and 1.02 were obtained for the ratio between the change in the cadmium ion concentration in each cell. Tests were also carried out using the cadmium ion solution in one cell and 0.0025 *M* thallous nitrate with 0.1 *M* potassium chloride in the other cell. Ratios obtained were 0.487, 0.500, 0.515 and 0.526. The reduction of several organic compounds was also studied. With the cadmium chloride solution in the one cell and 0.0026 *M* fumaric acid with 0.12 *M* hydrochloric acid in the second cell, ratios obtained were 0.97, 0.99, 1.01 and 1.04. The average value 1.00 gives $n = 2.00$ which is reasonable for fumaric acid reduction on the basis to other experimental evidence. Another series of determinations were made with 0.0011 *M* *p*-nitrobenzoic acid in a potassium hydrogen phthalate buffer with a *p*H of 2.65 and containing about 10% ethanol to increase the solubility of the acid. In this case the ratios obtained gave values of *n* as follows: 3.92, 3.96, 4.16 and 4.22. The average value of 4.07 is within 2% of the literature value of 4 (necessarily an integer) for similar mono-nitroaromatics.

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Theory of Electrolysis at Constant Current with Partial or Total Control by Diffusion—Application to the Study of Complex Ions[1]

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A mathematical analysis is made for the potential–time curves which are observed in electrolysis at constant current with mass transfer partially or totally controlled by semi-infinite linear diffusion. Three cases are considered: (1) reversible electrochemical process; (2) irreversible electrochemical process; (3) electrochemical process preceded by a first-order chemical reaction. The potential–time curves are characterized by a *transition time* whose value is derived for the above three cases. The transition time for given conditions of electrolysis is the same whether the electrode process is reversible or irreversible (cases 1 and 2). In the third case mentioned above, the transition time depends on the kinetics of the reaction preceding the electrochemical process. Conditions under which the theoretical treatment can be applied to the reduction of complex ions are stated. It is shown that for certain complexes (cadmium cyanide) dissociation must precede the electrochemical reaction, whereas other complexes (copper ethylenediamine) are reduced directly. The rate of recombination of Cd^{++} and CN^- ions is evaluated as being of the order of 4×10^9 (moles per l.)$^{-1}$ sec.$^{-1}$. Experimental methods are briefly discussed, and the potentialities of the method as a tool in electrochemical studies are evaluated.

Electrolysis at constant current density with mass transfer partially or totally controlled by diffusion has been studied for many years. Early investigations[2–5] were concerned with the verification of Fick's laws of diffusion, but more recent work[6–8] has been oriented toward the study of electrode processes and toward analytical applications. Recently, Gierst and Juliard[8] developed a very ingenious method for the oscillographic recording of voltage–time curves. These authors made some very interesting observations on electrode processes, and their study brought to light some of the potentialities of electrolysis at constant current. The theoretical treatment of this type of electrolysis is rather limited at the present, and it is the purpose of this paper to give a mathematical analysis of the boundary value problems encountered in this method. Only cases involving semi-infinite linear diffusion in an unstirred solution will be discussed, since cases of spherical or cylindric diffusion can be treated as linear diffusion problems provided that the duration of electrolysis is sufficiently short (1 second)—a condition which is generally fulfilled in the present type of electrolysis. Convection effects will be neglected on account of the short duration of electrolysis. Furthermore, it will be assumed that the solution being electrolyzed contains a large excess of supporting electrolyte, and that migration effects can be neglected. The discussion is divided in three parts according to the nature of the electrode process involved; a fourth part deals with the application of the method to the study of complex ions.

Reversible Electrode Processes

Potential–Time Variations.—Consider the reduction of a substance Ox, and assume that the reduction product Red is soluble either in solution (or in mercury in the case of the deposition of an amalgam forming metal on a mercury electrode). The value of the concentration of substance Ox during electrolysis at constant current was calculated by Weber,[2] Sand,[3] and Rosebrugh and Miller.[9] Karaoglanoff[5] derived the equation of the complete potential–time curve. His treatment need not be discussed here, but it is worth noticing that the curve representing the potential *versus* the square root of the electrolysis time is similar to a polarographic wave for the reversible process being considered here. If one assumes that the concentration of substance Red is equal to zero before elec-

(1) Paper to be presented at the 13th International Congress of Pure and Applied Chemistry, Physical Chemistry Division, Stockholm, July, 1953.

(2) H. F. Weber, *Wied. Ann.*, **7**, 536 (1879).

(3) H. J. S. Sand, *Phil. Mag.*, **1**, 45 (1901).

(4) F. G. Cottrell, *Z. physik. Chem.*, **42**, 385 (1902).

(5) Z. Karaoglanoff, *Z. Elektrochem.*, **12**, 5 (1906).

(6) J. A. V. Butler and G. Armstrong, *Proc. Roy. Soc. (London)*, **139A**, 406 (1933); *Trans. Faraday Soc.*, **30**, 1173 (1934).

(7) For a survey see "Electrical Phenomena at Interfaces," J. A. V. Butler, Editor, Methuen and Company, London, 1951, Chapters VIII and IX.

(8) (a) L. Gierst and A. Juliard, "Proceedings of the 2nd Meeting of the International Committee of Electrochemical Thermodynamics and Kinematics," 1950, Tamburini, Milan, pp. 117 and 279. (b) L. Gierst, Thesis, University of Brussels, 1952. We are indebted to Dr. Gierst for sending us a copy of his thesis.

(9) T. R. Rosebrugh and L. Miller, *J. Phys. Chem.*, **14**, 816 (1910).

trolysis, the potential of the electrode on which substance Ox is reduced is as follows, t seconds after the beginning of the electrolysis

$$E = E^0 + \frac{RT}{nF} \ln \frac{f_0 D_r^{1/2}}{f_r D_0^{1/2}} + \frac{RT}{nF} \ln \frac{C^0 - Pt^{1/2}}{Pt^{1/2}} \quad (1)$$

where E^0 is the standard potential for the couple Ox–Red,[10] the f's are the activity coefficients of substances Ox and Red, and P is defined as

$$P = \frac{2i_0}{\pi^{1/2} nFD_0^{1/2}} \quad (2)$$

In equation (2), i_0 is the constant current density for the polarizable electrode, D_0 the diffusion coefficient of substance Ox, and the other notations are conventional. The sum of the first two terms on the right-hand of equation (1) is identical to the polarographic half-wave potential $E_{1/2}$, when a mercury electrode is used in the constant current electrolysis. This observation enables one to predict from polarographic data the position of the potential–time wave in the range of potentials. For the experimental verification of equation (1), see reference 5.

