Noting that the first term of each of the right hand members of equations (5)–(8) is constant

$$\log K_m = \log K + (n+1)k_1 - (n+1)(\alpha_{[21]} + \alpha_{[12]})\mu_{[1]} + (n+1)(\alpha_{12} + \alpha_{21})\mu_1 \quad (9)$$

The α's of equation (9) are constant at any given total ionic strength. Combining the constants of equation (9)

$$\log K_m = k_2 + k_3\mu_{[1]} + k_4\mu_1 \quad (10)$$

Noting that the ionic strength of an electrolyte is proportional to its molality

$$\log K_m = k_2 + k_5 m_{[1]} + k_6 m_1 \quad (11)$$

The concentration of electrolyte 1 in the resin phase is proportional to the quantity that has been absorbed from the solution. Or

$$m_{[1]} = W(m_1^0 - m_1)/R = W\, m_2/R \quad (12)$$

where m_1^0 is the concentration of electrolyte 1 in the aqueous phase before equilibration; W = grams of water involved in the equilibration; R = grams of resin involved in the equilibration. Consequently

$$\log K_m = k_2 + k_5 W m_2/R + k_6 m_1 \quad (13)$$

Equation (13) can be tested by using the data of Boyd, Schubert and Adamson[1] (Table IV) for sodium–hydrogen equilibrations at constant total ionic strength. It was found that the equation

$$\log K_m = 0.413 - 0.110 W m_{H^+}/R \quad (14)$$

fits the data for samples 7–9 within an average deviation of 0.3%. The data for samples 1–5 show an average deviation of 1.3% from the equation

$$\log K_m = 0.137 + 0.114 W m_{Na^+}/R \quad (15)$$

If sample 4 were omitted from consideration, the average deviation would be 0.2%. (The average deviation obtained by Boyd, *et al.*,[1] without making the complete correction for mixed electrolyte activity coefficients, was 4.4%.)

It is known that $(\alpha_{12} + \alpha_{21})$ for sodium chloride and hydrochloric acid mixtures is small.[3] When the concentrations of sodium chloride and hydrochloric acid are not high, the product $(\alpha_{12} + \alpha_{21})m_1$, does not vary sufficiently to cause significant change in the calculated values of K_m. For that reason, equations (14) and (15) are accurate, notwithstanding the omission of the m_1 variable.

The observation of Tompkins and Mayer[4] that K_m is constant for exchange between $< 10^{-4}$ m cerous ion and 0.5 M ammonium ion can be explained on the basis of the considerations in this note. The concentration of cerous ion varied through the range of 10^{-10} m to 10^{-4} m; however, the total ionic strength of the solution did not vary significantly. Accordingly, equation (9) can be applied, with $Ce(ClO_4)_3$ as electrolyte 1. Because μ_1 and $[\mu_1]$ are very small, the terms containing μ_1 and $[\mu_1]$ become negligible. Accordingly, log K_m must be constant in the range below 10^{-4} m cerous perchlorate.

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[4] Tompkins and Mayer, THIS JOURNAL, **69**, 2859 (1947).

Precise Measurement of Polarographic Half-Wave Potentials

BY LOUIS MEITES

The recent polarographic literature contains many examples of half-wave potential measurements apparently accurate to ±5 mv. or better. Because of the increasing interest in refined polarographic measurements, a method has been developed which yields values with a probable error of about ±0.2 mv.

The residual current is measured at 10-mv. intervals over a range including the previously determined approximate value of the half-wave potential in question, and also at several points corresponding to the plateau of the wave. The reducible material is added and its diffusion current secured from the average of several measurements on the plateau. The applied potential is then adjusted so that the measured diffusion current is roughly half that on the plateau, and the current is measured at 1-mv. intervals on either side of this potential. After correction for the (interpolated) residual current at this potential, the half-wave potential (including, of course, the IR drop in the cell circuit) is most easily found by a short linear interpolation.

The application of the method is illustrated by the data on the tetrammino-cadmium(II) complex given in Table I. The ammonia solution was standardized against recrystallized sodium tetraborate decahydrate *via* perchloric acid. Volumetric equipment was calibrated by standard methods. Polarographic measurements were made with

TABLE I

HALF-WAVE POTENTIAL OF CADMIUM IN 0.812 F AMMONIA–0.10 F POTASSIUM NITRATE

The cadmium concentration was 0.65 millimolar. Measurements were made at 25.00 ± 0.01°

$E_{d.e.}$ *vs.* S. C. E., volt	i_r	Microamperes $i_l + i_r$		
−0.770	0.522			
− .775		2.458		
− .776	(0.526)	2.546	2.020	
− .777		2.641	2.115	
− .778		2.727		
− .780	.528			
− .950	.653	4.738	4.085	4.086
−1.000	.688	4.776	4.088	

$$E'_{1/2} = -0.776 - \left(\frac{2.043 - 2.020}{2.115 - 2.020}\right)(0.001) = -0.7762 \text{ v.}$$

$$E_{1/2} = E'_{1/2} + \frac{i_d R}{2} = -0.7762 + (2.034 \times 10^{-6})(210) = -0.7758 \text{ v.}$$

a manual instrument, using a Leeds and Northrup Type HS galvanometer as current-measuring instrument. A diagram of the circuit will be presented elsewhere. All electrical components were calibrated, and the bridge potential was checked with a Type K potentiometer at the time of use. The internal resistance of the cell under the conditions employed was found to be 210 ohms, while the additional resistance contributed by the galvanometer and its shunts was only 0.3 ohm.

