THE STUDY OF COMPLEXED METAL IONS BY POLAROGRAPHIC METHODS

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1. Introduction

The polarographic reduction wave of a simple (aquo) metal ion is usually shifted in the direction of more-negative potential on addition of a complexing agent. Direct measurement of the shift in half-wave potential can serve for the determination of stability constants of complexes in solution, provided that reactions at the dropping-mercury electrode occur reversibly. With suitable modifications, however, irreversible cases can be dealt with in many instances.

Comparatively few systems are such that direct application of simpler theory serves for stability constant determination. In many instances, reduction waves are both kinetically and diffusion controlled, and the rates of dissociation of complex species control, to a greater or lesser extent, the shapes of the waves. Systems consisting of several complexes are encountered in which both reducible and non-reducible species occur, in which equilibria between some species are less mobile than others. The overall kinetics of several such systems have been elucidated and the nature, structure, and behaviour of each species identified in addition to the calculation of their stability constants. From such applications, the polarograhic method has been developed as a useful tool for the determination of the structure of complexes. In the past, stability constant data, and little more, resulted from the study of complex systems. While there is still a lack of such important data, work in recent years has more constructively turned to the problem of determining the overall mechanism by which complexes of different, known, structures undergo reduction. Unknown structures may then be inferred from similar polarographic behaviour or confirmation may be given for structures already indicated by other techniques.

2. Stability Constant Determinations from Reversible Reductions

(a) Formation of a Single Complex.—The Heyrovsky–Ilkovic equation[1] expresses the half-wave potential ($E_{\frac{1}{2}}$) for the reduction of a metallic species in terms of the diffusion current (i_d) and the current(i) at any other point on the polarographic wave, corresponding to the potential ($E_{d.e.}$) applied to the mercury drops.

$$E_{d.e.} = E_{\frac{1}{2}} - \frac{RT}{nF} \ln \frac{i}{i_d - i} \qquad (1)$$

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[1] J. Heyrovsky and D. Ilkovic, *Coll. Czech. Chem. Comm.*, 1935, 7, 198.

The validity of this equation has received ample experimental verification.[2,3]

Provided that the reductions occur reversibly, the $E_{\frac{1}{2}}$ value of a complexed species, MX_j, will have a more-negative value than that of the "simple" (aquo) species M. A measure of this shift serves to determine both the co-ordination number and the stability constant of the complex. It can fairly simply be shown that the shift, to a first approximation, by ignoring activity coefficients, may be expressed in the following relationship:[4]

$$(E_{\frac{1}{2}})_S - (E_{\frac{1}{2}})_C = \frac{0{\cdot}0591}{n} \log_{10} \beta_j + j\,\frac{0{\cdot}0591}{n} \log_{10} C_X \text{ (at 25°)}, \qquad (2)$$

in which $(E_{\frac{1}{2}})_S$ and $(E_{\frac{1}{2}})_C$ are the half-wave potentials of the simple and complexed species, respectively, j, is the co-ordination number of the complex, β_j its stability constant, and C_X the ligand concentration.

Half-wave potentials of complexed metal ions shift with changing activity of the complexing ligand in accordance with:

$$\frac{\Delta E_{\frac{1}{2}}}{\Delta \log_{10} C_X \gamma_X} = -j.\,\frac{0{\cdot}0591}{n} \text{ (at 25°)} \qquad (3)$$

Hence the number of ligands, j, bound in the complex is found from a plot of $\log_{10} C_X$ against $(E_{\frac{1}{2}})_C$, which, in the present case, should be linear. By the application of eqn. (2), Lingane[4] showed the presence of the hydrogen plumbite ion, in a strongly alkaline solution of lead hydroxide, whose reversible reduction is represented by

$$HPbO_2^- + H_2O + 2e \rightleftharpoons Pb(Hg) + 3\ OH^- \qquad (4)$$

(b) Formation of a Series of Complexes with a Single Ligand Type.—In this category, there are essentially two classes of systems, *viz*, (i) those in which each complex species exists only within a definite region of ligand concentration (*i.e.*, two or more complexes, with different co-ordination numbers, are not present together), and (ii) systems which consist of a series of complexes in step-equilibrium (*i.e.*, two or more complexes co-exist, but different species predominate at particular ligand concentrations).

(i) Occasionally, a plot of $\log_{10} C_X$ against $(E_{\frac{1}{2}})_C$ produces a segmented curve, indicating the presence of a series of complexes whose stability constants and formulae may be found from the various segments. Such behaviour is shown, for example, in the ferro–ferri–oxalate,[4,5] the zinc–ammonia,[6] and cadmium–pyrazole systems.[7] It has been demonstrated

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[2] I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, 1939, **24**, 1.

[3] J. Tomes, *Coll. Czech. Chem. Comm.*, 1937, **9**, 150.

[4] J. J. Lingane, *Chem. Rev.*, 1941, **29**, 1.

[5] M. von Stackelberg and H. von Freyhold, *Z. Elektrochem.*, 1940, **46**, 120.

[6] R. Cernatescu, I. Popescu, A. Cracium, M. Bostan, and N. Iorga, *Studii si Cercetari Sti. Chim.* (*Fil. Iasi*), 1958, **9**, 1.

[7] A. C. Andrews and J. K. Romary, *Inorg. Chem.*, 1963, **2**, 1060.

that, for the segmentation of the curves to be sufficiently pronounced for the calculation of stability constant data, the constants must differ by a power of ten or more.

(ii) For a system of complexes in step-equilibrium, the plot of $\log_{10}C_X$ against $(E_{\frac{1}{2}})_C$ is a continuous curve. The first serious attempt to consider the full implications of step-equilibria in the study of complex-formation by the polarographic method was made by DeFord and Hume[8] who obtained the following relation between the change in half-wave potential and the free-ligand concentration [X] for a reversible metal deposition:

$$\text{Antilog}_{10}\left[\frac{0{\cdot}4343nF}{RT}\cdot\Delta E_{\frac{1}{2}}+\log_{10}\cdot\frac{I_M}{I_C}\right]=\gamma_M\sum_{0}^{N}\frac{\beta_j[\mathrm{X}]^j\gamma_X{}^j}{\gamma_{MX_j}} \tag{5}$$

$$=\beta_0+\beta_1\,[\mathrm{X}]\cdot\frac{\gamma_M\gamma_X}{\gamma_{MX}}+\beta_2\,[\mathrm{X}]^2\cdot\frac{\gamma_M(\gamma_X)^2}{\gamma_{MX_2}}+\dots\dots+\beta_N[\mathrm{X}]^N\cdot\frac{\gamma_M(\gamma_X)^N}{\gamma_{MX_N}} \tag{6}$$

$$[\Delta E_{\frac{1}{2}}=(E_{\frac{1}{2}})_s-(E_{\frac{1}{2}})_c]$$

Here, I_M and I_C are the diffusion-current constants for aquo and complex metal ions, respectively, the γ's are activity coefficients, the β's are stability constants ($\beta_0 = 1$ for the "zero" complex), and [X] = free-ligand concentration.