Determination of the Transition Time.—After an electrolysis time τ such that $C^0 = P\tau^{1/2}$, the potential E given by equation (1) becomes infinite. The *transition time* τ—a term coined by Butler and Armstrong[6]—is characteristic of the electrolysis conditions: $\tau^{1/2}$ is proportional to the concentration of reducible species and inversely proportional to the current density, etc. It is therefore important to determine τ in a reliable manner. This determination of τ would be obvious from the shape of the E *vs.* $t^{1/2}$ curve, if it were not for the distortion of voltage–time curves by the capacity current (double layer).[8] This effect of the capacity current is taken into account in the method of determining τ of Fig. 1-A, which is inspired from polarographic practice. Note that the potential $E_{1/2}$ corresponds to an electrolysis time $t = \tau/4$. When the potential-time curve has the shape of Fig. 1B, the construction of Fig. 1A leads to abnormally low values of the transition time. It is then necessary to apply the somewhat empirical method shown in Fig. 1B. The selection of point E is a matter of common sense.

By introducing the value of the transition time from $C^0 = P\tau^{1/2}$ in equation (1), the third term on the right-hand becomes

$$(RT/nF) \ln (\tau^{1/2} - t^{1/2})/t^{1/2}$$

Therefore, a plot of the logarithm of the quantity $(\tau^{1/2} - t^{1/2})/t^{1/2}$ against potential should yield a straight line whose slope is nF/RT (see theory of reversible polarographic waves).

Irreversible Electrode Processes

The theoretical treatment of this case has not been reported before, as far as we know. If the reduction Ox → Red involves only one rate-determining step, the rate of the electrochemical reaction is

$$\frac{i_0}{nF} = k_{f,h} f_0 C_{ox}(0,t) - k_{b,h} f_r C_{red}(0,t) \quad (3)$$

where the C's are the concentrations at the electrode surface ($x = 0$), and the k's are the rate constants for the forward and backward electrochemical reactions, respectively. Note that these k's are rate constants for an *heterogeneous* process and are consequently expressed in cm. sec.$^{-1}$. Furthermore, the k's depend on the electrode potential as is shown below. No hypothesis regarding the kinetics of the reduction of substance Ox was made by Karaoglanoff[5] in the derivation of the concentrations of substances Ox and Red, and consequently the values of $C_{ox}(0, t)$ and $C_{red}(0, t)$ obtained by this author can be introduced in equation (3). This yields the following relationship ($i_0 = 0$ for $t < 0$, $C_{red} = 0$ for $t < 0$)

$$i_0/nF = k_{f,h} f_0(C^0 - Pt^{1/2}) - k_{b,h} f_r Q t^{1/2} \quad (4)$$

where the expression for Q is the same as for P (equation (2)) except that D_0 is replaced by the diffusion coefficient D_r of substance Red. Since the electrode potential is implicitly contained in the rate constants $k_{f,h}$ and $k_{b,h}$, equation (4) gives formally the dependence of the electrode potential on time. Detailed equations are obtained by expressing $k_{f,h}$ and $k_{b,h}$ in terms of the electrode potential. Only the case in which $k_{f,h}$ is much larger than $k_{b,h}$ at the current density i_0 will be considered here for the sake of simplicity. The restriction imposed by the condition $k_{f,h} >> k_{b,h}$ is minor, since this inequality is verified for overvoltages of the order of at least 0.1 v., whilst much larger voltages are generally encountered.

As in the case of the reversible electrode process the transition time obeys the relationship $C^0 = P\tau^{1/2}$ (see equation (4), $k_{f,h} = \infty$, $k_{b,h} = 0$). By dropping the term in $k_{b,h}$ in equation (4) and introducing the transition time, one obtains

$$k_{f,h} = \pi^{1/2} D_0^{1/2} / 2f_0(\tau^{1/2} - t^{1/2}) \quad (5)$$

Equation (5) is important because it enables one to calculate the rate constant $k_{f,h}$ from experimental data. Values of E are measured on the E–t curve for various values of t and the corresponding rate constants $k_{f,h}$ are calculated. A plot of the results yields the rate constant $k_{f,h}$ as a function of the electrode potential E. The diffusion coefficient D_0 needed in the application of equation (5) can be readily calculated from the transition time (see equation (2)). The variations of $k_{f,h}$ with E can be interpreted by considering the value of $k_{f,h}$ derived from the absolute rate theory. Thus

$$k_{f,h} = k^0_{f,h} \exp [-(\alpha n_a F/RT)E] \quad (6)$$

where $k^0_{f,h}$ is a constant related to the free energy of

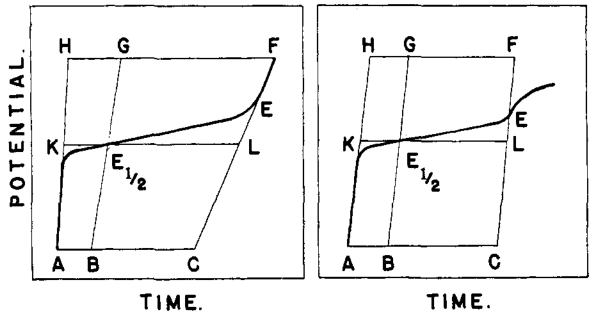

Fig. 1A (left) and 1B (right).—Graphic determination of the transition time (see text): HG = 1/4 HF; AB = 1/4 AC; KL = transition time.

(10) If an amalgam is involved, E^0 is the standard potential for the amalgam electrode.

activation for the forward electrode process,[11] α is the transfer coefficient, and n_a the number of electrons involved in the rate-determining step. The slope of the log $k_{f,h}$ *vs.* E line established from experimental results yields the product αn_a, and the intercept at $E = 0$ for the same diagram yields $k^0_{f,h}$ and, consequently, the free energy of activation for the forward electrode process. The electrode potential can be written as a function of time by combining equations (5) and (6). Furthermore, a plot of ln $[1 - (t/\tau)^{1/2}]$ against E yields a straight line having a slope of $- RT/\alpha n_a F$. Finally, the potential at time zero

$$E_{t=0} = \frac{RT}{\alpha n_a F} \ln \frac{nFk^0_{f,h}C^0f_0}{i_0} \quad (7)$$

depends on the bulk concentration of substance Ox, and on the transfer coefficient α.

As an example, potential–time curves have been plotted in Fig. 2 for various values of α and for the following data: $C^0 = 10^{-4}$ mole cm.$^{-3}$, $i_0 = 10^{-1}$ amp. cm.$^{-2}$, $D_0 = 10^{-5}$ cm.^{2} sec.$^{-1}$, $k_f^0 = 10^{-8}$ cm. sec.$^{-1}$, $n = n_a = 1$.

