and vanadates[14] and the respective peroxy compounds[15] is also inadequate, and no quantitative interpretation of the effect of the various factors presented in this paper can be given.

(14) G. Jander and K. Jahr, *Z. anorg. allgem. Chem.*, **211**, 49 (1933); **212**, 1 (1933); G. Jander, K. Jahr and H. Witzmann, *ibid.*, **217**, 65 (1934); J. Meyer and A. Pawletta, *Z. angew. Chem.*, **39**, 1284 (1926); P. Souchay and G. Carpeni, *Bull. soc. chim.*, 160 (1946).

(15) K. Jahr, *Fiat Rev. Germ. Science*, III, p. 180, 1939–1946, *Ing. chim.*; *Angew Chem.*, **54**, 94 (1941); M. E. R. Nordmann, *Compt. rend.*, **212**, 485 (1946); K. Jahr, *Ber. Ges. Freund Tech. Hochschule*, Berlin, 1941, No. 1, 55; *Z. Elektrochem.*, **47**, 810 (1941); J. Meyer and A. Pawletta, *Z. physik. Chem.*, **125**, 49 (1927); M. E. Rumpf, *Ann. chim.*, 11E, 485 (1937).

MINNEAPOLIS, MINN. RECEIVED MAY 7, 1951

---

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF KANSAS]

# The Determination of Consecutive Formation Constants of Complex Ions from Polarographic Data

BY DONALD D. DEFORD[1] AND DAVID N. HUME[2]

**A method for the mathematical analysis of the change in half-wave potential of a metal ion with changes in the concentration of the complexing agent is derived. The identification of the successive complex ions formed and the determination of their formation constants are thus made possible.**

The polarograph has been extensively used in the study of complex ions which are reversibly electroreduced at the dropping mercury electrode. If a metal ion forms only one complex over a considerable range of ligand concentration, it is possible to determine from a plot of half-wave potential against the logarithm of ligand concentration, the number of ligands bound in the complex, and by the shift in half-wave potential from that of the simple ion, the dissociation constant.[3] Hitherto, data derived from systems involving mixtures of consecutively formed complex ions have not been interpretable. During the last ten years a great deal of interest has been developed in the study of consecutively formed complex ions largely through the pioneering work of Bjerrum.[4] Leden[5] has described an ingenious and useful method of taking and interpreting potentiometric data for the evaluation of consecutive formation constants. In this paper is described a method of mathematical analysis of the shift of half-wave potential with ligand concentration which makes possible the identification of the successive complex ions formed and the evaluation of their formation (or dissociation) constants. The sign conventions are those of reference 3.

For complex ions of a metal which is soluble in mercury, the reduction to the metallic state (amalgam) at the dropping mercury electrode may be represented by

$$MX_j^{+(n-jb)} + ne \rightleftarrows M(\text{amalgam}) + jX^{-b} \quad (1)$$

where $X^{-b}$ is the complex-forming substance. For convenience, this reaction may be regarded as the sum of the partial reactions

$$MX_j^{+(n-jb))} \rightleftarrows M^{+n} + jX^{-b} \quad (2)$$

and

$$M^{+n} + ne \rightleftarrows M(\text{amalgam}) \quad (3)$$

where $M^{+n}$ symbolizes the simple (hydrated) metal ions. If the electrode reactions are reversible, the potential of the dropping electrode is given by

$$E_{d.e.} = E^0_a - \frac{RT}{nF}\ln\frac{C^0_a f_a}{C^0_M f_M} \quad (4)$$

where $C^0_a$ is the concentration of the amalgam at the electrode surface, $C^0_M$ is the concentration of simple metal ions at the electrode surface, and the $f$'s are the corresponding activity coefficients. Since the amalgams formed at the electrode surface are very dilute, $f_a$ may be considered to be unity and will be neglected hereafter.

