Kinetics of Fast Electrode Reactions

By Talivaldis Berzins[1] and Paul Delahay

A method is described for the study of the kinetics of fast electrode reactions. The working electrode, whose kinetics is being studied, is coupled with an unpolarized electrode, and the potential of the former electrode is adjusted at its equilibrium value. A current impulse represented by a step function is passed through the electrolytic cell, and the potential of the working electrode is recorded. The parameters characterizing the kinetics of electron transfer—the rate constant k_s at the standard potential and the transfer coefficient α—are determined from potential–time curves. A rigorous mathematical analysis, which takes into account the double layer capacity, is developed for potential–time curves. Values of k_s up to 10^2 cm. sec.$^{-1}$ can be determined, and application to the study of the kinetics of so-called "reversible" electrode reactions in aqueous solutions and in fused salts is thus possible. Experimental methods are described in detail: cell with hanging drop electrode, generator of current impulses having the shape of a step function (transients shorter than one microsec.), compensation of ohmic drop, etc. The application to the reduction of cadmium ions on cadmium amalgam yielded experimental results which were in excellent agreement with theory.

Introduction

In a recent note and a more detailed paper[2] a method was described for the kinetic study of fast electrode reactions. In this method, the potential of the electrode whose kinetics is being studied is adjusted at its equilibrium value, and a current impulse represented by a step function flows through the electrolytic cell. This cell may be composed of two identical polarized electrodes or one polarized and one unpolarized electrode. The solution is not stirred, and a large excess of supporting electrolyte is present: diffusion is thus the sole mode of mass transfer. The polarized electrode is a plane, and conditions of semi-infinite linear diffusion are assumed to prevail. The voltage across the cell is recorded during electrolysis, and parameters characterizing the kinetics of electron transfer are calculated from voltage–time curves. A theoretical analysis of these curves was presented in our previous publications for the simplified case in which the double layer capacity is neglected. A rigorous analysis in which this simplification is not made is now presented, and experimental methods are discussed in detail.

The rate of an electrode reaction represented by the symbolic equation, $O + ne^- = R$, and involving only a single rate-determining step is

$$i_t = nF \left\{ C_O k_f^0 \exp\left[-\frac{\alpha n FE}{RT} \right] - C_R k_b^0 \exp\left[\frac{(1-\alpha) nFE}{RT} \right] \right\} \quad (1)$$

where the notations are as follows: i_f, the current density, which is positive for a cathodic reaction; n, the number of electrons involved in the electrode reaction; F, the faraday; R, the gas constant; T, the absolute temperature; C_O and C_R, the concentrations of substances O and R, respectively, at the electrode–solution interface; E, the electrode potential referred to the normal hydrogen electrode; α, the transfer coefficient; k^0 and k_b^0, the formal rate constants at $E = 0$ for the forward and backward reactions, respectively. Equation 1 is written on the assumption that the number of electrons involved in the rate-determining step is equal to the number of electrons in the over-all reaction. Fur-

thermore, it is assumed that substance O is soluble in solution, and that the reduction product is soluble either in solution or in the electrode as in the deposition of an amalgam-forming metal on a mercury electrode. The modification of equation 1 and the subsequent treatment is trivial when R is an insoluble species (metal).[3]

At the equilibrium potential E_e the current is equal to zero, and one has

$$C_O k_f^0 \exp\left[-\frac{\alpha n FE_e}{RT} \right] = C_R^0 k_b^0 \exp\left[\frac{(1-\alpha) nFE_e}{RT} \right] \quad (2)$$

where C_O^0 and C_R^0 are the concentrations at equilibrium. The quantities equated in (2) can also be written in the form

$$C_O^{0(1-\alpha)} C_R^{0\alpha} k_s$$

where k_s is defined by

$$k_s = k_f^0 \exp\left[-\frac{\alpha n FE^0}{RT} \right] = k_b^0 \exp\left[\frac{(1-\alpha) nFE^0}{RT} \right] \quad (3)$$

In view of equations 2 and 3 the current–potential relationship (1) can now be written in a form containing only the rate constant k_s, i.e.