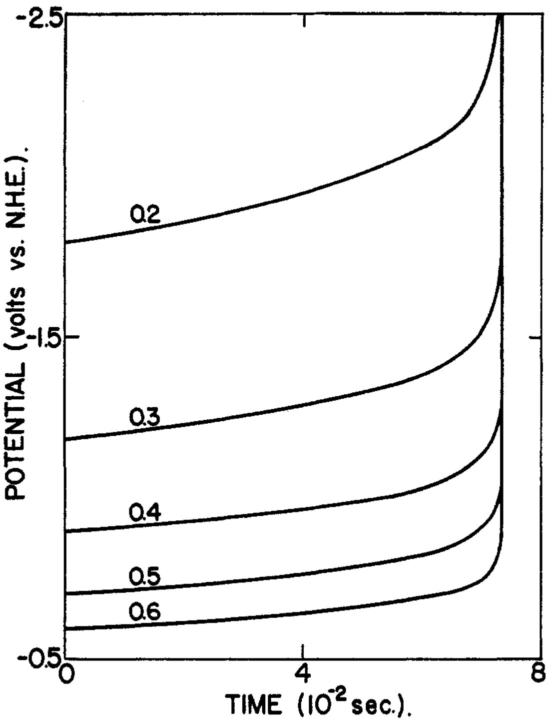

Fig. 2.—Potential–time curve for an irreversible electrode process. See data in text. Number on each curve is the value of transfer coefficient.

The present treatment is valid only when the effect of the backward process can be neglected (see above). When this is not so, the E–$t^{1/2}$ curve has a shape similar to that observed in a reversible process, although the curve is somewhat more drawn out. A detailed analysis of such a case will not be presented here since the corresponding equation is too cumbersome to be of any practical value.

In the case of an irreversible wave, the potential $E_{1/2}$ corresponding to $t = \tau/4$ has no particular significance, and the graphic determination of τ by the method of Fig. 1A is devoid of any theoretical basis. It is, however, reasonable to apply the method of Fig. 1A in the determination of τ, since any other method which might be proposed would probably not be less empirical.

Electrode Process Preceded by a Chemical Reaction

Consider the electrode process in which a substance Z is in equilibrium with a substance Ox, the latter substance being reduced at markedly less cathodic potentials than Z. The transition time corresponding to the reduction of substance Ox is determined by the diffusion of substance Z toward the electrode and by the rate of transformation Z $\rightleftarrows$ Ox. This case was treated by Gierst and Juliard[8] who introduced a kinetic term in the expression of the transition time $C^0 = P\tau^{1/2}$. Such a treatment is questionable on two counts: (1) It is assumed that Fick's differential equation is applicable without modification; (2) A rate constant for an heterogeneous process is introduced to characterize a process which occurs in solution. Such a treatment has its merits, but a more rigorous approach is desirable and leads to new results.

Boundary Conditions.—As in the previous two sections, the transition time for the reduction of substance Ox is calculated from the condition $C_{ox}(0,t) = 0$. Consequently, it is necessary to determine the function $C_{ox}(x,t)$. The latter is obtained by following a method similar to the one applied by Koutecky and Brdicka in the treatment of kinetic polarographic currents.[12] However, the derivation given below is different from that of Koutecky and Brdicka because one of the boundary condition is not the same as in the case of kinetic polarographic currents.

Kinetic terms have to be added on the right-hand of the differential equation for linear diffusion, because of the occurrence of the transformation Z $\rightleftarrows$ Ox in solution. Thus

$$\frac{\partial C_{ox}(x,t)}{\partial t} = D_o \frac{\partial^2 C_{ox}(x,t)}{\partial x^2} + k_f C_z(x,t) - k_b C_{ox}(x,t) \quad (8)$$

$$\frac{\partial C_z(x,t)}{\partial t} = D_z \frac{\partial^2 C_z(x,t)}{\partial x^2} - k_f C_z(x,t) + k_b C_{ox}(x,t) \quad (9)$$

where the D's are the diffusion coefficients, and the k's the formal rate constants for the transformation Z $\rightleftarrows$ Ox. Note that the k's in equations (8) and (9) are conventional rate constants (in sec.$^{-1}$).

The boundary conditions are obtained by expressing that the flux at the electrode surface is constant, and that substance Z is not reduced at the electrode. Thus

$$(\partial C_{ox}(x,t)/\partial x)_{x=0} = \lambda \quad (10)$$

with

$$\lambda = i_0/(nFAD_o) \quad (11)$$

and

$$(\partial C_z(x,t)/\partial x)_{x=0} = 0 \quad (12)$$

The initial conditions are

$$C_{ox}(x,0)/C_z(x,0) = K \quad (13)$$

$$C_{ox}(x,0) + C_{red}(x,0) = C^0 \quad (14)$$

(11) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941, p. 577.

(12) J. Koutecky and R. Brdicka, *Collection Czechoslov. Chem. Communs.*, **12**, 337 (1947).

where K is the equilibrium constant for the transformation $Z \rightleftarrows Ox$.

Variations of Concentrations.—In order to solve the system of equations (8) and (9) it is useful to make several substitutions, as was done by Koutecky and Brdicka. Furthermore, it will be assumed for the sake of simplicity that the diffusion coefficients of substances Ox and Z are equal; this coefficient is represented by D in the subsequent equations. The following functions are introduced

$$\psi(x,t) = C_{ox}(x,t) + C_z(x,t) \quad (15)$$

$$\varphi(x,t) = C_z(x,t) - (k_b/k_f)C_{ox}(x,t) \quad (16)$$

By using the Laplace transformation[13] it can be shown (see Appendix) that the transforms corresponding to the equations (8) and (9) are

$$\bar{\psi}(x,s) = \frac{C^0}{s} + N \exp\left(-\frac{s^{1/2}}{D^{1/2}}x\right) \quad (17)$$

$$\bar{\varphi}(x,s) = M \exp\left[-\frac{(s + k_f + k_b)^{1/2}}{D^{1/2}}x\right] \quad (18)$$