If the formation of the complex ions is rapid and reversible, then for each individual complex

$$C_{MXj} f_{MXj} = K_j C_M f_M (C_X)^j (f_X)^j \quad (5)$$

where $K_j$ is the formation constant of the complex $MX_j^{+(n-jb)}$, $C_{MXj}$ is the concentration of the complex in the body of the solution, $C_M$ is the concentration of the simple metal ion in the body of the solution, $C_X$ is the concentration of the complex-forming substance, and the $f$'s are the corresponding activity coefficients. Also

$$C^0_{MXj} f_{MXj} = K_j C^0_M f_M (C_X)^j (f_X)^j \quad (6)$$

where the zero superscripts refer to concentrations at the electrode surface. It is assumed that the complex-forming substance is present in relatively large excess so that the concentration of this substance at the electrode surface is virtually equal to the concentration in the body of the solution.

Addition of the equations for the individual complexes as represented by equation (6) and rearrangement of the resulting equation shows that

$$C^0_M f_M = \frac{\sum\limits_j C^0_{MXj}}{\sum\limits_j \frac{K_j (C_X)^j (f_X)^j}{f_{MXj}}} \quad (7)$$

Combination of equations (4) and (7) gives

$$E_{d.e.} = E^0_a - \frac{RT}{nF}\ln\frac{C^0_a \sum\limits_j \frac{K_j (C_X)^j (f_X)^j}{f_{MXj}}}{\sum\limits_j C^0_{MXj}} \quad (8)$$

When an excess of supporting electrolyte is pres-

---

[1] Department of Chemistry, Northwestern University, Evanston, Illinois.

[2] Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Massachusetts.

[3] I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941.

[4] J. Bjerrum, "Metal Amine Formation in Aqueous Solution," P. Maase and Son, Copenhagen, 1941.

[5] I. Leden, *Z. physik. Chem.*, **188A**, 160 (1941).

ent to eliminate the migration current, the current at any point on the wave is given by

$$i = \sum_{j} i_j = k \sum_{j} I(C_{jMX_j} - C^0_{MX_j}) \qquad (9)$$

where $k$ is the capillary constant, $m^{2/3}t^{1/6}$, and $I_j$ is the diffusion current constant, $607nD^{1/2}$ of the complex $MX_j$. From equations (5), (6) and (9), it follows that

$$i = kI_c \sum_{j} (C_{MX_j} - C^0_{MX_j}) \qquad (10)$$

where $I_c$ is the apparent (measurable) diffusion current constant, which is related to the individual $I_j$ values by

$$I_c = \frac{\sum\limits_{j} \frac{I_j k_j (C_X)^j (f_X)^j}{f_{MX_j}}}{\sum\limits_{j} \frac{k_j (C_X)^j (f_X)^j}{f_{MX_j}}} \qquad (11)$$

Similarly, the diffusion current is given by

$$i_d = k\,I_c \sum_{j} C_{MX_j} \qquad (12)$$

It is also known that the concentration of the amalgam at the electrode surface is related to the current by

$$i = kI_M C^0_a \qquad (13)$$

where $I_M$ is the diffusion current constant of the metal atoms in mercury. Combination of equations (8), (10), (12) and (13) shows that the half-wave potential of the reducible ion in the presence of the complex-forming substance is given by

$$(E_{1/2})_c = E^0_a - \frac{RT}{nF} \ln \frac{I_c}{I_M} \sum_{j} \frac{k(C_X)^j f_X{}^j}{f_{MX_j}} \qquad (14)$$

Similar considerations show that the half-wave potential of the simple metal ion is given by

$$(E_{1/2})_s = E^0_a - \frac{RT}{nF} \ln \frac{I_s}{f_s I_M} \qquad (15)$$

The half-wave potential of the simple metal ion when its activity coefficient is unity is given by

$$(E^0{}_{1/2})_s = (E_{1/2})_s - \frac{RT}{nF} \ln f_s = E^0_a - \frac{RT}{nF} \ln \frac{I_s}{I_M} \qquad (16)$$

Combination of equations (14) and (16) gives, on rearrangement

$$F_0(X) = \sum_{j} \frac{K_j C_X^j f_X^j}{f_{MX_j}} =$$
$$\text{antilog} \left\{ 0.435 \frac{nF}{RT} [(E^0{}_{1/2})_s - (E_{1/2})_c] + \log \frac{I_s}{I_c} \right\} \qquad (17)$$

where the symbol $F_0(X)$ is introduced for convenience to represent the experimentally measurable quantity on the right-hand side of the equation.