The current–potential curve for such a deposition has been shown to be:[9]

$$E_{\mathrm{d.e.}}=E^0-\frac{RT}{nF}\ln\sum_{0}^{N}\beta_j[\mathrm{X}]^j-\frac{RT}{nF}\ln\frac{i}{i_d-i} \tag{7}$$

The graphical method due to Leden[10] is then applied. If all measurements are made at the same ionic strength and the activity quotients dropped from eqn. (6), the right-hand side may be denoted by $F_0[\mathrm{X}]$, indicating that it is a function of free-ligand concentration, and written as follows:

$$F_0[\mathrm{X}]=\beta_0+\beta_1[\mathrm{X}]+\beta_2[\mathrm{X}]^2+\dots\dots+\beta_N[\mathrm{X}]^N \tag{8}$$

A new function, $F_1[\mathrm{X}]$, may then be defined by:

$$F_1[\mathrm{X}]=\left[\frac{F_0[\mathrm{X}]-\beta_0}{[\mathrm{X}]}\right]=\beta_1+\beta_2[\mathrm{X}]+\beta_3[\mathrm{X}]^2+\dots\dots \tag{9}$$

In a similar manner, other functions may be derived, giving finally:

$$F_N[\mathrm{X}]=\left[\frac{F_{N-1}[\mathrm{X}]-\beta_{N-1}}{[\mathrm{X}]}\right]=\beta_N \tag{10}$$

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[8] D. D. DeFord and D. N. Hume, *J. Amer. Chem. Soc.*, 1951, **73**, 5321.

[9] P. Kivalo and H. A. Laitinen, *J. Amer. Chem. Soc.*, 1955, **77**, 5205.

[10] I. Leden, *Z. phys. Chem.*, 1941, **188**, 160.

From eqn. (9), a plot of $F_1[X]$ against [X] gives a curve having a limiting slope of β_2 at [X] $= 0$, and an intercept of β_1. Such plots are made for each function until all the complex species are accounted for, the penultimate graph being linear with positive slope and that for the highest complex a straight line parallel to the concentration axis. Fig. 1 is a schematic representation of a set of graphs expected for such a system with three complex species formed. In the original DeFord–Hume derivation,[8] $(E_{\frac{1}{2}})_S$ was designated $(E_{\frac{1}{2}}{}^0)_S$ to indicate that it was the half-wave potential of the simple ion when its activity was unity. There is then little justification for assuming that the first term in eqn. (6) is unity, it is, in fact, β_0/γ_M. As used above, $(E_{\frac{1}{2}})_S$ refers to the value obtained in a medium of the same ionic strength as that used in the measurements on the complexed cation.

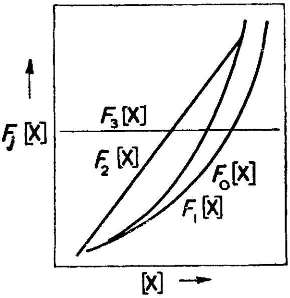

FIG. 1. *Schematic plots of* F[X] *functions for a system of three complex species in step-equilibrium.*

For a particular system, the ligand number, $\bar{n}$, is defined[11] by:

$$\bar{n} = \frac{d(\log_{10}F_0[X])}{d(\log_{10}[X])}, \qquad (11)$$

so that a plot of $\log_{10}F_0[X]$ against $\log_{10}[X]$ gives a curve whose slope at any point gives the value of $\bar{n}$ corresponding to a particular value of [X]. $\bar{n}$ then represents the average composition, $MX_{\bar{n}}$, of the species present in solution. On increasing [X], the composition will approach that of the highest complex, MX_N, and eqn. (5) may be expressed in the form

$$\frac{0{\cdot}4343nF}{RT}\cdot\Delta E_{\frac{1}{2}} + \log_{10}\frac{I_M}{I_C} = \log_{10}\beta_N + N\log_{10}[X] \qquad (12)$$

Eqn. (12) is identical with eqn. (2) under these limiting conditions if it is assumed that $I_M = I_C$ and $[X] = C_X$. The earliest practical applications of the theoretical work of DeFord and Hume were to the cadmium and

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[11] H. Irving, "Advances in Polarography," Pergamon, London, 1960, vol. 1, p. 49.

zinc thiocyanate complexes. Hume *et al.*[12] determined the half-wave potentials of the cadmium ion in potassium nitrate–thiocyanate mixtures over a thiocyanate concentration range 0·1—2·0 M at a constant ionic strength of 2 M. The above treatment revealed the presence of four complex species, $CdSCN^+$, $Cd(SCN)_2$, $Cd(SCN)_3^-$, and $Cd(SCN)_4^{2-}$, with consecutive stability constants 11, 56, 6, and 60, respectively. Over this thiocyanate concentration range, the half-wave potential was observed to change from —0·5724 v to —0·6646 v [against standard calomel electrode (S.C.E.)], with a corresponding decrease in the diffusion current from 7·56 μA to 7·03 μA. Such small shifts in $E_{\frac{1}{2}}$ values demand very careful measurement and this can only satisfactorily be done by the use of manual equipment. In the case of the zinc complexes, the overall shift was from —0·9977 v to —1·079 v (against S.C.E.),[13] so small that earlier investigators had reported the absence of complex-formation.[14] A recent study of the cadmium–azide system[15] revealed the presence of the five complex species CdN_3^+, $Cd(N_3)_2$, $Cd(N_3)_3^-$, $Cd(N_3)_4^{2-}$, and $Cd(N_3)_5^{3-}$.

(c) Formation of Mixed-ligand Complexes.—Since the above early applications, many other systems have been studied. A notable contribution, which seems to have aroused little interest, is the extension of the DeFord–Hume approach by Schaap and McMasters[16] to deal with mixed-ligand systems. For a complexing reaction of the type

$$M + iX + jY + \ldots\ldots = MX_iY_j\ldots\ldots \qquad (13)$$

in which $i, j, \ldots\ldots$ are stoicheiometry numbers, and X, $Y, \ldots\ldots$ are different ligands, the DeFord–Hume expression for the $F_0[X]$ function may be extended to give a new function, $F_{00\ldots\ldots}[X,Y,\ldots\ldots]$, given by:

$$F_{00\ldots\ldots}[X,Y\ldots\ldots] = \sum_{0}^{N} \beta_{i,j}\ldots[X]^i[Y]^j\ldots\ldots/\gamma_{MX_iY_j}\ldots \qquad (14a)$$

$$= \text{antilog}\left\{\frac{nF}{RT}\cdot\Delta E_{\frac{1}{2}} + \log\frac{I_M}{I_c\gamma_M}\right\} \qquad (14b)$$

As before, each term in eqn. (14*a*) is determinable except for γ_M,which is included in the resultant equilibrium constants. For a total of three bound ligands, of the type X and Y, factorisation of the F_{00} function leads to:

$$F_{00}[X,Y] = \{\beta_0 + \beta_{01}[Y] + \beta_{02}[Y]^2 + \beta_{03}[Y]^3\}[X]^0$$
$$+ \{\beta_{10} + \beta_{11}[Y] + \beta_{12}[Y]^2\}[X] + \{\beta_{20} + \beta_{21}[Y]\}[X]^2 \qquad (15)$$
$$+ \{\beta_{30}\}[X]^3$$

$$\text{or } F_{00}[X,Y] = A + B[X] + C[X]^2 + D[X]^3 \qquad (16)$$

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[12] D. N. Hume, D. D. DeFord, and G. C. B. Cave, *J. Amer. Chem. Soc.*, 1951, **73,** 5323.