The integration constants N and M are determined from the transforms of the boundary conditions (see Appendix). By inverse transformation one obtains the functions $\psi(x,t)$ and $\varphi(x,t)$. Thus (see Appendix)

$$\psi(x,t) = C^0 - 2\lambda\left(\frac{Dt}{\pi}\right)^{1/2}\exp\left(-\frac{x^2}{4Dt}\right) + \lambda x \operatorname{erfc}\left(\frac{x}{2D^{1/2}t^{1/2}}\right) \quad (19)$$

and by applying the convolution for $\bar{\varphi}(x,s)$

$$\varphi(x,t) = \frac{\lambda D^{1/2}\frac{k_b}{k_f}}{2(k_b + k_f)^{1/2}}\left\{\begin{array}{l}\exp\left[-x\left(\frac{k_f + k_b}{D}\right)^{1/2}\right] \\ + \exp\left[-x\left(\frac{k_f + k_b}{D}\right)^{1/2}\right]\operatorname{erf}\left[(k_f + k_b)^{1/2}t^{1/2} - \frac{x}{2(Dt)^{1/2}}\right] \\ - \exp\left[x\left(\frac{k_f + k_b}{D}\right)^{1/2}\right]\operatorname{erfc}\left[(k_f + k_b)^{1/2}t^{1/2} + \frac{x}{2(Dt)^{1/2}}\right]\end{array}\right\} \quad (20)$$

The notations "erf" and "erfc" in equations (19) and (20) represent the error function having the quantity between brackets as argument, and the complement of this function, respectively. In view of the definition of the functions $\psi(x,t)$ and $\varphi(x,t)$, the concentrations $C_{ox}(x,t)$ and $C_Z(x,t)$ can be calculated from equations (19) and (20), but it suffices to determine the function $C_{ox}(0,t)$ in order to calculate τ; the value of $C_Z(0,t)$ could be obtained in the same manner, but it is of little interest in the present case. From (15), (16), (19) and (20) one deduces

$$C_{ox}(0,t) = \frac{1}{1 + (k_b/k_f)}\left\{\begin{array}{l}C^0 - 2\lambda(Dt/\pi)^{1/2} \\ - \lambda\frac{k_f}{k_b}\frac{D^{1/2}}{(k_f + k_b)^{1/2}}\operatorname{erf}[(k_f + k_b)^{1/2}t^{1/2}]\end{array}\right\} \quad (21)$$

Dependence of the Transition Time on the Constants k_f, k_b and K.—The transition time is obtained by equating to zero the right-hand member of (21). The resulting equation in τ can be solved graphically, but it is more fruitful to consider plots of $i_0\tau^{1/2}$ vs. i_0. This type of diagram was first used by Gierst and Juliard.[8] From equation (21) one deduces the following equation for the product $i_0\tau^{1/2}$

$$i_0\tau^{1/2} = \frac{\pi^{1/2}}{2}nFC^0D^{1/2} - \frac{\pi^{1/2}}{2}i_0\frac{1}{K(k_f + k_b)^{1/2}}\operatorname{erf}[(k_f + k_b)^{1/2}\tau^{1/2}] \quad (22)$$

Cases in which the error function is virtually equal to unity will be considered first. This simplification is permissible when the argument of the error function, $(k_f + k_b)^{1/2}\tau^{1/2}$, is larger than 2. The product $i_0\tau^{1/2}$ is then a linear function of the current density, and one can calculate the value of $K(k_f + k_b)^{1/2}$ from the slope

$$-\frac{\pi^{1/2}}{2}\frac{1}{K(k_f + k_b)^{1/2}}$$

of the line $i_0\tau^{1/2}$ vs. i_0 without having to know the diffusion coefficient D and the concentration C^0. If the equilibrium constant K is known, the rate constants k_f and k_b are readily obtained ($K = k_f/k_b$).

When the quantity $[(k_f + k_b)^{1/2}\tau^{1/2}]$ is smaller than 2, the error function in equation (22) is smaller than unity. A limiting value of the product $i_0\tau^{1/2}$ for large current densities is obtained by expanding the error function for small arguments[14] (≤ 0.1) and by retaining only the first term in the series. Thus, if $[(k_f + k_b)^{1/2}\tau^{1/2}]$ is smaller than 0.1, equation (22) reduces to

$$i_0\tau^{1/2} = \frac{\pi^{1/2}}{2}\frac{nFC^0D^{1/2}}{(1 + (1/K))} \quad (23)$$

Under these conditions the quantity $i_0\tau^{1/2}$ is independent of the current density. Equation (23) shows that the equilibrium constant K for the transformation $Z \rightleftarrows Ox$ can be calculated from experimental data provided that the limiting value of $i_0\tau^{1/2}$ can be determined. It is to be noted that when $K = \infty$, formula (23) reduces to the equation $C^0 = P\tau^{1/2}$ previously derived for the case in which there is no chemical reaction preceding the electrode process (see equations (1) and (2)).

The conclusions of the above discussion are summarized in Fig. 3. This diagram was constructed on the basis of the following data: $K = 10^{-1}$, $C^0 = 1.1 \times 10^{-4}$ mole. cm.$^{-3}$, $D = 10^{-5}$ cm.^{2} sec.$^{-1}$.

It is of interest to note that in the treatment of Gierst and Juliard,[8] the $i_0\tau^{1/2}$ vs. τ relationship is represented by a straight line which intersects the abscissa axis at a current equal to nFC^0k_h where k_h is an heterogeneous rate constant. The value of this current was simply obtained by expressing that the rate of the transformation $Z \rightleftarrows Ox$ is proportional to the concentration of substance Ox (C_z being assumed to be negligible). From the treatment developed in the present paper one concludes that the heterogeneous rate constant k_h used by Gierst and Juliard actually is equal to the quantity $D^{1/2}K(k_f + k_b)^{1/2}$. Thus k_h has no real physical significance, but is rather a mathematical device.

Application to the Determination of K, k_f, k_b.—The upper limit in the measurement of the quantity $K(k_f + k_b)^{1/2}$ by the present method (see equation (22)) can be evaluated in the following manner. The value of the quantity $i_0\tau^{1/2}$ at $i_0 =$

(13) R. V. Churchill, "Modern Operational Mathematics in Engineering," McGraw-Hill Book Co., Inc., New York, N. Y., 1944. Note that Koutecky and Brdicka used the original Heaviside transform $\bar{f}(s) = s\int_0^\infty \exp(-st)\, f(t)dt$ whereas in our calculations the transform is $\bar{f}(s) = \int_0^\infty \exp(-st)\, f(t)\, dt$.

(14) B. O. Peirce, "A Short Table of Integrals," Ginn and Company Boston, Mass., 1929, p. 120.