Plots of $-E_{\text{d.e.}}$ against $\log (i/(i_d - i))$ for these and similar data indicate that the reduction is thermodynamically reversible.[1] Independent diffusion current measurements, made with the same capillary, gave $I = 3.205 \pm 0.009$ in 0.10 F potassium nitrate and 3.85 ± 0.01 in 0.10 F potassium nitrate–0.88 F ammonia. Then, by the fundamental equation for the reduction of a complex to the metal[1]

$$(E_{1/2})_c - (E_{1/2})_s = 0.02957 \log \frac{3.205\, K f_c}{3.85 f_s} - 0.1183 \log C_{\text{NH}_3} \quad (1)$$

where the subscripts c and s refer to the ammino- and aquo- complexes, respectively, K is the dissociation constant of the ammino- complex, and f_c and f_s the activity coefficients of the two complexes, which, for want of experimental data, we shall consider to be equal.

Table II summarizes the measurements at ammonia concentrations between 0.12 and 3.6 F. From these data and equation (1), one computes $K = 1.26\ (\pm 0.02) \times 10^{-7}$, and, with the value of the cadmium–cadmium ion standard potential given by Harned and Fitzgerald[2]

$$\text{Cd} + 4\text{NH}_3 \longrightarrow \text{Cd(NH}_3)_4{}^{++} + 2e;\quad E^0 = 0.606_0 \text{ v. (N. H. E.)}$$

TABLE II

EFFECT OF AMMONIA CONCENTRATION ON HALF-WAVE POTENTIAL OF CADMIUM(II) IN 0.10 F POTASSIUM NITRATE

All measurements were made with *ca.* 0.6 millimolar cadmium at 25.00 ± 0.01°

C_{NH_3}, F	$E_{1/2}$ *vs.* S. C. E., volt	$(E_{1/2})_c - (E_{1/2})_s + 0.1183 \log C_{\text{NH}_3}$
0	−0.5777	......
0.1267	− .6776	−0.2065
.310	− .7243	− .2066
.433	− .7407	− .2060
.550	− .7535	− .2064
.812	− .7758	− .2068
1.120	− .7899	− .2065
1.389	− .8033	− .2078
1.890	− .8206	− .2103
2.79_0	− .8441	− .2135
3.56_5	− .8604	− .2172
	Mean ($C_{\text{NH}_3} < 1.2$ F)	−0.2064 ± 0.0002

Further, with the standard free energy of NH_3 (aq.) given by Latimer,[3] $F_{\text{Cd(NH}_3)_4{}^{++}} = -53{,}280$ cal.

$$F^0_{\text{Cd(NH}_3)_4{}^{++}} = -53{,}280 \text{ cal.}$$

Previously Lingane had found −0.578 v. for the half-wave potential of cadmium in 0.1 F potassium nitrate[4] and −0.81 v. in 1 F ammonia–1 F ammonium chloride.[5] Neglecting, as here, correction for activity effects, Euler[6] found 1×10^{-7} for the dissociation constant of the ammino- complex from potentiometric measurements.

The deviation in concentrated ammonia solutions is probably to be attributed to the formation of such complexes as $\text{Cd(NH}_3)_5{}^{++}$.

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[1] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946, pp. 161–165.

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

[3] W. M. Latimer, "The Oxidation States of the Elements and Their Potentials in Aqueous Solution," Prentice-Hall, Inc., New York, N. Y., 1938, p. 305.

[4] J. J. Lingane, THIS JOURNAL, **61**, 2099 (1939).

[5] J. J. Lingane, *Ind. Eng. Chem., Anal. Ed.*, **15**, 583 (1943).

[6] H. Euler, *Ber.*, **36**, 3400 (1903).

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The Preparation of Calcium D-Arabonate from Calcium 2-Keto-D-gluconate by Electrolytic Bromine Oxidation

BY C. L. MEHLTRETTER, W. DVONCH AND C. E. RIST

Isbell and Frush and others[1] have shown that aqueous solutions of D-glucose in the presence of calcium carbonate can be oxidized to calcium D-gluconate in nearly quantitative yield with bromine generated electrolytically. By prolonging the electrolysis so as to consume twice the current required for the conversion of D-glucose to D-gluconic acid, Cook and Major[2] were able to isolate calcium 5-keto-D-gluconate in small amount.

In a study of the oxidation of calcium D-gluconate by electrolytic bromine whereby 4 faradays of electricity per mole of gluconate was used, we obtained calcium D-arabonate as well as the calcium salts of 5-keto-D-gluconic and oxalic acids. The crude calcium D-arabonate was converted to D-arabobenzimidazole,[3] from which the yield was calculated to be 9%. Electrolysis with 8 faradays per mole of calcium D-gluconate resulted in a 17% yield of calcium D-arabonate. The presence of 2-keto-D-gluconic acid could not be detected in any of the oxidized solutions.

The transformation of calcium D-gluconate to arabonate suggested that calcium 2-keto-D-gluconate is first formed and is then rapidly decarboxylated and oxidized to calcium D-arabonate. Honig and Tempus[4] proposed such a mechanism for the hypobromite oxidation of D-glucose because both 2-keto-D-gluconic and D-arabonic acids were

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[1] (a) Isbell and Frush, *J. Research Nat. Bur. Standards*, **6**, 1145 (1931); (b) Helwig (to Rohm and Haas Co.) U. S. Patent 1,937,273 (Nov. 28, 1933); (c) Fink and Sommers, *Trans. Electrochemical Soc.*, **74**, 625 (1938).

[2] Cook and Major, THIS JOURNAL, **57**, 773 (1935).

[3] Moore and Link, *J. Biol. Chem.*, **133**, 293 (1940).

[4] Honig and Tempus, *Ber.*, **57**, 787 (1924).