[13] R. E. Frank and D. N. Hume, *J. Amer. Chem. Soc.*, 1953, **75,** 1736.

[14] P. R. Stout and J. Levy, *Coll. Czech. Chem. Comm.*, 1938, **10,** 136.

[15] P. Senise and E. F. de Almeida Neves, *J. Amer. Chem. Soc.*, 1961, **83,** 4146.

[16] W. B. Schaap and D. L. McMasters, *J. Amer. Chem. Soc.*, 1961, **83,** 4699.

where, for a given [Y], A, B, C, and D are constants. The original graphical solution may be applied to the F_{00} data if the activity of one of the ligands is held constant while that of the other is varied. For the copper- and cadmium–ethylenediamine–oxalate systems, the oxalate concentration was held constant (at several fixed values) while that of ethylenediamine was varied. Thus, $[X] \equiv [en]$, and $[Y] \equiv [ox]$. For the Cd–en–ox system, in which possible mixed complexes are Cd(en)(ox), $Cd(en)_2(ox)$, and $Cd(en)(ox)_2^{2-}$, values of A and D were known from studies of the simple Cd–en and Cd–ox systems. B was obtained graphically from the F_{10} function, defined by

$$F_{10} = \left[\frac{F_{00} - A}{[en]}\right] = B + C[en] + D[en]^2, \qquad (17)$$

by plotting F_{10} against [en]. Similarly, C is given by the F_{20} function:

$$F_{20} = \left[\frac{F_{10} - B}{[en]}\right] = C + D[en] \qquad (18)$$

With a knowledge of C, the mixed-complex stability constant, β_{21}, may be calculated, but, in order to determine β_{11} and β_{12}, B must be evaluated for at least two different oxalate concentrations.

3. Stability Constant Data from Irreversible Waves

There are two essential approaches to the determination of stability constants from irreversible waves. These involve the use, on the one hand, of diffusion-current measurements and of half-wave-potential data on the other. In the majority of cases, a process of competition for a ligand by the metal studied and an "indicator ion" is used.

(a) The Use of Current Measurements.—In all the relations so far given, it is usually assumed that the diffusion coefficients of the various species in solution do not differ to any great extent from one another and that the limiting current is therefore independent of ligand concentration. Should there be a measurable difference between the diffusion coefficients of a metal M and its complex MX, the stability constant of the latter species may be determined by observing the change of diffusion current with ligand concentration[17,18] and applying the relation[19]

$$\bar{D} = \frac{D_M + D_{MX}\,\beta_{MX}\,[X]}{1 + \beta_{MX}[X]}, \qquad (19)$$

where D_M and D_{MX} are the diffusion coefficients of the free and complexed metal ions, respectively, and $\bar{D}$ is the observed mean coefficient in a solution containing the two species. Eqn. (19) can only be used for systems containing a complex with one bound ligand, but, since no poten-

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[17] V. Kačena and L. Matoušek, *Coll. Czech. Chem. Comm.*, 1953, **18**, 294.

[18] Z. Zabransky, *Coll. Czech. Chem. Comm.*, 1959, **24**, 3075.

[19] J. Koryta, "Progress in Polarography," ed. P. Zuman, Interscience, New York, 1962, vol. 1, p. 291.

tial measurements are needed, it may be applied to irreversible processes. Use of the method assumes a rapid attainment of equilibrium between the metal ion and the complex.

In the case of very stable complexes, for which completely non-labile equilibria may be assumed, current measurements may also serve to provide stability constant data, by use of a method of competitive complex-formation largely developed by Schwarzenbach and his co-workers.[20–22] Suppose that a metal complex MX is irreversibly reduced or is even electro-inactive at the dropping-mercury electrode. In order that the stability constant of MX may be determined, it is necessary to have access to a complex NX whose stability constant is known and is of the same order as that of MX. The wave for uncomplexed N must be reversible, occur at a more positive potential than that of M, and be undetectable in the presence of NX when N and X are present together in equivalent concentrations. Briefly, the experimental procedure is as follows: polarograms are obtained for N in both the presence and absence of X. A measured quantity of M is now added, which competes for the ligand X, some of which it abstracts from the previously formed NX, finally setting up the equilibrium

$$\mathrm{M} + \mathrm{NX} \rightleftharpoons \mathrm{MX} + \mathrm{N} \tag{20}$$

By this action, ions of N are liberated and reduction waves are observed for both N and NX, whose heights are directly proportional to the concentrations (Fig. 2). By observing the above conditions, waves for M and X do not interfere; that of MX might well appear after that of hydrogen. The equilibrium constant for reaction (20) is given by

$$K = \frac{i_b{}^2 . C_N}{(i_N - i_b)(C_M i_N - C_N i_b)} = \frac{K_{NX}}{K_{MX}} \tag{21}$$

Hence, when K_{NX} is known, K_{MX} is determinable. This technique has been used by Schwarzenbach and Sandera[23] in studies of vanadium complexes with ethylenediaminetetra-acetic acid (E.D.T.A.), using copper as the indicator ion N, MX being Na_2VOY and NX, Na_2CuY. Many metals have been employed as the auxiliary cation in this method, *e.g.*, manganese, zinc, cadmium, mercury, copper, and iron in the determination of stability constants of aminopolycarboxylate complexes of many metal ions including the lanthanides.[24–28]

[20] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta.*, 1952, **35**, 485.

[21] G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta.*, 1954, **37**, 937.

[22] K. Bril and P. Krumholz, *J. Phys. Chem.*, 1953, **57**, 874.

[23] G. Schwarzenbach and J. Sandera, *Helv. Chim. Acta.*, 1953, **36**, 1089.

[24] L. Holleck and G. Liebold, *Naturwiss*, 1957, **22**, 582.

[25] D. M. H. Kern, *J. Amer. Chem. Soc.*, 1959, **81**, 1563.

[26] F. H. Spedding, J. E. Powell, and E. J. Wheelwright, *J. Amer. Chem. Soc.*, 1956, **78**, 34.

[27] G. Schwarzenbach and R. Gut, *Helv. Chim. Acta.*, 1956, **39**, 1589.

[28] E. J. Wheelwright, F. H. Spedding, and G. Schwarzenbach, *J. Amer. Chem. Soc.*, 1953, **75**, 4196.