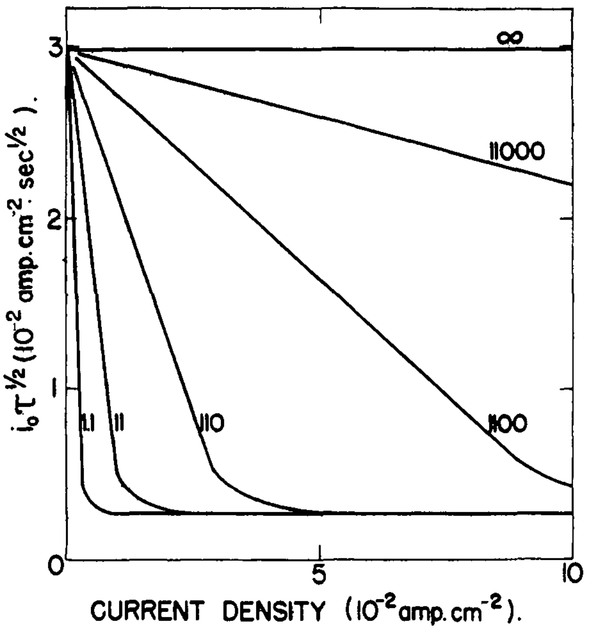

Fig. 3.—Variations of $i_0\tau^{1/2}$ with current density. See data in text. Number on each curve is the value of $(k_f + k_b)$ in sec.$^{-1}$.

0 is simply (see equation (22))

$$\frac{1}{2}\pi^{1/2}nFC^0D^{1/2}$$

The order of magnitude of the maximum value of this quantity is ($C^0 \leq 10^{-5}$ mole cm.$^{-3}$, $D \leq 10^{-5}$ cm.^{2} sec.$^{-1}$, $n = 2$) approximately 6×10^{-3} amp. cm.$^{-2}$ sec.$^{1/2}$. On the other hand, the maximum current density which can be utilized is of the order of 10^{-1} amp. cm.$^{-2}$.[8] Furthermore, it can be conservatively assumed that a 10% decrease in the quantity $i_0\tau^{1/2}$ can be detected as i_0 is varied from 0 to 0.1 amp. cm.$^{-2}$. The corresponding slope of the $i_0\tau^{1/2}$ *vs.* i_0 line is therefore $-0.1 \times 6 \times 10^{-3}/0.1$ or -6×10^{-3} sec.$^{1/2}$. By comparing this value with the slope deduced from equation (22) one deduces that the quantity $K(k_f + k_b)^{1/2}$ should be smaller than approximately 150 sec.$^{-1/2}$ in order to observe with certainty the effect of the chemical reaction preceding the electrochemical process. If the equilibrium constant K is appreciably smaller than unity this condition can be written: $Kk_b^{1/2} < 150$ sec.$^{-1/2}$.

It is of interest to compare this criterion with the corresponding condition for polarographic kinetic currents. In the latter method the average limiting current is virtually diffusion controlled when the quantity $Kk_b^{1/2}$ is smaller than 5 sec.$^{-1/2}$.[15] Actually this limit is somewhat smaller because of the uncertainty about the diffusion coefficient of the substance being studied. Thus a kinetic process which causes a 10% decrease in the limiting current will generally be overlooked.[16] Therefore, it is reasonable to regard the value $Kk_b^{1/2} = 1$ sec.$^{-1/2}$ as the upper limit for which a kinetic effect can be detected by the polarographic method. The value $Kk_b^{1/2} = 1$ sec.$^{-1/2}$ corresponds to a slope of approximately -1 sec.$^{1/2}$ in the $i_0\tau^{1/2}$ *vs.* i_0 diagram. Since the minimum detectable slope is approximately -6×10^{-3} sec.$^{1/2}$, systems which yield an apparently normal polarographic wave might exhibit the characteristics of kinetic complications in electrolysis at constant current.

In conclusion, the conditions for the study of kinetic processes by electrolysis at constant current are far more favorable than in polarography when a rapid chemical transformation is involved.

Second-order Processes.—Under certain conditions which are stated below, the previous treatment can be applied to cases in which the chemical transformation preceding the electrochemical reaction is one of the two processes

$$Z + X \rightleftarrows Ox \quad (24)$$

or

$$Z \rightleftarrows Ox + X \quad (25)$$

where substance X is neither reduced nor oxidized at the potential at which substance Ox is reduced. The rate of the transformation Z to Ox is

$$k'_fC_z(x,t)C_X(x,t) - k'_bC_{ox}(x,t)$$

for reaction (24), and

$$k''_fC_z(x,t) - k''_bC_{ox}(x,t)C_X(x,t)$$

for reaction (25). If the concentration of substance X is a function of x and t the boundary value problem is arduous to solve. In practice, however, it is often possible to carry out the electrolysis in presence of a large excess of substance X (say 100 times the bulk concentration of Z), and under these conditions the concentration $C_X(x,t)$ in the above equations can be replaced by the bulk concentration C^0_X of substance X. Equations (8) to (23) can be applied provided that the constants k_f, k_b and K in these equations are defined as

$$k_f = k'_fC^0_X; \quad k_b = k'_b; \quad K = K'C^0_X \quad (26)$$

$$k_f = k''_f; \quad k_b = k''_bC^0_X; \quad K = K''/C^0_X \quad (27)$$

K' and K'' being the equilibrium constants for (24) and (25).

The slopes of the $i_0\tau^{1/2}$ *vs.* i_0 diagram are then ($k'_f \ll k'_b$; $k''_f \ll k''_b$)

$$-\frac{\pi^{1/2}}{2}\frac{1}{K'k'^{1/2}_bC^0_X}$$

for process (24), and for reaction (25)

$$-\frac{\pi^{1/2}}{2}\frac{(C^0_X)^{1/2}}{K''(k''_b)^{1/2}}$$

From the above values one concludes that the slope of the $i_0\tau^{1/2}$ *vs.* i_0 line decreases when the concentration of substance X is increased in the case of reaction (24), and that this slope increases with C^0_X for reaction (25).

A classical example of electrode process involving a chemical reaction of the type represented by equation (24) is the reduction of pyruvic acid. The polarographic behavior of this substance was thoroughly investigated by Brdicka and coworkers[12] and the findings of these investigators can be readily transposed to the method at constant current. Examples of reaction (25) can be found by studying the reduction of complex ions as shown in the next section.

(15) Compare ref. (12) with P. Delahay, THIS JOURNAL, **73**, 4944 (1951).

(16) It could, however, be detected by studying the dependence of the limiting current on the head of mercury.

Application to the Study of Complex Ions

Mechanism of Reduction.—The theoretical treatment developed in the last section leads to interesting conclusions with regard to the mechanism of the electrolytic reduction of complex ions. Three hypotheses can be made about the reduction of complex ions. It can be assumed: (1) that the complex is the entity which is reduced; (2) that dissociation of the complex must precede the electrochemical reaction; (3) that the previous two modes of reduction occur simultaneously.

