[CONTRIBUTION FROM THE LADD CHEMICAL LABORATORY OF THE NORTH DAKOTA AGRICULTURAL COLLEGE]

The Simultaneous Evaluation of the Stability Constant for the $CdCl^+$ Ion and the Standard State Potential of the Cell $Cd-Hg/CdCl_2(m)/AgCl/Ag$ at 25°

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The potential at 25° of the cell $Cd-Hg/CdCl_2(m)/AgCl/Ag$ has been measured at various concentrations of cadmium chloride. Values for the stability constant of $CdCl^+$, K, were calculated at each concentration using various provisional values for the standard state potential E^0. The value of E^0 which yielded the most nearly constant value of K was selected as the best value for the standard state potential. In this manner E^0 was evaluated as 0.5745 ± 0.0002 absolute volt and the corresponding value of K was 90 ± 4.

Introduction

The determination of accurate values for standard state potentials by extrapolation to infinite dilution of functions suggested by the Nernst and Debye–Hückel equations, using the methods of Lewis and Randall,[2] Hitchcock[3] or of Brown and MacInnes[4] is not feasible if association occurs to appreciable but unknown extents between ions which are involved in the net cell reaction. The cell $Cd-Hg$(2-phase amalgam)$/CdCl_2(m)/AgCl/Ag$ is a case in point because of the existence and moderate stability of the $CdCl^+$ ion in dilute solutions. This cell was investigated by Harned and Fitzgerald,[5] who evaluated the stability constant K of the $CdCl^+$ ion, and the standard state potential E^0 by special methods which they described. The subsequent publication by Kielland[6] of calculated values for the individual ion activity coefficients for a large number of ions, including Cd^{++}, Cl^- and $CdCl^+$, allows the simultaneous evaluation, from electromotive force data, of K and E^0 at 25° by an alternate method.

If one makes conventional choices of standard state for Ag, AgCl and aqueous $CdCl_2$, and chooses the two-phase equilibrium amalgam as the standard state environment for the cadmium metal, the reversible potential of the cell E may be expressed as

$$E = E^0 - (RT/2F)\ln(m - m_{CdCl^+})(2m - m_{CdCl^+})^2\gamma_{Cd^{++}}\,\gamma^2_{Cl^-} \quad (1)$$

where m is the analytical molality of $CdCl_2$, m_{CdCl^+} is the actual molality of the $CdCl^+$ ion, and the other symbols have their usual meaning. The stability constant K of the $CdCl^+$ ion may be represented by the equation

$$K = \frac{m_{CdCl^+}\,\gamma_{CdCl^+}}{(m - m_{CdCl^+})(2m - m_{CdCl^+})\gamma_{Cd^{++}}\,\gamma_{Cl^-}} \quad (2)$$

TABLE I

VALUES OF K CALCULATED AT VARIOUS CONCENTRATIONS OF $CdCl_2$ USING SEVERAL ARBITRARILY SELECTED VALUES OF E^0

E^0 used, abs. v.	$10^3 m$, mole/kg.	E, abs. v.	$10^4 m_{CdCl^+}$, mole/kg.	K
0.57390	1.089	0.82760	1.602	108
	2.4392	.80115	5.906	103
	7.0941	.76870	28.57	96.6
	11.043	.75626	52.63	95.7
	15.047	.74793	79.85	96.3
	21.645	.73845	128.2	97.1
.57430	1.089	.....	1.445	95.5
	2.4392	.....	5.579	95.1
	7.0941	.....	27.73	91.4
	11.043	.....	51.34	90.9
	15.047	.....	78.23	91.8
	21.645	.....	126.2	93.1
.57440	1.089	.....	1.406	92.4
	2.4392	.....	5.501	93.2
	7.0941	.....	27.47	90.0
	11.043	.....	51.07	88.8
	15.047	.....	77.87	90.9
	21.645	.....	125.8	92.2
.57450	1.089	.....	1.369	89.4
	2.4392	.....	5.422	91.4
	7.0941	.....	27.28	88.9
	11.043	.....	50.69	88.8
	15.047	.....	77.51	89.9
	21.645	.....	125.2	91.2
.57460	1.089	.....	1.331	86.4
	2.4392	.....	5.331	89.3
	7.0941	.....	27.04	87.4
	11.043	.....	50.39	87.6
	15.047	.....	77.12	88.9
	21.645	.....	124.7	90.2
.57470	1.089	.....	1.292	83.4
	2.4392	.....	5.238	87.2
	7.0941	.....	26.85	86.4
	11.043	.....	50.13	86.6
	15.047	.....	76.70	87.8
	21.645	.....	124.3	89.3
.57510	1.089	.....	1.09	68.6
	2.4392	.....	4.874	79.4
	7.0941	.....	25.85	80.8
	11.043	.....	48.65	81.8
	15.047	.....	75.88	84.0
	21.645	.....	121.8	86.1

If E^0 were known, m_{CdCl^+} could be calculated from eq. 1 by successive approximations for each value of m using the corresponding measured value of E and Kielland's[6] individual ion activity coefficients. The stability constant could then be calculated from eq. 2. From an arbitrarily chosen value of E^0, values of K can be calculated using the experi-

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[1] Taken from part of a thesis submitted in 1955 by L. M. Ferris in partial fulfillment of the requirements for the degree of Master of Science at the North Dakota Agricultural College.