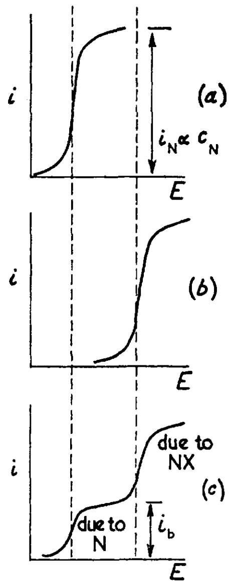

FIG. 2. (*a*) *Polarogram of metal ion* N. (*b*) *Polarogram of complex-ion* NX. (*c*) *Superposition of wave due to* N *upon that of* NX *on addition of metal ion* M.

(b) The Use of Potential Data.—A method due to Subrahmanya[29] utilises a modification of the treatment of Lingane by Tamamushi and Tanake[30] for an irreversible process, *i.e.*,

$$\frac{\Delta E}{\Delta \log C_{\mathrm{X}}} = \frac{-j \times 2{\cdot}303\boldsymbol{RT}}{\alpha n\boldsymbol{F}} \tag{22}$$

By using the modified Heyrovsky–Ilkovic equation for an irreversible reduction:

$$E_{\mathrm{d.e.}} = E_{\frac{1}{2}} - \frac{\boldsymbol{RT}}{\alpha n\boldsymbol{F}} . \ln \frac{i}{i_{\mathrm{d}} - i}, \tag{23}$$

$$i.e., E_{\frac{3}{4}} - E_{\frac{1}{4}} = \frac{2\boldsymbol{RT}}{\alpha n\boldsymbol{F}} . \ln 3, \tag{24}$$

from which αn was evaluated. Thus j was solved and the dissociation constant K_{c} deduced from the expression:

$$(E_{\frac{1}{2}})_{\mathrm{c}} - (E_{\frac{1}{2}})_{\mathrm{s}} = \frac{\boldsymbol{RT}}{\alpha n\boldsymbol{F}} \ln K_{\mathrm{c}} - \frac{j\boldsymbol{RT}}{\alpha n\boldsymbol{F}} \ln C_{\mathrm{X}} \tag{25}$$

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[29] R. S. Subrahmanya, "Advances in Polarography," Pergamon, London, 1960, vol. 2, p. 674.

[30] R. Tamamushi and N. Tanaka, *Bull. Chem. Soc. Japan*, 1949, **22**, 227.

The method has been applied to the study of the mono-, di-, and triethanolamines of iron, cadmium, nickel, cobalt, copper, lead, and zinc at 30° in alkaline media. A few of the mono- and di-ethanolamine compounds are reversible, but the triethanolamine complexes are invariably irreversible. In addition, at higher pH values, OH^-, NH_3, and CO_3^{2-} tend to enter the complex, and, by variation of the concentration of these species, with constant amount of complexing agent in the base solution, some of these additional species have been identified and their dissociation constants calculated. However, the success of the method relies upon the reversibility of the simple ion in eqn. (24), and conditions giving a constant value of α, so that it was inapplicable to cobalt and nickel, although the formulae of the complexes, including the mixed-ligand complexes, were deduced.

A further technique, based on theoretical suggestions of Ringbom and Eriksson,[31,32] also uses an indicator ion to compete, with the ion studied, for the complexing ligand. The method can be used, in principle at least, for studying systems containing a single complex or a series of complexes in mobile equilibrium which are electro-inactive or which give irreversible waves. If the indicator metal ion N is present in solution with an excess of ligand, addition of ions M will decrease the free-ligand concentration and give a consequent shift of the wave for the N–X system to more-positive values. It is necessary that M should react very rapidly with the ligand and that the complex equilibrium is established almost instantaneously. That the latter may not occur, is a weak feature of the method. A preliminary experiment is performed in which the shift in half-wave potential for the system NX is determined with increasing free-ligand concentration. The position of $E_{\frac{1}{2}}$ for the system NX when M has been added then gives directly the free-ligand concentration from the preliminary calibration.

The ligand number for the system MX is given by

$$\bar{n} = \frac{C_X - [X] - \frac{\bar{n}' C_N}{2}}{C_M} \tag{26}$$

at the half-wave potential,[33] where $\bar{n}'$ is the ligand number of the system NX, [X] the free-ligand concentration, C_X the total ligand concentration, C_N the concentration of N, and C_M the concentration of M.

If the activity coefficients are neglected, the DeFord–Hume F_1 function is expressed by

$$F_1[X] = K_1 + K_2[X] + K_3[X]^2 + \ldots . = \sum_{1}^{N} K_j[X]^{j-1} \tag{27}$$

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[31] A. Ringbom and L. Eriksson, *Acta. Chem. Scand.*, 1953, 7, 1105.

[32] L. Eriksson., *Acta. Chem. Scand.*, 1953, 7, 1146.

[33] F. J. Rossotti and H. Rossotti, "The Determination of Stability Constants," McGraw-Hill, New York, 1961, ch. 8, p. 185.

It was shown by Fronaeous[34] that

$$\sum_{0}^{N} K_j[X]^j + \exp\int_0^{[X]} \frac{\bar{n}}{[X]} \,.\, d[X] = F_0[X] \tag{28}$$

$$\text{and } F_1[X] = \frac{\exp\int_0^{[X]} \frac{\bar{n}}{[X]} \,.\, d[X] - 1}{[X]} \tag{29}$$

Then the graph of $F_1[X]$ against [X] gives K_1 as intercept and K_2 as limiting slope. The process is continued up to F_N. In this way, Zabransky[18] determined the stability constants of the sodium and lithium E.D.T.A. complexes by using thallium as the indicator metal. Plumbic lead has also been used as the auxiliary cation for the determination of the stability constants of the chloro-complexes of nickel and zinc.[35]

The tedious nature of the technique when a series of complexes is formed, and the slow attainment of equilibria in many cases, may account for the somewhat limited application and exploitation.

4. Limitations of the Graphical Method

Graphical solutions of the $F[X]$ functions involve cumulative errors, and this is reflected in the increased scattering of points in the graphs for higher complexes. This becomes even more apparent in the case of mixed-ligand complex-formation.

Some attempt has been made, for example by Irving,[36] to use algebraic solutions for the various β's. If more simultaneous equations of type (8) than there are unknowns can be set up from the polarographic data, a least-squares treatment can be employed to find the best set of values.

The ultimate equations in the DeFord–Hume and Eriksson techniques possess properties which allow of their being treated by the relaxation method. Examples of the use of the method with data obtained by using the above techniques are given in an excellent Paper by Watkins and Jones.[37]

Although the preceding refinements are of great importance, it should be borne in mind that much improved data can be obtained by correct control of experimental conditions. Approximations valid for some sets of conditions do not hold in others. For example, in the original treatment of the Cd–SCN system, the total ligand concentration was used as an approximation for that of the free ligand (in terms of which the Leden functions are expressed). In this case, the assumption was valid, since the thiocyanate concentration was so large, compared with those of the complexes, that, in the most dilute solutions with respect to the ligand, the

[34] S. Fronaeous, *Acta. Chem. Scand.*, 1950, **4**, 72.
[35] B. Kivalo and R. Luoto, *Suomen Kem.*, 1957, **30B**, 163.
[36] H. Irving, ref. 11, p. 52.
[37] K. O. Watkins and M. M. Jones, *J. Inorg. Nuclear Chem.*, 1961, **16**, 187.

greatest error introduced was no more than 0·5 per cent. In cases where this assumption is no longer valid, the ligand number, $\bar{n}$, must first be found, assuming at this stage that $[X] = C_X$. Then true (or truer) values of [X] may be calculated by substitution into the relation

$$\bar{n} = \frac{C_X - [X]}{C_M}. \tag{30}$$

The fraction I_M/I_C [see eqn. (5)] should be included in the calculations, since, although small, its neglect produces a significant positive error in the final consecutive stability constants. Many workers have ignored this fraction in their studies.