$$i_t = nF k_s C_O^{0(1-\alpha)} C_R^{0\alpha} \left\{ \frac{C_O}{C_O^0} \exp\left[-\frac{\alpha n F(E-E_e)}{RT} \right] - \frac{C_R}{C_R^0} \exp\left[\frac{(1-\alpha) nF(E-E_e)}{RT} \right] \right\} \quad (4)$$

E^0 being the standard potential for the system $O + ne^- = R$. The product

$$nF k_s C_O^{0(1-\alpha)} C_R^{0\alpha} = i_0 \quad (5)$$

is the exchange current density, and can be used to characterize the kinetics of electrode reactions. The main drawback in the use of the exchange current density results from the dependence of i_0 on the equilibrium concentrations C_O^0 and C_R^0, i.e., on the potential. This is not the case for the rate constant k_s which is therefore more characteristic of the kinetics of electron transfer.[4]

The kinetic parameters α and k_s or i_0 can be determined by conventional polarization experiments for values of k_s up to about 10^{-3}–10^{-2} cm. sec.$^{-1}$. Faster reactions with values of k_s up to about 1 cm. sec.$^{-1}$ can be studied by electrolysis with superim-

(1) Predoctoral fellow, 1953–1955.

(2) (a) T. Berzins and P. Delahay, J. Chem. Phys., 23, 972 (1955); (b) T. Berzins and P. Delahay, Z. Elektrochem., in press (proceedings of the 1955 annual meeting of the Bunsen Gesellschaft).

(3) For a detailed discussion of equation 1 see an electrochemistry text.

(4) J. E. B. Randles, Trans. Faraday Soc., 48, 828 (1952).

posed alternating voltage.[5] Such processes and possibly faster reactions can be studied by the method at constant potential recently developed by Vielstich and Gerischer.[6]

Boundary Value Problem

The electrolysis current density i_t is the sum of a faradaic component i_t corresponding to electron transfer and the capacity current density i_c used to charge, or discharge, the double layer. The faradaic component is given by equation 4 in which the exchange current density, as written in equation 5, can be introduced for the sake of simplicity. The capacity current density is

$$i_c = - c_1 \, d \, (E - E_e)/dt \qquad (6)$$

where c_1 is the differential capacity of the double layer. Since the sum of the faradaic and capacity currents is constant, one has

$$i_t + i_c = i_t \qquad (7)$$

The potential–time relationship is derived by solving Fick's equation for linear diffusion for the following initial and boundary conditions

$$C_O = C_O^0 \text{ and } C_R = C_R^0 \text{ for } x \geqslant 0 \text{ and } t = 0 \quad (8)$$

$$C_O \longrightarrow C_O^0 \text{ and } C_R \longrightarrow C_R^0 \text{ for } x \longrightarrow \infty \text{ and } t \geqslant = 0 \qquad (9)$$

$$i_t = - c_1 d(E - E_e)/dt + nFD_O(\partial C_O/\partial x)_{x=0} \quad (10)$$

$$nFD_O(\partial C_O/\partial x)_{x=0} = i_0$$

$$\left\{ \begin{array}{l} \dfrac{(C_O)_{x=0}}{C_O^0} \exp\left[- \dfrac{\alpha nF(E - E_e)}{RT} \right] \\[2mm] - \dfrac{(C_R)_{x=0}}{C_R^0} \exp\left[\dfrac{(1 - \alpha)nF(E - E_e)}{RT} \right] \end{array} \right\} \qquad (11)$$

$$D_O(\partial C_O/\partial x)_{x=0} = - D_R(\partial C_R/\partial x)_{x=0} \qquad (12)$$

The new notations in the above conditions are as follows: the D's, the diffusion coefficients; x, the distance from the electrode; and t, the time elapsed since the beginning of electrolysis. Condition (10), in which the second term on the right-hand side is the faradaic current density written in terms of the flux of substance O at the surface of the electrode, expresses the condition that the total current density is constant (see equation 7). Condition (11) expresses the equality of the flux of substance O at the electrode surface to the faradaic current density calculated from (4) and (5). Finally, condition (12) expresses the equality of the fluxes of substances O and R at the electrode surface.