[2] (a) G. N. Lewis and M. Randall, THIS JOURNAL, **43**, 1112 (1921); (b) G. N. Lewis and M. Randall, "Thermodynamics and the Free Energy of Chemical Substances," McGraw-Hill Book Co., Inc., New York, N. Y., 1923, pp. 333–335.

[3] D. I. Hitchcock, THIS JOURNAL, **50**, 2076 (1928).

[4] (a) A. S. Brown and D. A. MacInnes, *ibid.*, **57**, 1356 (1935); (b) D. A. MacInnes, "Principles of Electrochemistry," Reinhold Publ. Corp., New York, N. Y., 1939, pp. 185–186.

[5] H. S. Harned and M. E. Fitzgerald, THIS JOURNAL, **58**, 2624 (1936).

[6] J. Kielland, *ibid.*, **59**, 1675 (1937).

TABLE II

VALUES OF K CALCULATED AT VARIOUS CONCENTRATIONS OF $CdCl_2$ USING SEVERAL ARBITRARILY SELECTED VALUES OF E^0 (BASED ON THE DATA OF HARNED AND FITZGERALD[5])

E^0 used, abs. v.	10^3 m, mole/kg.	E, abs. v.	10^4 m_{CdCl^+}, mole/kg.	K
0.57339	1.0	0.83025	1.485	118
	5.0	.77877	17.79	103
	7.0	.76888	.....	...
	10.0	.75872	46.54	98.2
	20.0	.74001	115.9	97.0
.57400	1.0	.....	1.265	97.4
	5.0	.....	16.83	93.5
	7.0	.....	.....	...
	10.0	.....	44.74	90.6
	20.0	.....	113.1	91.1
.57410	1.0	.....	1.230	94.1
	5.0	.....	16.64	91.8
	7.0	.....	27.11	90.8
	10.0	.....	44.57	89.6
	20.0	.....	112.7	90.2
.57420	1.0	.....	1.190	90.4
	5.0	.....	16.47	90.4
	7.0	.....	26.91	89.7
	10.0	.....	44.23	88.5
	20.0	.....	112.1	89.1
.57430	1.0	.....	1.160	87.7
	5.0	.....	16.32	89.0
	7.0	.....	26.70	88.5
	10.0	.....	43.97	87.6
	20.0	.....	111.5	87.9
.57440	1.0	.....	1.123	84.4
	5.0	.....	16.17	87.6
	7.0	.....	26.50	87.3
	10.0	.....	43.73	86.6
	20.0	.....	111.1	87.1
.57450	1.0	.....	1.077	80.3
	5.0	.....	16.02	86.3
	7.0	.....	.....	...
	10.0	.....	43.40	85.4
	20.0	.....	110.7	86.4

mental data obtained at several molalities. A systematic drift, with concentration, of the calculated values of K would suggest that a better choice of E^0 could be made.

Experimental

The anode of the cell was a saturated two-phase cadmium amalgam which had been prepared by slow electrolytic deposition of cadmium into a pool of distilled mercury from a saturated solution of cadmium chloride. The amalgam was contained in a J-shaped glass vessel which previously had been constructed and used by Schroeder.[7] This vessel also contained purified cyclohexane which protected the amalgam from air oxidation and also allowed the operator to extrude at will into contact with the $CdCl_2$ solution fresh droplets of the liquid phase of the amalgam. Two amalgams were used, one containing 9.9 wt. % cadmium, the other 11.4%. These amalgams were found to yield identical potentials within the limits of experimental error, ±0.01 mv. The silver–silver chloride electrodes, prepared according to the procedure of Brown,[8] exhibited identical potentials within 0.02 millivolt. The aqueous solutions of cadmium chloride were prepared by introducing weighed portions of the anhydrous salt into glass-stoppered flasks containing appropriate quantities of freshly distilled conductivity water and weighing the resulting solutions. The cells were allowed to reach equilibrium in a bath maintained at a temperature of 24.96 ± 0.02°. Potential measurements were made using a Leeds and Northrup Type K-2 potentiometer, a galvanometer having a sensitivity of 0.0015 microamp. per mm., and Weston cells which recently had been calibrated at the National Bureau of Standards. Measurements were repeated, using fresh droplets of amalgam, until a constant potential was obtained over a period of several hours.