Above all, temperature and ionic strength must be maintained strictly constant over the entire ligand-concentration range. Any effect causing a potential shift, which can be superimposed on that due to complex-formation, must be rigorously excluded.

5. Structural and Kinetic Factors affecting Reduction

The overall redox process occurring at the electrode and in its immediate vicinity may be represented diagrammatically (Fig. 3), division into the stages being quite formal.[38]

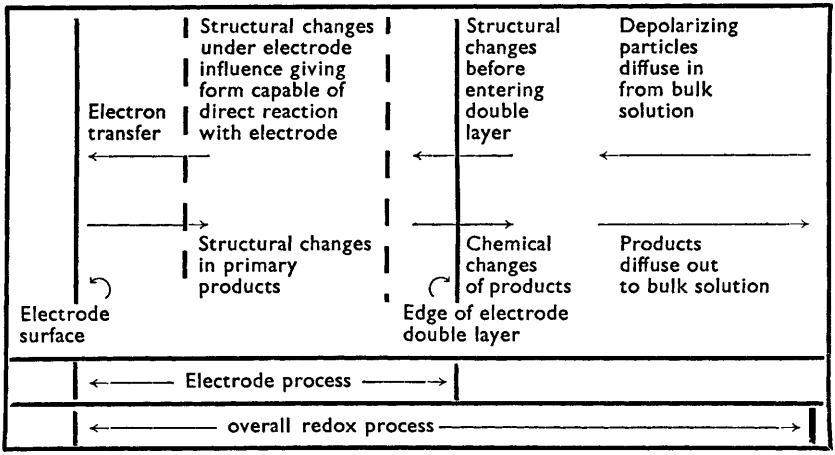

FIG. 3

(a) Structural Factors.—Both the mechanism and rate of the overall electrode process depend on the energy and localization of the lowest unoccupied (or singly occupied) orbital on the reducible species. It is into such orbitals that the electrons, provided at the electrode in a reduc-

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[38] A. A. Vlcek, *Progr. Org. Chem.*, 1963, **5**, 216.

tion process, are received.[39,40] Should the depolarizing particle have a high electron affinity, direct transfer of electrons to these vacant orbitals may take place. If such a condition does not hold, the electronic energy of the complex may change in such a manner that direct reaction with the electrode is made possible.[41] The energy necessary to produce this change constitutes an important, and sometimes the major, part of the activation energy of the electrode process. Configurational changes occurring immediately after the electron transfer cannot be directly determined, and have to be inferred from the structures of secondary products derived from them.[41,42]

In attempting to correlate the structure of complexes with polarographic behaviour, recent studies have considered cases that reluctantly undergo substitution reactions so that the structure in solution may be assumed to be little different from that in the solid state. The most useful complexes in this respect have proved to be those of trivalent cobalt and chromium. Changes, such as aquation, which may occur in solution can, in fact, be of more help than hindrance, since they usually take place to a sufficient extent to allow the change in morphology of the waves with time to be followed.

Recent studies by Vlcek[43,44] have shown important correlations between polarographic and spectroscopic behaviour. The energy of the "reactive" or "transition" state (capable of taking part in the electron transferences) depends on the energy differences between the ground and excited states of the central metal ion. Thus the energy depends on the ligand-field strength of the complex, and, if this is too large, the complex may well be non-reducible. Any effect which decreases the energy difference leads to easier reduction. Vlcek's studies involved substitution in octahedral cobalt(III) complexes of the type CoX_6 to form CoX_5Y. In many cases, a CoX_6-type complex is non-reducible, whereas a substituted form may be reducible, owing to the splitting of the e_g and t_{2g} levels caused by the substituent Y. Should both forms of the complex be reducible, the substituted form has the more-positive half-wave potential. The larger the separation of the ligands X and Y in the Spectrochemical Series, the larger the potential shift. Similar trends are found for the complexes of chromium(III) and rhodium(III).

(b) Distinction between Isomeric Species.—A study of cobaltammine isomers by Willis, Friend, and Mellor[45] showed that polarographic half-wave potentials may sometimes be used to distinguish between the two structural types in solution. Since this work, several studies of both

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[39] A. A. Vlcek, *Coll. Czech. Chem. Comm.*, 1955, **20**, 894.
[40] A. A. Vlcek, *Nature*, 1956, **177**, 1043.
[41] A. A. Vlcek, *Coll. Czech. Chem. Comm.*, 1957, **22**, 948.
[42] A. A. Vlcek, *Coll. Czech. Chem. Comm.*, 1957, **22**, 1736.
[43] A. A. Vlcek, *Discuss. Faraday Soc.*, 1958, **26**, 164.
[44] A. A. Vlcek, *Coll. Czech. Chem. Comm.*, 1959, **24**, 181.
[45] J. B. Willis, J. A. Friend, and D. P. Mellor, *J. Amer. Chem. Soc.*, 1945, **67**, 1680.

octahedral and planar isomeric species have been carried out. Holtzclaw and Sheetz[46,47] found that, in six-co-ordinated complexes of cobalt(III) containing two negative groups, the *trans*-isomer was reduced at a more-negative potential than was the *cis*-form.

For octahedral cobalt complexes, the reductions proceed irreversibly in two main stages, *viz.*, cobalt(III)→cobalt(II) and cobalt(II)→cobalt. However, the first stage, cobalt(III)→cobalt(II), is, in many cases, represented by a doublet wave, and in others by a single wave. For example, in the case of the isomers of $[Co(NH_3)_4(NO_2)_2]^+$, a single wave is obtained for the cobalt(III) to cobalt(II) step, with $E_{\frac{1}{2}}$ values of −0·05 and −0·21 v (against S.C.E.) for the *cis*- and *trans*-forms, respectively. The same relationship between $E_{\frac{1}{2}}$ values and structure occurs with the first waves of the doublets, as shown in Table 1.

