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^{++}.

Acknowledgment.—The authors wish to express their appreciation to the Research Corporation for the Frederick Gardner Cottrell grant which supported this investigation.

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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]

BY WILLIAM B. TREUMANN AND LESLIE M. FERRIS

RECEIVED MARCH 26, 1958

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

Cd–Hg(2-phase amalgam)/$CdCl_2(m_1)$, $Na_3Cit(m_2)$/ AgCl/Ag (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.

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may be represented as

$$\log K' = \log K_2 - 6A'\mu^{1/2} \qquad (4)$$

At low ionic strengths a plot of log K' *versus* $\mu^{1/2}$ should yield a straight line with log K_2 as the ordinate intercept.

If the ionic strength is below about 0.05 the predominating equilibria[4-6] are

$$Cd^{++} + Cl^- = CdCl^+ \qquad (5)$$

$$Cd^{++} + Cit^{\equiv} = CdCit^- \qquad (6)$$

Therefore the molalities of the ionic species needed to calculate log K' are best expressed in terms of m_{CdCl^+} and $m_{Cd^{++}}$

$$m_{CdCit^-} = m_1 - m_{Cd^{++}} - m_{CdCl^+} \qquad (7)$$

$$m_{Cl^-} = 2m_1 - m_{CdCl^+} \qquad (8)$$

$$m_{Cit^{\equiv}} = m_2 - m_1 + m_{Cd^{++}} + m_{CdCl^+} \qquad (9)$$

Thus expressions

$$m_{CdCl^+} = K_1(m_{Cd^{++}})(2m_1 - m_{CdCl^+})\gamma_{Cd^{++}}\gamma_{Cl^-}/\gamma_{CdCl^+} \qquad (10)$$

$$m_{Cd^{++}} = \frac{(m_1 - m_{Cd^{++}} - m_{CdCl^+})\gamma_{CdCit^-}}{K_2(m_2 - m_1 + m_{Cd^{++}} + m_{CdCl^+})\gamma_{Cd^{++}}\gamma_{Cit^{\equiv}}} \qquad (11)$$

containing the stability constants of $CdCl^+$ and $CdCit^-$, K_1 and K_2, respectively, may be solved simultaneously to evaluate $m_{Cd^{++}}$ and m_{CdCl^+}. The desired ionic concentrations may then be obtained from eq. 7, 8 and 9. Because K_2 appears in eq. 11 successive extrapolations of eq. 4 must be made until the value of K_2 obtained as the ordinate intercept agrees with that chosen for use in eq. 11. As better approximations for K_2 are obtained, the calculated value of the ionic strength

$$\mu = 6m_2 - 3m_1 + 6m_{Cd^{++}} + 4m_{CdCl^+} \qquad (12)$$

changes slightly, requiring a corresponding adjustment of the activity coefficients before the next calculation of log K' is made.

An alternate method, which does not require the evaluation of a standard state potential, is based on data which can be obtained from the concentration cell without liquid junction

$$\underbrace{Cd\text{–}Hg/CdCl_2(m_1)/AgCl/Ag}_{\text{Cell B}}\text{–}\underbrace{Ag/AgCl/CdCl_2(m_1),\ Na_3Cit(m_2)/Cd\text{–}Hg}_{\text{Cell A}} \quad \text{(Cell A-B)}$$

The reversible potential of Cell A-B is

$$\Delta E = E_A + E_B = RT/2F \ln \frac{(m_{Cd^{++},B})(m_{Cl^-,B})^2(\gamma_{Cd^{++},B})(\gamma_{Cl^-,B})^2}{(m_{Cd^{++},A})(m_{Cl^-,A})^2(\gamma_{Cd^{++},A})(\gamma_{Cl^-,A})^2} \qquad (13)$$

Appropriate successive approximation calculations involving eq. 7–10 and 13 allow evaluation of the molalities of the Cd^{++}, $Cit^{\equiv}$ and $CdCit^-$ ions. K_2 may then be calculated from eq. 11.

Experimental

Solutions.—The solutions, which ranged in *p*H from 6.2 to 7.8, were prepared using reagent grade cadmium chloride and sodium citrate and freshly distilled conductivity water. According to Meites[4] the predominating complex ion species in this *p*H range is the $CdCit^-$ ion. In solutions of *p*H 4–5.6 the $HCit^-$ ion predominates, while the main species in the range of 8–11 is the $Cd(OH)Cit^=$ ion. The molality ratio of sodium citrate to cadmium chloride was about 1.2 in each solution (see Table I).