Results and Discussion

Table I contains the potentials measured for 6 cells covering the cadmium chloride molality range

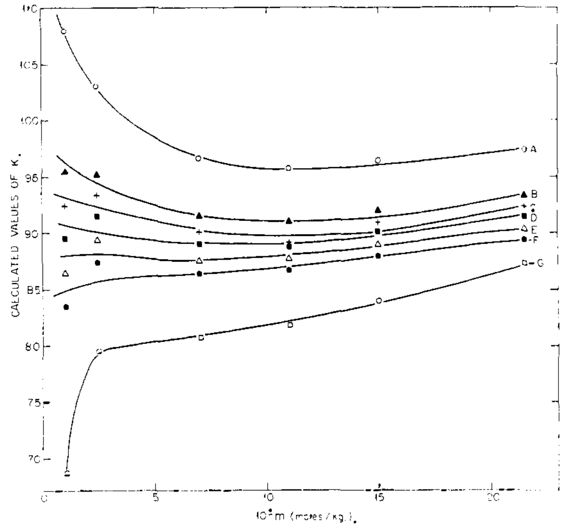

Fig. 1.—Calculated values of K as functions of the molality of $CdCl_2$ using various arbitrarily selected values of E^0. Curve A, E^0 = 0.57390 abs. volt; curve B, E^0 = 0.57430 abs. volt; curve C, E^0 = 0.57440 abs. volt; curve D, E^0 = 0.57450 abs. volt; curve E, E^0 = 0.57460 abs. volt; curve F, E^0 = 0.57470 abs. volt; curve G, E^0 = 0.57510 abs. volt.

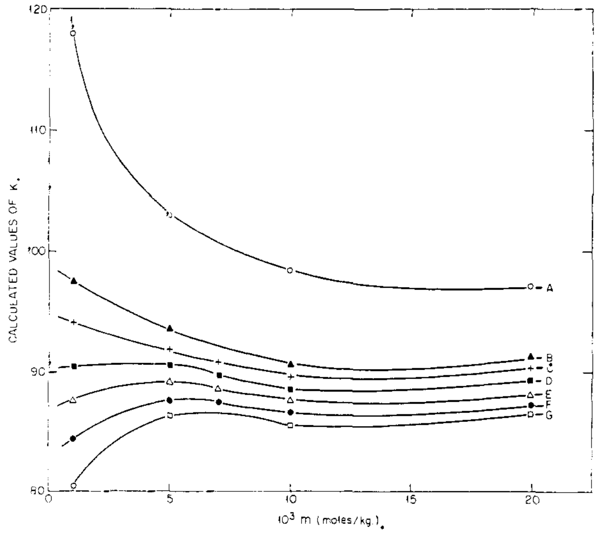

Fig. 2.—Calculated values of K as functions of the molality of $CdCl_2$ using various arbitrarily selected values of E^0 (based on the data of Harned and Fitzgerald).[5] Curve A, E^0 = 0.57339 abs. volt; curve B, E^0 = 0.57400 abs. volt; curve C, E^0 = 0.57410 abs. volt; curve D, E^0 = 0.57420 abs. volt; curve E, E^0 = 0.57430 abs. volt; curve F, E^0 = 0.57440 abs. volt; curve G, E^0 = 0.57450 abs. volt.

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[7] R. A. Schroeder, M.S. Thesis, North Dakota Agricultural College, 1953.

[8] A. S. Brown, THIS JOURNAL, 56, 646 (1934).

of 0.001 to 0.022 and the corresponding values of K calculated using various selected values of E^0. A plot of these values of K *versus* the molality of cadmium chloride appears in Fig. 1. Similar data calculated from the smoothed e.m.f. data of Harned and Fitzgerald[5] appear in Table II and are plotted in Fig. 2.

Neither the present data nor those of Harned and Fitzgerald yield a truly horizontal plot of K *vs.* m with any one value of E^0. This may be due, in part, to systematic errors in the activity coefficients used. Probably of greater importance, an upward shift in the calculated values of K for the more concentrated solutions is to be expected from inspection of eq. 1 and 2 if the species $CdCl_2$, $CdCl_3^-$ or $CdCl_4^=$ are not of negligible importance.