TABLE 1. *Comparison of* $E_{\frac{1}{2}}$ *values for* cis *and* trans *cobalt*(III) *isomers containing two negative groups.*[47]

Complex	Reduction cobalt(III)→cobalt(II) First wave $-(E_{\frac{1}{2}})_1$ (v) (*vs.*S.C.E.)	 Second wave $-(E_{\frac{1}{2}})_2$ (v) (*vs.*S.C.E.)
$[Co(en)_2(NO_2)_2]^+$	*cis* 0·24	*cis* 0·41
	trans 0·27	*trans* 0·40
$[Co(en)_2(NCS)(NO_2)]^+$	*cis* 0·04	*cis* 0·38
	trans 0·12	*trans* 0·36

The second wave, which in each case appears at about −0·4 v, may correspond to the reduction of an aquated form of the parent complex, the reduction of the parent complex itself being represented by the first wave of the doublet. Slight discrepancies between half-wave-potential values for the second waves in Table 1 would tend to suggest that these correspond to the reduction of different intermediate forms. The aquated species may be a hydroxo-complex of some sort.[47] A study of similar complexes with less than two negative groups was also carried out by the above workers, and $E_{\frac{1}{2}}$ values are given in Table 2 for two representative pairs.

TABLE 2. *Comparison of* $E_{\frac{1}{2}}$ *values for* cis *and* trans *cobalt*(III) *isomers with one negative group.*[47]

Complex	Reduction cobalt(III)→cobalt(II) First wave $-(E_{\frac{1}{2}})_1$ v (*vs.*S.C.E.)	 Second wave $-(E_{\frac{1}{2}})_2$ v (*vs.*S.C.E.)
$[Co(en)_2NO_2NH_3]^{2+}$	*cis* 0·21	*cis* 0·40
	trans 0·20	*trans* 0·40
$[Co(en)_2NH_3NCS]^{2+}$	*cis* 0·13	*cis* 0·39
	trans 0·10	*trans* 0·39

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[46] H. F. Holtzclaw, jun., *J. Amer. Chem. Soc.*, 1951, **73**, 1821.

[47] H. F. Holtzclaw, jun., and D. P. Sheetz, *J. Amer. Chem. Soc.*, 1953, **75**, 3053.

In their original publication, the authors stated that, in octahedral complexes containing only one or no negative groups, there was no apparent difference between the polarographic behaviour of isomeric species. However, as has been shown,[48] the data tend to suggest that slightly easier reduction of the *trans*-isomer occurs in such cases.

Recent studies[49] of *cis*- and *trans*-$[Rh(en)_2Cl_2]^+$ have shown that the half-wave potential of the *cis*-isomer is considerably more-negative than that of the *trans*-form. This is in contradistinction to the case of cobalt(III) complexes of similar type. (See Figs. 4 and 5 for polarograms of the two cases.) In our view, it seems reasonable to explain the effect in terms of reduction occurring on different sides of the electrocapillary maximum for the cobalt and rhodium cases.

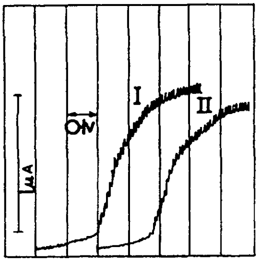

FIG. 4. *Polarograms of* trans (I) *and* cis (II) $[Co(en)_2(NO_2)_2]^+$ (ca. 2·5 × 10^{-4} M) *in* 0·1 M-$NaClO_4$. *Both waves start at* 0·0 v.

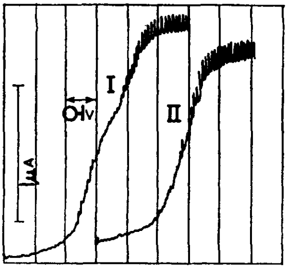

FIG. 5. *Polarograms of* trans (I) *and* cis (II) $[Rh(en)_2Cl_2]^+$ (ca. 2·3 × 10^{-4} M) *in* 0·1M-$NaClO_4$. *Wave* I *starts at* 0·3 v; *wave* II *at* 0·5 v.

In view of the greater internal dipole which exists within the *cis*-isomer of an octahedral complex containing two negative groups, Holtzclaw[50] suggested that, in the absence of a supporting electrolyte, this isomer, on account of its correspondingly greater orientation in the unsymmetrical field around the dropping-mercury electrode, should migrate to this electrode at a rate different from that of the *trans*-form. Investigations of

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[48] J. R. Hall and R. A. Plowman, *Austral. J. Chem.*, 1956, **9**, 14.

[49] D. R. Crow and J. V. Westwood, to be published.

[50] H. F. Holtzclaw, jun., *J. Phys. Chem.*, 1955, **59**, 300.

various pairs of isomers in solution under these conditions showed that the different migration effects were not reliable as a means of distinguishing between the two structures. Half-wave-potential data, on the other hand, have found use in the identification of the different species.[51,52]

Similar studies have been carried out on the four-co-ordinated complexes of platinum and palladium.[48,53] Platinum(II)-tetra-amine ions, in which the ligands are ammonia, methylamine, dimethylamine, ethylenediamine, pyridine, aniline, or combinations of these, show a polarographic distinction between *cis*- and *trans*-isomers. *Trans*-forms undergo easier reduction than do the *cis*-forms, suggesting the greter thermodynamic stability of the latter. Chakravarty and Banerjea[53] observed that, for platinum(II) and palladium(II) complexes containing two negative groups, there is a significant difference (of the order of 60 mv or more) in the $E_{\frac{1}{2}}$ values of the isomeric forms, the *cis*- now being reduced at a more-positive potential than is the *trans*-form. The general behaviour of such complexes is very similar to that of six-co-ordinated cobalt(III) complexes. For diaquo- and chloroaquo-complexes, $E_{\frac{1}{2}}$ values are almost identical. A striking difference between the planar and octahedrally co-ordinated structures is that, for the former, a definite difference between the behaviour of *cis*- and *trans*-forms is observed even when all groups are neutral.

(c) **Kinetic Factors.**—Very often, the rate of dissociation of a complex, as well as the rate of diffusion, controls the limiting current. It has proved possible to determine stability constants from the half-wave potentials and kinetic limiting currents obtained from dissociation-rate-controlled waves. The half-wave potential of the kinetic wave is less negative than that of the hypothetical diffusion-controlled wave, and the difference can be used to compute consecutive stability constants in the normal way, provided that the dissociation reaction is followed by a reversible discharge process. The relation for a diffusion-controlled deposition [see eqn. (7)] has been modified by Koryta[54–56] and Matsuda and Ayabe[57] to:

$$E = E^0 - \frac{RT}{nF}\ln\sum_{0}^{N}\beta_j[\mathrm{X}]^j - \frac{RT}{nF}\ln\frac{i}{i_{\mathrm{k}} - i} + \frac{RT}{nF}\ln\frac{i_{\mathrm{d}}}{i_{\mathrm{k}}} \qquad (31)$$

Here, i_{k} replaces i_{d} of eqn. (7), and a new term is added. This, in effect, "corrects" the half-wave potential of the kinetic wave for the slowness of dissociation, relative to the diffusion rate, of a particular complex. Then

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[51] Z. E. Gol'braikh, *Zhur. neorg. Khim.*, 1956, **1**, 1739.

[52] E. A. Maksimyuk and G. S. Ginzburg, *Doklady Akad. Nauk S.S.S.R.*, 1959, **124**, 1069.

[53] B. Chakravarty and D. Banerjea, *J. Inorg. Nuclear Chem.*, 1961, **16**, 288.

[54] J. Koryta, *Coll. Czech. Chem. Comm.*, 1958, **23**, 1408.

