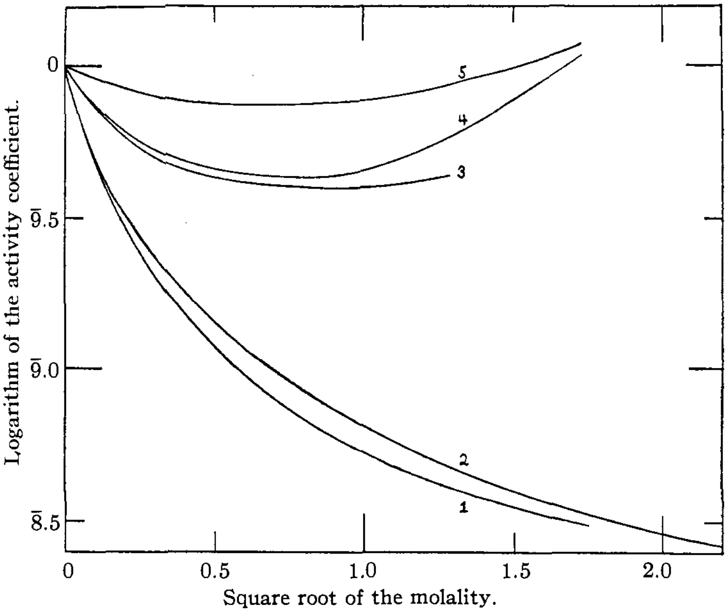
[13] Debye and Hückel, *Physik. Z.*, **24**, 185 (1923); see also Brönsted and La Mer, THIS JOURNAL, **46**, 555 (1924).

[14] Harned, *ibid.*, **48**, 326 (1926).

[15] Harned, *ibid.*, **42**, 1808 (1920); **44**, 252 (1922); Taylor, "Treatise on Physical Chemistry," D. Van Nostrand Company, New York, **1924**, p. 744.

concentration ranges could be obtained. This would be without point, however, in view of the uncertainty of the extrapolation.

How different the behavior of the cadmium halides is from that of typical strong electrolytes can be seen further from Fig. 1, where the logarithms of the activity coefficients of cadmium chloride and bromide from Tables I and II, of lithium chloride from the data of MacInnes and Beattie[16] and of barium and strontium chloride are plotted against the square root of the molality. The curves of the alkaline earth chlorides all exhibit minima at concentrations below 0.7 *M*.[17] The activity coefficients of the cadmium halides show little if any such tendency even at very high concentrations. The point determined by Horsch at 6.62 *M* cadmium chloride leads to the value 0.025 for the activity coefficient and taken in conjunction with the values given in Table I might indicate a slight minimum in the region of the nearly saturated solution. However, from the general form of the three curves this seems unlikely. At moderate and high concentrations the values of the activity coefficients of the cadmium halides fall much below those of a typical bi-univalent electrolyte. Thus the values for cadmium chloride at 0.01, 0.1 and 1 *M* are 0.503, 0.219 and 0.065 as against



1, $CdBr_2$; 2, $CaCl_2$; 3, $BaCl_2$; 4, $SrCl_2$; 5, LiCl.

Fig. 1.—The activity coefficients of cadmium chloride and bromide and typical strong electrolytes.

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[16] MacInnes and Beattie, This Journal, **42**, 1117 (1920).

[17] Lucasse, *ibid.*, **47**, 743 (1925).

0.723, 0.499 and 0.397 calculated by Harned for barium chloride at the same concentrations.

By the nature of their assumption the values of the activity coefficient of cadmium chloride calculated by Lewis and Randall lie everywhere below those of barium chloride except at very high dilutions, where they are considered to be equal. Thus the values given at the first four concentrations in Table IB are considered to be the same for both salts. It seems not unlikely, however, that at very high dilutions the values for cadmium chloride might rise slightly higher than those for barium chloride. However, in view of the uncertainty of the data in this region and the very slight differences in the values of the activity coefficients of the alkaline earth chlorides at 0.0001 *M* (all very nearly 0.961) as calculated by the equation of Hückel, using the constants determined by Harned, it cannot be regarded as significant that the values given in Table IB cross in the neighborhood of 0.0003 *M*, below which concentration the values for cadmium chloride are markedly higher (0.970 at 0.0001 *M*) than those for barium chloride.

If the cadmium halides behave like typical strong electrolytes at all, it is only at extremely low concentrations. At moderate and high concentrations their behavior becomes such as to preclude them unquestionably from consideration as completely dissociated.

Summary

In the above paper are given values of the electromotive force at 25° of the cell Hg, Cd | CdX_2 | AgX | Ag. The concentrations of the cadmium chloride and bromide, represented by CdX_2, were varied from 0.01 to 6 *M* and from 0.01 *M* to 3 *M*, respectively.

From these data values of the activity coefficients of the salts have been calculated over these concentration ranges.

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