Electrodes.—The silver-silver chloride electrodes, prepared by a method which was essentially that of Brown,[7] exhibited potentials which agreed within the limits of experimental error, ±0.01 mv. For use as anodes two saturated two-phase amalgams,[8] containing 11.4 and 9.9 wt. % cadmium, respectively, were prepared by electrolytic deposition of cadmium from saturated cadmium chloride solutions. These amalgams exhibited identical potentials within ±0.01 mv.

Apparatus.—All potential measurements were made at 24.96 ± 0.02° using a Leeds and Northrup Type K potentiometer and a sensitive galvanometer (0.0015 microamp. per mm.). A more detailed description of the apparatus and experimental procedure appears elsewhere.[6,9]

Calculations.—The activity coefficients used were calculated by Kielland.[10] In this connection the effective diameter of the $CdCit^-$ ion was assumed to be the same as that for the H_2Cit^- ion, 3.5×10^{-8} cm. The necessary physical constants were taken from those reported by Rossini, *et al.*[11] The stability constant for the $CdCl^+$ ion ($K_1 = 90$) and the standard state potential of Cells A and B ($E^0 = 0.5745$ abs. volt) were those determined by Treumann and Ferris.[6]

Results and Discussion

Table I contains the measured potentials for Cell A and the calculated quantities needed for the graphical evaluation of K_2 at 25°. A least squares plot of log K' *vs.* $\mu^{1/2}$ is found in Fig. 1. The slope of this plot is −3.00 kg. mole^{-1} which is within 2% of that expected theoretically from eq. 4, −3.051 kg. mole^{-1}. The ordinate intercept, log K_2 = 5.37, corresponds to a value of 2.3×10^5 for K_2. This value lies between the value of 2×10^4 obtained by Meites[4] from polarographic data, and that, 2×10^6, obtained by Schroeder[3] using essentially the same methods used in this investigation. However, Schroeder considered the concentration of $CdCl^+$ to be negligible, and, also, the slope of his plot of log K' *vs.* $\mu^{1/2}$ was three times that predicted from the theory.

TABLE I

DATA FROM CELL A USED IN THE EVALUATION OF K_2

$10^3 m_1$ (moles/kg.)	$10^3 m_2$ (moles/kg.)	E (abs. v.)	$10^2 \mu^{1/2}$ (moles/kg.)$^{1/2}$	log K'
4.0972	5.2310	0.8293	13.967	4.962
4.9487	7.6584	.82803	17.724	4.810
5.0353	6.3399	.82089	15.312	4.882
5.6126	7.1657	.81870	16.339	4.877
6.5715	7.7265	.81021	16.580	4.891
7.2661	8.8274	.80792	17.883	4.830
7.8425	10.012	.80722	19.311	4.779
8.4232	10.551	.80476	19.718	4.792

Potentials for Cell A-B at selected values of m_1 are found in Table II. These potentials were not obtained by actual measurements on Cell A-B but were computed from those reported by Treumann

TABLE II

VALUES OF K_2 CALCULATED USING DATA FROM CELL A-B

$10^3 m_1$ (moles/kg.)	$10^3 m_2$ (moles/kg.)	$10^2 \mu$ (moles/kg.)	E_A (abs. v.)	E_B (abs. v.)	ΔE (abs. v.)	$K_2 \times 10^{-5}$
4.0972	5.2310	1.97	0.7849	−0.8293	−0.0444	1.87
4.9487	7.6584	3.17	.7793	− .8280	− .0487	1.54
5.0353	6.3399	2.37	.7773	− .8209	− .0436	1.83
5.6126	7.1657	2.71	.7753	− .8187	− .0434	1.70
6.5715	7.7265	2.80	.7704	− .8102	− .0398	1.76
7.2661	8.8274	3.26	.7675	− .8079	− .0404	1.60
7.8425	10.012	3.80	.7660	− .8072	− .0412	1.40
8.4232	10.551	3.95	.7631	− .8048	− .0417	1.61

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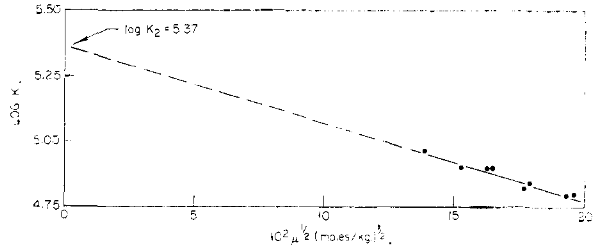

Fig. 1.—Evaluation of the stability constant of the CdCit$^-$ ion by extrapolation of equation 4 to infinite dilution.