We now introduce the function $F_1(X)$ defined by the relationship

$$F_1(X) = [F_0(X) - (k_0/f_s)]/C_X f_X \qquad (18)$$

where $K_0$ is the formation constant of the zero complex, which is, of course, unity. If $F_1(X)$ is plotted against $C_X f_X$ and is extrapolated to $C_X = 0$, it is apparent that the value of $F_1(X)$ at the intercept is equal to $K_1/f_{MX}$. Likewise, the value of $K_2/f_{MX_2}$ is given by the value of $F_2(X)$ at the intercept when the function $F_2(X)$, defined by the relationship

$$F_2(X) = [F_1(X) - (K_1/f_{MX})]/C_X f_X \qquad (19)$$

is plotted against $C_X f_X$ and is extrapolated to $C_X = 0$. The formation constants of higher complexes may be determined in a similar manner.

It is apparent from equation (17) that the first derivative of $F_0(X)$ with respect to $C_X f_X$ is equal to $F_1(X)$, when $C_X = 0$. If $F_0(X)$, including the value $F_0(X) = 1$ at $C_X = 0$, is plotted as a function of $C_X f_X$, the slope of this curve at $C_X = 0$ will be equal to the value of $F_1(X)$ at $C_X = 0$. Similarly, at $C_X = 0$ the slope of the curve obtained by plotting $F_1(X)$ as a function of $C_X f_X$ gives a value for $F_2(X)$ at $C_X = 0$, and so on for the higher complexes. Measurement of the limiting slope of the previous $F(X)$ curves serves as a useful check on the value of $K_j$ obtained by extrapolation.

The mathematical form of the $F$-functions has several interesting consequences. It will be observed that a plot of the $F(X)$ *versus* $C_X f_X$ for the *last* complex will be a straight line parallel to the concentration axis. A similar plot for the immediately preceding complex will be a straight line with a positive slope, and all previous $F$-function plots will show curvature. These characteristics aid in establishing the number of complex ions formed in a given system and also provide a qualitative check on the validity of the data.

At the time of the development of the above relations, the only precise data available to the authors for the testing of the theory were some measurements on the half-wave potential of the cadmium ion as a function of thiocyanate concentration in the range of 0.1 to 6.0 *M*.[6] These measurements were, unfortunately, not made at constant ionic strength. Application of the method, ignoring all activity coefficients, gave values of $K_1 = 16$, $K_2 = 63$ and $K_3 = \sim 1$ with indications of one or more higher complexes of relatively low stability. It was felt that although the data did not justify quantitative interpretation beyond the first two or three formation constants, the essential validity of the method had been demonstrated.

More recently we have studied the cadmium–thiocyanate system at constant ionic strength in another laboratory and the results of these experiments, which show clearly the application of method, are described in the following paper.[7]

Subsequently, with the aid of other collaborators we have applied the method successfully to the study of the lead–nitrate, lead–thiocyanate, thallous–thiocyanate, lead–acetate and cadmium–acetate systems. These investigations will be described in later communications.

EVANSTON, ILLINOIS
CAMBRIDGE, MASSACHUSETTS
RECEIVED APRIL 23, 1951

---

[6] D. D. DeFord, M.A. Thesis, University of Kansas, 1947.

[7] D. N. Hume, D. D. DeFord and G. C. B. Cave, THIS JOURNAL, **73**, 5323 (1951).