From the foregoing considerations one deduces that the quantity $i_0\tau^{1/2}$ is a function of the current density if dissociation precedes the electrochemical reaction. The dissociation process generally involves several consecutive steps. Thus, if MX_n is the complex being studied, dissociation proceeds stepwise with the formation of the intermediates MX_{n-1}, $MX_{n-2} \ldots M_0$.[17] Each of the consecutive steps in the dissociation is characterized by two rate constants k_f and k_b. If the rate constants k_f for the consecutive steps are sufficiently different, it can be assumed that the over-all dissociation of the complex involves essentially one rate-determining step. The treatment developed in the present section is then *approximately* valid. In applying this treatment it should be kept in mind that the equilibrium constant K in equation (22) corresponds to the equilibrium between two species involved in the slow step; *K is not the over-all unstability constant of the complex.* Furthermore, values of k_f obtained in this manner are too low since the effect of the various consecutive steps is accounted for by assuming one single slow step. However, the results can be of interest in deciding whether or not dissociation precedes the electrochemical reaction as is shown in the following two examples.

Reduction of Ethylenediamine–Copper Complexes.—The characteristic $i_0\tau^{1/2}$ *vs.* i_0 were determined for the reduction of the copper ethylenediamine complexes on a mercury electrode, and the results are shown in Table I (see description of the apparatus in the Experimental part).

TABLE I

DATA FOR THE REDUCTION OF COPPER–ETHYLENEDIAMINE COMPLEXES[a] AT 20°

Current (i), 10^{-3} amp.	Transition time (τ) sec.	$i\tau^{1/2}$, 10^{-3} amp. sec.$^{1/2}$
1.048	2.24	1.57
1.272	1.50	1.55
2.044	0.587	1.56
2.636	.360	1.57
3.078	.260	1.57
4.584	.113	1.54
6.060	.0522	1.38
7.455	.0332	1.36
8.835	.0298	1.53

[a] Solution composition: 4 mM copper sulfate, 1.04 M ethylenediamine, 1 M potassium nitrate, temperature 20°.

It is seen from Table I that the product $i\tau^{1/2}$ is independent of the current through the cell,[18] and it can be concluded from this observation that either the complex involved is directly reduced or that the dissociation is so rapid that no kinetic effect is observed. The second hypothesis can be ruled out on the following grounds. The formation constants at 25° for the copper(+2)–ethylenediamine system which are defined by the relationship (en = ethylenediamine)

$$K_1 = C_{M(en)_n}/C_{M(en)_{n-1}}\, C_{en} \quad n = 1,2 \ldots$$

are according to Bjerrum[17,19]: $\log K_1 = 10.72$, $\log K_2 = 9.31$, $\log K_3 = -1.0$. If one assumes that the process corresponding to the highest formation constant ($\log K_1 = 10.72$) is the slow step, one concludes that the rate constant k_b for this step would be larger than 10^{26} sec.$^{-1}$ (slope of the $i_0^{1/2}$ *vs.* i_0 diagram smaller than 10^{-2} sec.$^{-1/2}$, see above; $K'' = 10^{-10.72}$). Such unreasonably large values for a rate constant ($kT/h \approx 6 \times 10^{12}$ sec.$^{-1}$) cannot be accepted, and consequently one concludes that *the copper–ethylenediamine complexes are directly reduced.*

Reduction of the Cadmium Cyanide Complexes.—The example of the copper–ethylenediamine complexes was selected to give an *ab absurdo* proof of the direct electrolytic reduction of a complex. There are cases in which the above theoretical principles enables one to establish the occurrence of a dissociation process prior to the electrochemical reaction. This is the case in the reduction of cadmium cyanide complexes on a mercury electrode. Gierst and Juliard[7] observed that the product $i_0\tau^{1/2}$ for this process decreases very quickly when the current density increases, and these authors interpreted this variation of $i_0\tau^{1/2}$ by assuming that dissociation precedes the electrochemical reaction. This interpretation can now be stated quantitatively on the basis of the above treatment. According to Bjerrum,[17] the formation constants for the cadmium–cyanide complexes are: $\log K_1 = 5.54$, $\log K_2 = 5.06$, $\log K_3 = 4.65$, $\log K_4 = 3.59$. If one takes the reaction corresponding to K_1 as the slow step, the rate constant k_b for the combination of Cd^{++} with one CN^- ion is[20] 4×10^9 (moles per l.)$^{-1}$ sec.$^{-1}$ at 25°. It should be emphasized that this value of k_b is *very approximate* on account of the simplification made by assuming the existence of a single rate-determining step in the dissociation of the cadmium cyanide complexes. Nevertheless, *the above treatment shows that the cadmium cyanide complex must undergo dissociation before electrochemical reduction.*

It can be concluded from these two examples that certain complexes are directly reduced, whereas other complexes are dissociated before being reduced electrolytically. The explanation for this difference in behavior results possibly from the

(17) J. Bjerrum, *Chem. Revs.*, **46**, 381 (1950).

(18) Currents (i) rather than current densities (i_0) are used here. This is permissible since a plot of $i\tau^{1/2}$ *vs.* i has the same slope as a plot $i_0\tau^{1/2}$ *vs.* i_0.

(19) Bjerrum's values are approximately the same as those of G. A. Carlson, J. P. McReynolds and F. H. Verhoek, THIS JOURNAL, **67**, 1334 (1945).

(20) Calculated from a slope equal to 2.6 as measured on the $i_0\tau^{1/2}$ *vs.* i_0 for the reduction of a solution having the following composition: 0.03 M in cadmium, 0.3 M in potassium cyanide. These data are taken from Fig. 8 in the paper of Gierst and Juliard.[1a] Note that there must have been some concentration polarization for the cyanide, since the bulk concentration of the latter ion was only ten times the concentration of cadmium ion. This effect can, however, be neglected in the present approximate calculation.

nature of the bond between the metal and the complexing substance or from differences in structure (copper–ethylenediamine complexes are plane, $Cd(CN)_4^-$ is tetrahedral[17]).