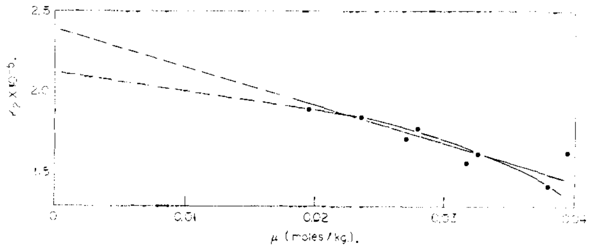

Fig. 2.—Alternate extrapolations to infinite dilution of the values of K_2 calculated from data derived from Cell A-B.

and Ferris[6] for Cell B and those obtained for Cell A during this investigation. Table II also contains the values of K_2 calculated at each selected molality of cadmium chloride. A plot of K_2 *vs.* μ is found in Fig. 2 where a rather systematic decrease in K_2 with increasing ionic strength is observed. This effect may be attributable to errors in the activity coefficients used.[10] Alternate extrapolations to infinite dilution, where activity coefficients are necessarily unity, lead to a value of about 2×10^5 for K_2. This value is obtained by any reasonable extrapolation and is consistent with that obtained by the other method discussed above.

It was unfortunate that reproducible e.m.f. readings could be made only over a narrow range of ionic strength. At ionic strengths less than 0.02 the amount of cadmium in solution was insufficient for satisfactory electrode operation, while at ionic strengths greater than 0.04 a precipitate formed in the solutions. This precipitate was found by chemical analysis to be $Cd_3Cit_2 \cdot 4H_2O$. Calcd. for $Cd_3C_{12}H_{18}O_{18}$: Cd, 42.8; C, 18.3; H, 2.30; O, 36.6. Found: Cd, 43.4; C, 18.0; H, 2.38; O (by difference), 36.2.

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FARGO, NORTH DAKOTA

[CONTRIBUTION FROM THE DEPARTMENT OF PHYSICS, D. I. MENDELEJEV CHEMICAL-TECHNOLOGICAL INSTITUTE]

The Heat Capacities of Sodium Tetraborate on the Basis of the Theory of the Specific Heat of Chain Structures

BY V. V. TARASSOV

RECEIVED MARCH 6, 1958

The heat capacity of anhydrous crystalline sodium tetraborate is analyzed on the basis of the theory of the heat capacity of chain structures earlier advanced by the author. The heat capacity of crystalline $Na_2B_4O_7$ is treated as the sum of contributions from the high-polymer chain anions $(B_4O_7)_\infty$ and the Na^{1+} cations. When the contribution of the Na^{1+} cations is subtracted from the experimental values of the heat capacity of $Na_2B_4O_7$, a strictly linear dependence is obtained, which expresses the limiting law of the heat capacity for a chain structure. The value of the characteristic temperature thus obtained $\theta_{B_4O_7} = 1890°$ coincides exactly with the earlier established value for B_2O_3 and points to the large value of the force constants of binding in the $(B_4O_7)_\infty$ chains.

The theory of the heat capacity of chain and layer structures developed by us (1945–1950)[1] has withstood the test of extensive experimental verification in a number of our papers[1d–j] and in the papers of other authors (De Sorbo,[2] Dworkin, Sasmor, Van Artsdalen, Smith, Brown,[3] Fukuroi and Muto,[4] etc.). In addition, several theoretical investigations, based on a method analogous to that of Born and Karman, have given additional confirmation of our simple laws of distribution of the fundamental frequencies of the lattice in the spectrum of elastic vibrations of chain and layer crystals.

Recently Fukuroi and Muto[4] announced that Yoshimori in analyzing the spectrum of the elastic vibrations of crystalline selenium carried out theoretical calculations which confirm our conception.

Komatsu's paper[5] on the dynamics of the vibrations of the graphite layer lattice is also of considerable interest.

Stockmayer and Hecht considered the spectrum of vibrations of a simple tetragonal lattice composed of high-molecular monoatomic chains. They arrived at results closely approaching ours. The authors mention this circumstance in their paper.[6]

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