In Figs. 1 and 2 the extreme curvatures of curves A and G in the more dilute region show that, for each set of data, the correct value of E^0 and the corresponding value of K, lies within the 0.4 mv. range defined by curves B to F. On this basis, from the data of the authors, K was evaluated as 90 ± 4 and E^0 as 0.5745 ± 0.0002 abs. volt. Values of 88 ± 2 and 0.5742 ± 0.0002 abs. volt were obtained for K and E^0, respectively, from the data of Harned and Fitzgerald.

Using their own method, Harned and Fitzgerald[5] obtained values of 0.5741 abs. volt and about 90 for E^0 and K, respectively. The K obtained in this investigation, although in agreement with the value reported by Harned and Fitzgerald, is somewhat lower than the value of 99 reported by Righellato and Davies[9] and that of 100 reported by Vanderzee and Dawson.[10]

Use of an average value of 0.5744 abs. volt as the standard state potential of the cell Cd–Hg(2-phase amalgam)/$CdCl_2(m)$/AgCl/Ag, Bates and Bower's[11] value of −0.2223 abs. volt for the standard oxidation potential of the electrode Ag/AgCl/Cl^-, and Parks and LaMer's[12] value of 0.0505 abs. volt for the potential of the cell Cd/$CdSO_4(m)$/Cd-Hg-(2-phase amalgam) yields a value of 0.4026 abs. volt for the standard state potential of the electrode Cd/Cd^{++}.

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[9] E. C. Righellato and C. W. Davies, *Trans. Faraday Soc.*, **26**, 592 (1930).

[10] C. E. Vanderzee and H. J. Dawson, Jr., THIS JOURNAL, **75**, 5659 (1953).

[11] R. G. Bates and V. E. Bower, *J. Research Natl. Bur. Standards*, **53**, 283 (1954).

[12] W. G. Parks and V. K. LaMer, THIS JOURNAL, **56**, 90 (1934).

FARGO, NORTH DAKOTA

[CONTRIBUTION FROM THE LADD CHEMICAL LABORATORY OF THE NORTH DAKOTA AGRICULTURAL COLLEGE]

The Determination of a Thermodynamic Stability Constant for the Cadmium Citrate ($CdCit^-$) Complex Ion at 25° by an E.M.F. Method[1]

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The stability constant of the $CdCit^-$ complex ion was determined to be 2.3×10^5 at 25° using the e.m.f. method developed by Harned and Ehlers.

Introduction

The e.m.f. method of Harned and Ehlers[2] for the determination of dissociation constants for weak acids and bases consists essentially of the extrapolation to infinite dilution of suitable forms of the Nernst equation which contain the desired equilibrium constants. Cells without liquid junction are employed, but activity coefficients for the various ionic species must either be known or estimated. The method is applicable, in principle, to any type of equilibrium involving one or more ionic species of the net reaction of a thermodynamically reversible voltaic cell. Schroeder[3] concluded that for 1-1 complex ions the method can best be adapted to the investigation of the stability of complex ions having stability constants in the range of 10^4 to 10^6. The cadmium citrate ($CdCit^-$) complex ion appeared[4] to meet this requirement and was, therefore, selected for study. The cell used was

$$\text{Cd–Hg(2-phase amalgam)}/CdCl_2(m_1),\ Na_3Cit(m_2)/AgCl/Ag \quad \text{(Cell A)}$$

where m_1 and m_2 are the analytical molalities of cadmium chloride and sodium citrate, respectively. If one chooses the saturated two-phase amalgam as the standard state for cadmium and makes the conventional choices of standard state for the other components of the net cell reaction, the reversible potential E may be expressed as

$$E = E^0 - RT/2F \ln (m\gamma)_{Cd^{++}}(m\gamma)^2_{Cl^-} \quad (1)$$

If eq. 1 is combined with the expression for the stability constant of the $CdCit^-$ complex ion

$$K_2 = (m\gamma)_{CdCit^-}/(m\gamma)_{Cd^{++}}(m\gamma)_{Cit^{\equiv}} \quad (2)$$

and the limiting form of the Debye–Hückel equation for the individual ion activity coefficients one obtains

$$2F(E - E^0)2.3026RT + \log(m_{CdCit^-}m^2_{Cl^-}/m_{Cit^{\equiv}}) = \log K_2 - 6A'\mu^{1/2} \quad (3)$$

where μ is the ionic strength and A' is the molal Debye–Hückel constant. For convenience, this

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[1] Taken from a portion of the M.S. thesis of L. M. Ferris, North Dakota Agricultural College, 1955.

[2] H. S. Harned and R. W. Ehlers, THIS JOURNAL, **54**, 1350 (1932).

[3] R. A. Schroeder, M.S. thesis, North Dakota Agricultural College, 1953.

[4] L. Meites, THIS JOURNAL, **73**, 4727 (1951).