Experimental

The present paper is chiefly concerned with theoretical principles and only a brief description of the experimental methods will be given here. The apparatus was fundamentally the same as that of Gierst and Juliard,[8a] although it was much simpler. The latter authors used a dropping mercury electrode whose operation had to be synchronized with the recording of the voltage–time curve. A mercury pool of constant area was used as polarizable electrode in our instrument, and consequently a synchronization device was not necessary. The mercury pool was found entirely satisfactory provided that the mercury is renewed before each recording and that wetting of the glass by the solution is avoided (silicone coating). The mercury pool electrode had the form of a U-tube having two arms of unequal lengths. One arm of this tube was used for connection with the polarization circuit (platinum wire in mercury). The lid of the arm of the tube immersed in solution extended at least 0.5 cm. above the level of the mercury in order to reproduce as well as possible the conditions of semi-infinite linear diffusion. The exposed area of the electrode was of the order of 1 square centimeter. This electrode was immersed in one compartment of an H polarographic cell. A platinum electrode immersed in the other compartment of this cell, was the anode. Both arms of the cell were filled with the solution being studied. The potential of the mercury pool was recorded from the voltage between this electrode and an external saturated calomel electrode whose tip was in the vicinity of the mercury pool (approximately 1 cm.; not too close to avoid a perturbation in the field of diffusion). The solution was freed of oxygen by bubbling nitrogen through it for 15 minutes. This gas was also passed through the cell before each measurement in order to eliminate any gradient of concentration.

The apparatus for electrolysis at constant current (Fig. 4) was assembled from commercially available components. The electrolytic cell was fed at constant current by a regulated power supply P (250 v.) connected in series with the variable resistances R_1 and R_2. The current was adjusted by means of R_1, and the current intensity was determined by measuring the ohmic drop in the calibrated resistance R_2 by means of a Leeds and Northrup student potentiometer. The voltage between the mercury pool (e_3) and the reference electrode (e_2) was recorded by means of cathode-ray oscillograph (DuMont oscillograph 304 H; amplifiers not represented in Fig. 4). A 10 megohm resistor was inserted between electrode e_2 and the "Y" input of the oscillograph in order to lower the current drawn from the cell e_2e_3. The single-sweep time T basis of the oscillograph was operated by means of S_2, the necessary signal being applied to terminal B. A D.P.S.T. relay was used for S_1S_2, and this relay was adjusted in such a manner as to close S_2 slightly before S_1 in order to avoid missing the zero time point. A switch could be used for S_1 and S_2, but a relay can be more easily adjusted to obtain a short lag between the closing of S_1 and S_2. The horizontal axis of the oscillograph was calibrated by applying a sinusoidal signal of known frequency (Hewlett Packard audio oscillator, model 200 I) to the "Z" modulation input of the oscillograph, and by actuating the relay S_1S_2, the "Y" input amplifier being turned off. An horizontal trace composed of a succession of bright spots was recorded in this fashion, and the distance between two successive bright spots was readily calculated from the frequency of "Z" modulation. Oscillograms were photographed on 35 mm. film and readings were made from enlarged images.

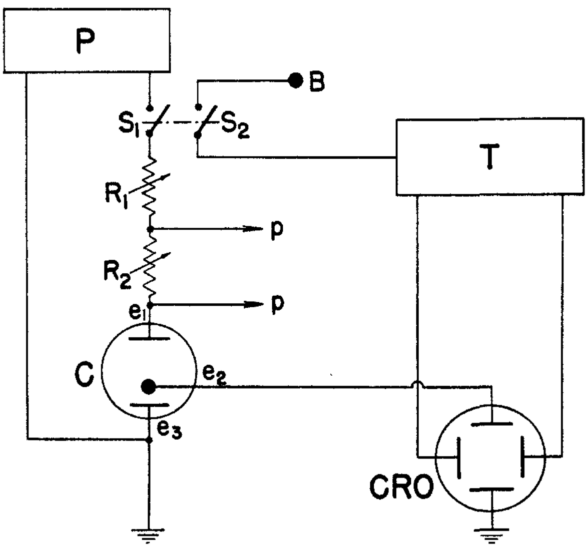

Fig. 4.—Schematic diagram of the apparatus for the oscillographic recording of potential–time curves: P, regulated power supply; C, electrolytic cell; CRO, cathode-ray oscillograph; T, time basis of the oscillograph; R_1, adjustable resistance, up to 1 megohm; R_2, 0–9999 ohm decade box; S_1S_2, D.P.S.T. relay; pp, terminals to student potentiometer; B, input for the signal actuating the time basis of the oscillograph; e_1, platinum anode; e_2, reference electrode (saturated calomel electrode); e_3, mercury pool electrode.

Conclusion

It is possible to develop a rigorous treatment for electrolysis at constant current with mass transfer partially or totally controlled by semi-infinite linear diffusion. The characteristics of the potential–time curves appear to be particularly useful in the study of irreversible electrode processes. *In such studies the method at constant current is more advantageous than polarography because the mass transfer problem can be treated rigorously; in polarography only an approximate solution of the boundary value problem can be given because of the complications resulting from the expansion of the mercury drop.* Likewise, the method at constant current appears very promising in the study of the mechanism of the reduction of complex ions.

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Appendix

By assuming that $D_r = D_o = D$ and introducing the functions $\psi(x,t)$ and $\varphi(x,t)$ defined by equations (15) and (16) one transforms the boundary value problem originally stated by equations (8) to (14) into the problem

$$\partial\psi(x,t)/\partial t = D(\partial^2\psi(x,t)/\partial x^2) \quad (28)$$

$$\partial\varphi(x,t)/\partial t = D(\partial^2\varphi(x,t)/\partial x^2) - (k_f + k_b)\varphi(x,t) \quad (29)$$

with the initial and boundary conditions as

$$\psi(x,0) = C^0 \quad (30)$$

$$\varphi(x,0) = 0 \quad (31)$$

$$\partial\psi(0,t)/\partial x - \partial\varphi(0,t)/\partial x = (\lambda + (k_b/k_f)) \quad (32)$$

$$\partial\varphi(0,t)/\partial x = -(k_b/k_f)(\partial\psi(0,t)/\partial x) \quad (33)$$

The new initial and boundary conditions (30) to (33) are easily derived from equations (10) to (14) by using the following values of $C_{ox}(x,t)$ and $C_r(x,t)$

$$C_{ox}(x,t) = \frac{\psi(x,t) - \varphi(x,t)}{1 + (k_b/k_f)} \quad (34)$$

$$C_r(x,t) = \frac{\varphi(x,t) + (k_b/k_f)\psi(x,t)}{1 + (k_b/k_f)} \quad (35)$$

which result from the definition of $\psi(x,t)$ and $\varphi(x,t)$ by (15) and (16).