[55] J. Koryta, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2903.

[56] J. Koryta, *Electrochim. Acta*, 1959, **1**, 26.

[57] H. Matsuda and Y. Ayabe, *Bull. Chem. Soc. Japan*, 1956, **29**, 134.

$$(E_{\frac{1}{2}})_{\text{kin.}} = E^0 - \frac{RT}{nF}\ln\sum_{0}^{N}\beta_j[\text{X}]^j + \frac{RT}{nF}\ln\frac{i_{\text{d}}}{i_{\text{k}}} \tag{32}$$

and

$$(E_{\frac{1}{2}})_{\text{kin.}} - (E_{\frac{1}{2}})_{\text{diff.}} = \frac{RT}{nF}\ln\frac{i_{\text{d}}}{i_{\text{k}}} \tag{33}$$

The method involves an estimated i_{d} value based on a reasonable value for D and a knowledge of n. These equations have found important uses for the determination of stability constant data for several systems. After "correcting" for the half-wave potential, the procedure follows the DeFord–Hume graphical method.[55,58,59]

It is rare, especially if faced with several step-wise equilibria, to be able to know precisely the nature of the species present in solution. Not only are there often many species, but added complications may arise, due to binuclear complex-formation and also the low mobility of equilibrium between some species in the step complexes. Further, not all the complexes may be electro-active at the mercury electrode. In some cases, it has proved possible to determine both the chemical reaction controlling the overall rate and its rate constant. Koryta[60] studied the cadmium-cyanide system ([CN] = 0·005—0·1 M) and obtained a limiting kinetic current, i_{k}, related to i_{d}, the limiting (diffusion) current for rapid dissociation, by use of the expression.

$$\ln\left[\frac{i_{\text{k}}}{i_{\text{d}} - i_{\text{k}}}\right] = \text{constant} \times (p - N - \tfrac{1}{2})\ln[\text{X}], \tag{34}$$

where p and N represent the composition of the complex whose dissociation is rate-determining, and that of the highest complex present, respectively. Experimental determination of the quotient $\text{d}\{\ln[i_{\text{k}}/(i_{\text{d}} - i_{\text{k}})]\}/\text{d}\{\ln[\text{X}]\}$ yields a value for p when N is known. In the system quoted, $N = 4$ and the quotient was found to have the value $-3/2$. Hence, $p = 3$ and the reaction

$$\text{Cd(CN)}_3^- = \text{Cd(CN)}_2 + \text{CN}^- \tag{35}$$

is rate-controlling.

Should there be, in a mobile system of complexes, a species whose reduction (electrode reaction proper) controls the overall rate, the composition of this species may be found by a similar treatment. If p again represents the composition of the unique species, and r_p the rate constant of its reduction process, the current relationship is

$$\frac{i}{i_{\text{d}} - i} = 0{\cdot}886\, r_p\, t^{\frac{1}{2}}\, D^{-\frac{1}{2}}\, (k_N \ldots . \, k_{p+1}.[\text{X}]^{N-p})^{-1}, \tag{36}$$

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[58] J. Koryta, *Coll. Czech. Chem. Comm.*, 1959, **24**, 3057.

[59] D. Konrad and A. A. Vlcek, *Coll. Czech. Chem. Comm.*, 1963, **28**, 808.

[60] J. Koryta, *Z. Elektrochem.*, 1957, **61**, 423.

where t and D have the usual significance, and the k's are stability constants. Again, p is found from the change in current with ligand concentration. In cases of more-complex behaviour, both equations above have to be combined to take account of the two effects.

6. Solvent Variables

In studies of complex-formation which involve measurements of half-wave-potential shifts, it is necessary that care be taken to ensure that the observed shifts are due to complex-formation—especially that involving the required ligand—without interference arising from other ligands. It has already been shown that the nature of the complexes present in solution can differ widely with changing concentrations of the complexing ligand. If indifferent electrolytes with good co-ordinating ability are used, these can have a pronounced effect on both half-wave potentials and diffusion currents. For example, Holtzclaw[46] investigated the behaviour of *cis*- and *trans*-dinitrotetramminecobalt(III) chloride with increasing concentrations of chloride, tartrate, and citrate, and Laitinen *et al.*[61] carried out similar studies on hexamminecobaltic chloride. Half-wave potentials were shifted in the negative-potential direction and diffusion-current constants were at the same time reduced. Such behaviour is attributed to "supercomplex" formation due to clustering of base electrolyte anions, by ion–dipole and electrostatic attraction, about the central complex. The formation of supercomplexes is closely allied with the phenomenon of ion-pairing, the nature of which has been largely clarified by the work of Bjerrum[62] and Fuoss and Kraus.[63]

Tur'yan and Bondarenko[64] studied the effect of non-aqueous solvents on the polarographic behaviour of many complexes. The main feature of this work was the use of various concentrations of methanol or ethanol in water. The dielectric constant was found to have a pronounced effect on the stability of cadmium thiocyanate complexes; the stability constants varied inversely as the dielectric constant. In such mixed-solvent systems, lower members of the Cd–SCN series of complexes are formed preferentially, with a lower concentration of higher complexes and a general increase in stability, with increasing concentration of non-aqueous solvent.

Solutions of ethanol, 2-methoxymethanol, and dioxan in water have been used as polarographic solvents for copper chelates of 1,3-diketones[65] and for copper and cadmium complexes with thiourea and its homologues.[66] Nightingale and Holtzclaw[65] derived the expression

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[61] H. A. Laitinen, J. C. Bailar, H. F. Holtzclaw jun., and J. V. Quagliano, *J. Amer. Chem. Soc.*, 1948, **70**, 2999.

[62] J. Bjerrum, *Kgl. danske Videnskab. Selskab. Mat.-fys. Medd.*, 1926, **7**, No. 9.

[63] R. M. Fuoss and C. A. Kraus, *J. Amer. Chem. Soc.*, 1933, **55**, 1019, 2387.

[64] Ya. I. Tur'yan and N. I. Bondarenko, *Zhur. neorg. Khim.*, 1959, **4**, 1070.

[65] E. R. Nightingale and H. F. Holtzclaw, jun., *J. Amer. Chem. Soc.*, 1959, **81**, 3523.

[66] T. J. Lane, J. W. Thompson, and J. A. Ryan, *J. Amer. Chem. Soc.*, 1959, **81**, 3569.

$$\Delta E_{\frac{1}{2}} = \text{constant} \times \Delta \left(\frac{1}{\epsilon}\right), \tag{37}$$

relating the half-wave-potential change and the corresponding change in dielectric constant ϵ. Experimentally, the value of the constant was found to be —3·5, in fair agreement with the calculated value of —4·09. The same workers investigated the effect of viscosity changes on the reduction of the ketone chelates and found that the Stokes–Einstein relation was, in general, obeyed. Values of diffusion coefficients, needed for computation of the Stokes–Einstein product $D\eta$, were obtained from the Lingane–Loveridge modification[67] of the Ilkovic equation, which had not been rigorously tested for non-aqueous-solvent systems until this study.