After Laplace transform with respect to the variable t, equations (28) and (29) are reduced to the following ordinary differential equations

$$D(\mathrm{d}^2\bar{\psi}(x,s)/\mathrm{d}x^2) - s\bar{\psi}(x,s) + C^0 = 0 \quad (36)$$

$$D(\mathrm{d}^2\bar{\varphi}(x,s)/\mathrm{d}x^2) - (s + k_f + k_b)\bar{\varphi}(x,s) = 0 \quad (37)$$

and the boundary conditions are accordingly

$$\frac{\mathrm{d}\bar{\psi}(0,s)}{\mathrm{d}x} - \frac{\mathrm{d}\bar{\varphi}(0,s)}{\mathrm{d}x} = \frac{\lambda(1 + (k_b/k_f))}{s} \quad (38)$$

$$\mathrm{d}\bar{\varphi}(0,s)/\mathrm{d}x = (k_b/k_f)(\mathrm{d}\bar{\psi}(0,s)/\mathrm{d}x) \quad (39)$$

The solutions of equations (36) and (37) ($\bar{\psi}(x,s)$ and $\bar{\varphi}(x,s)$ are bound for $x \to \infty$) were given above in equations (17) and (18).

The integration constants M and N are evaluated by satisfying the boundary conditions (38) and (39). Thus

$$\bar{\psi}(x,s) = (C^0/s) - \lambda(D^{1/2}/s^{3/2}) \exp(-s^{1/2}x/D^{1/2}) \quad (40)$$

$$\bar{\varphi}(x,s) = \lambda \frac{k_b}{k_f}\left(1/s\left(\frac{s + k_f + k_b}{D}\right)^{1/2}\right) \exp\left[-x\left(\frac{s + k_f + k_b}{D}\right)^{1/2}\right] \quad (41)$$

By inverse transformation one finally obtains the functions $\psi(x,t)$ and $\varphi(x,t)$. The inverse transform of $\bar{\psi}(x,s)$, as given in equation (19), is obtained directly from tables.[13] The inverse transform of $\bar{\varphi}(x,s)$ is obtained by applying the convolution.[13] Thus

$$\varphi(x,t) = \lambda(k_b/k_f)\int_0^t (D/\pi\epsilon)^{1/2} \exp\left[-(k_f + k_b)\xi - (x^2/4\xi)\right]\mathrm{d}\xi \quad (42)$$

For the evaluation of the integral in (42) see Horenstein.[21] By applying the result obtained by this author, equation (20) is readily derived.

As a final comment, it should be mentioned that the equation for the potential–time curve can be derived from the above results. If the reduction Ox to Red is irreversible, the potential during electrolysis is calculated by the same method as that exposed in the section entitled "Irreversible Electrode Processes." The concentration $C_{ox}(0,t)$ needed in this calculation is given in equation (21). If the process is reversible the potential is calculated from the Nernst formula. The concentration $C_{red}(0,t)$ needed in this calculation is determined from the flux of this substance (equal to $-D\partial C_{ox}(0,t)/\partial x$) at the electrode surface and by application of Duhamel's theorem.[22] This derivation is not given here for the sake of briefness, since it is the transition time which is of interest in the present case.

(21) W. Horenstein, *Quart. App. Math.*, **3**, 183 (1945).

(22) See for example H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, London, 1947, p. 18.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

Determination of the Valence of a Heteropoly Anion: Dodecamolybdoceric(IV) Acid and its Salts. Structural Considerations

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Solutions of pure 12-molybdoceric(IV) acid were prepared by the use of ion-exchange resin. Potentiometric titration confirmed the presence of eight replaceable hydrogen ions as indicated by the formulas of some of its salts. A new salt containing eight dimethylammonium groups was made from the free acid. A structural formula is suggested based on a central CeO_6 octahedron, which is consistent with the observed basicity.

Potentiometric titration of a solution of a free heteropoly acid offers a convenient method for determining approximate dissociation constants, and the number of replaceable hydrogen ions per molecule. The recent application of the ion-exchange method to the production of heteropoly acids from their recrystallized salts[2] has made it possible to prepare solutions of a number of these acids in a pure state. Heteropoly acids made by older methods could not be purified readily by recrystallization because of the high solubility characteristic of this class of compounds[3]; the presence of even small amounts of impurities, such as acids of low molecular weight, would introduce significant errors in the titrations because of the high molecular weight and polybasic nature of the heteropoly acids.

The purpose of the present work is to apply the method of potentiometric titration to a 12-molybdoheteropoly acid, and to one of its salts recently prepared in this Laboratory.

The dodecamolybdocerates(IV) were chosen for study because the free acid proved to be stable, and because the high basicity assigned to the anion by its discoverer seemed to offer interesting possibilities for discussing its structure.

Barbieri[4] has reported dodecamolybdocerates(IV) to which he assigned the following Miolati–Rosenheim formulas: $(NH_4)_8[Ce(Mo_2O_7)_6]\cdot 8H_2O$, $(NH_4)_6H_2[Ce(Mo_2O_7)_6]\cdot 10H_2O$, $Ag_8[Ce(Mo_2O_7)_6]$. Meinhard[5] has described the sodium salt: $4Na_2O$, $CeO_2\cdot 12MoO_3\cdot 6H_2O$, which may be formulated as $Na_8[Ce(Mo_2O_7)_6]\cdot 6H_2O$. All of these formulas indicate an octabasic anion.

Experimental

Yellow ammonium dodecamolybdocerate(IV) octahydrate, $(NH_4)_8[CeMo_{12}O_{42}]\cdot 8H_2O$, was prepared according to Barbieri[4] by adding 5% ammonium cerium(IV) nitrate solution to boiling 0.25 M ammonium paramolybdate solution. In order to obtain pure material the normal salt was converted to the light yellow acid salt, by saturating dilute sulfuric acid at 65° with the former, filtering, cooling, and adding a saturated ammonium nitrate solution. Light yellow crystals separated and were filtered and washed free of sulfate ion with saturated ammonium nitrate solution. The crystals were washed thoroughly with methyl alcohol, recrystallized from hot water, filtered and washed with methyl alcohol.

A warm solution of the light yellow crystals was converted to the free heteropoly acid by the ion-exchange method,[2] using Amberlite IR-200 (Rohm and Haas Company) which had been upflow regenerated and washed. The yellow

(1) Chemistry Department, Boston University, Boston 15, Massachusetts.

(2) L. C. W. Baker, B. Loev and T. P. McCutcheon, THIS JOURNAL, **72**, 2374 (1950).

(3) See, for example, R. D. Hall, *ibid.*, **29**, 690 (1907).

(4) G. A. Barbieri, *Atti Accad. Lincei*, [5] **23**, 1, 805 (1914).

(5) A. Meinhard, "Zur Kenntnis der Heteropolymolybdate des Mangans und einiger vierwertiger Elemente," Berlin, 1928.