In a more recent study, the effects of solvent isotopes have been examined. Light and heavy water were used as solvents for the polarographic determination of stability constants of cadmium and copper oxalate complexes.[68] The constants were found to be greater in heavy water than in the more-strongly-solvating light water.

Increase in the ionic strength of an electrolytic solution shifts the half-wave potentials to more-negative values. In using the DeFord–Hume method, activity coefficients are assumed to remain constant, and independent of the concentration of the complexing agent, by holding the ionic strength at a constant value. This assumption is not always justifiable in cases where concentrated solutions of mixed electrolytes are used. The polarographic method, indeed, has been applied to the determination of formation constants in $LiNO_3$–KNO_3 melts at 180°.[69] In this way, the chloro-complexes of nickel, cadmium, and lead were studied by the DeFord–Hume method. A similar application involved the formation of the species AgCl, $AgCl_2^-$, and Ag_2Cl^+ in molten KNO_3.[70]

7. Thermodynamic Quantities

Evaluation of ΔG^0, ΔH^0, and ΔS^0 is, in principle, possible from measurements of the formation constants at various temperatures, although relatively few of such studies have been made polarographically. Earlier work on the complexes of nickel and copper with glycine and valine, over the range 25—40°, gave results in reasonable agreement with those obtained from potentiometric studies.[71] The ΔH^0 values varied from —14·0 to —21·0 kcal., but the ΔS^0 values varied considerably, with both positive and negative results. A more recent study of cadmium–pyrazole complexes[7] confirmed the presence of 1:1, 1:2, and 1:3 metal:complex

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[67] J. J. Lingane and B. A. Loveridge, *J. Amer. Chem. Soc.*, 1950, **72**, 438.

[68] D. L. McMasters, J. C. Raimondo, L. H. Jones, R. P. Lindley, and E. W. Zeltmann, *J. Phys. Chem.*, 1962, **66**, 249.

[69] J. H. Christie and R. A. Osteryoung, *J. Amer. Chem. Soc.*, 1960, **82**, 1841.

[70] J. Braunstein, M. Blander, and R. M. Lindgren, *J. Amer. Chem. Soc.*, 1962, **84**, 1529.

[71] N. C. Li, J. M. White, and R. L. Yoest, *J. Amer. Chem. Soc.*, 1956, **78**, 5218.

ratios, with mean values of ΔH^0 of −3·94, −8·10, and −12·14 kcal., respectively, for the overall reactions over the temperature range 0—45°. A regular increase of ΔH^0 thus occurs with each ligand attachment, with a corresponding negative entropy increase. The variability in entropy values for complex-formation is well shown by the values obtained for the mercury(II), cadmium, and zinc complexes with ethylenediamine, with values of −5, +3·4, and +10·7 e.u., respectively,[72] and more recently by the cadmium complexes of histamine and related compounds,[73] where ΔS^0 varied from −19 e.u. for antistine to +4 e.u. for benadryl. The loss of translational degrees of freedom by ligand attachment would suggest a greater degree of order and hence a negative entropy value, but this may be offset by a loss of hydration of the metal ion. The latter may in fact be sufficient to swing the value over to the positive side. The field force due to the central ion may still be sufficient to maintain some degree of ordering of the solvent outside the sphere of the ligand (the "iceberg" concept of Frank and Wen[74]). With a multidentate ligand, more water tends to be displaced from the metal ion and the entropy changes are greater. The entropy values give some indications as to the nature of the complex and show whether inner-sphere or outer-sphere complexes are formed.

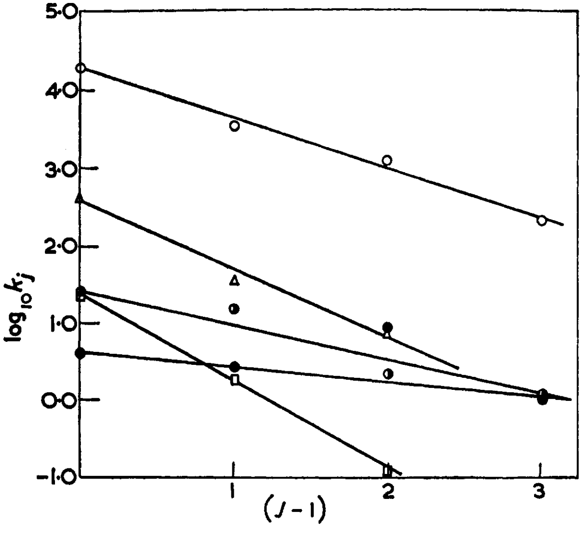

FIG. 6. *Plots of* $\log_{10} k_j$ *against* $(j - 1)$ *for several systems of complexes.* ○ Cu–NH_3 (ref. 5). △ Cd–OX^{2-} (ref. 16). ◑ Cd–N_3^+ (ref. 15). □ Cd–thiourea (T. J. Lane, "Advances in Polarography," Pergamon, London, 1960, vol. 2, p. 797). ● Pb–thiourea (ref. as for Cd–thiourea).

[72] D. K. Roe, D. B. Masson, and C. J. Nyman, *Analyt. Chem.*, 1961, **33**, 1464.

[73] A. C. Andrews and J. Kirk Romary, *J.*, 1964, 405.

[74] H. S. Frank and W. Y. Wen, *Discuss. Faraday Soc.*, 1957, **24**, 133.

The values of the stability constants for step-wise complexes show an interesting correlation. Van Panthaleon van Eck[75] suggested a relationship of the form

$$\log_{10} K_j = \log_{10} K_1 - \lambda(j - 1), \tag{38}$$

where λ is an empirical parameter for each system. This, however, appears to have been little exploited. Accordingly, values for some of the systems, which have been reported, have been calculated from the overall step constants and are shown in the form of a graph of $\log_{10} K_j$ against $(j - 1)$ (see Fig. 6). These systems give reasonably linear graphs, and this suggests an equal change in free energy at each increase in ligand. However, in some systems, *e.g.*, cadmium thiocyanate,[12] the results are not so encouraging.

8. Conclusion

Few methods are available for studying step-wise complex-formation in solution, and, of these, the polarographic method has some advantage over spectral methods, since the identification and the determination of the properties of more species is possible simultaneously. However, it must be admitted that, since the measurement of very small differences in half-wave potentials is often involved, the accuracy in the determination of the higher stability constants, so far obtained, is often not as great as is desired. This is unfortunate, since the potentialities for obtaining thermodynamic data are considerable. There are, however, indications that recent workers are realising these advantages, and greater care is being observed over solution factors.

More information is required for families of compounds of similar composition, to relate general electrode behaviour with structure. So far, only cobalt compounds have been studied in considerable detail particularly by Vlcek, but other elements, *e.g.*, chromium, rhodium, and iridium, would be interesting. In particular, there is wide scope for studying the electrode mechanisms of complex species. This is not an easy field, being somewhat bedevilled by the complications arising from the electrical double layer, but is a fascinating and rewarding one.

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[75] C. L. van Panthaleon van Eck, *Rec. Trav. chim.*, 1953, **72**, 529.