The solution of this boundary value problem will be given for the particular case in which the exponentials in (11) can be replaced without any appreciable error by the first two terms of their expansion in series. This is the case when the condition $E - E_e \ll RT/nF$ is fulfilled, i.e., when the departure from the equilibrium potential does not exceed a few millivolts. The boundary value problem is simplified when the relative concentrations[7]

$$\psi_O = (C_O - C_O^0)/C_O^0 \text{ and } \psi_R = (C_R - C_R^0)/C_R^0 \quad (13)$$

(5) For a survey see for instance P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954.

(6) (a) H. Gerischer and W. Vielstich, Z. physik. Chem., N. F., **3**, 16 (1955); (b) W. Vielstich and H. Gerischer, ibid., **4**, 12 (1955).

(7) Relative concentrations were first used in problems of this type by H. Gerischer, Z. physik. Chem., **198**, 286 (1951).

are introduced. After linearization the boundary conditions are

$$(\partial\psi_O/\partial x)_{x=0} = \lambda_O[(\psi_O)_{x=0} - (\psi_R)_{x=0} - nF(E - E_e)/RT] \qquad (14)$$

with

$$\lambda_O = i_0/nFD_O C_O^0 \qquad (15)$$

and a similar condition in terms of ψ_R. Furthermore one has

$$\psi_O = \psi_R = 0 \quad \text{for } x \geqslant 0 \text{ and } t = 0 \qquad (16)$$

$$\psi_O \longrightarrow 0 \text{ and } \psi_R \longrightarrow 0 \text{ for } x \longrightarrow \infty \text{ and } t \geqslant 0 \quad (17)$$

The solution, which is obtained by means of the Laplace transformation as shown in appendix, is

$$E - E_e =$$

$$\frac{i_t}{c_e(\gamma - \beta)} \left\{ \begin{array}{l} \dfrac{\gamma}{\beta^2} \left[\exp(\beta^2 t) \, \mathrm{erfc}\,(\beta t^{1/2}) + 2\beta\left(\dfrac{t}{\pi}\right)^{1/2} - 1 \right] \\[3mm] - \dfrac{\beta}{\gamma^2} \left[\exp(\gamma^2 t)\, \mathrm{erfc}\,(\gamma t^{1/2}) + 2\gamma\left(\dfrac{t}{\pi}\right)^{1/2} - 1 \right] \end{array} \right\} \qquad (18)$$

where the notation "erfc" represents the complement of the error function; β is defined by the following relationship

$$\beta = \frac{i_0}{2nF}\left(\frac{1}{D_O^{1/2}C_O^0} + \frac{1}{D_R^{1/2}C_R^0}\right) +$$
$$\left[\frac{i_0^2}{4n^2F^2}\left(\frac{1}{D_O^{1/2}C_R^0} + \frac{1}{D_R^{1/2}C_R^0}\right)^2 - \frac{nF}{RT} - \frac{i_0}{c_1}\right]^{1/2} \quad (19)$$

and γ is defined by the same equation as (19) but with a minus sign in front of the quantity between brackets.

Potential–Time Relationship

The potential–time relationship (18) will be first discussed for the case in which the conditions $C_O^0 = C_R^0 = C^0$ and $D_O = D_R = D$ are fulfilled. The interpretation is then greatly simplified. However, the general equation will be utilized in the calculation of k_s and α. In the simplified case the constants β and γ, which are now

$$\beta = \frac{k_s}{D^{1/2}}\left[1 + \left(1 - \frac{n^2F^2C^0D}{RTc_1k_s}\right)^{1/2}\right] \qquad (20)$$

$$\gamma = \frac{k_s}{D^{1/2}}\left[1 - \left(1 - \frac{n^2F^2C^0D}{RTc_1k_s}\right)^{1/2}\right] \qquad (21)$$

can be real or complex quantities according to whether the quantity

$$\frac{n^2F^2C^0D}{RTc_1k_s}$$

is smaller or larger than unity. By taking the following representative values, $n = 1$, $T = 300°K.$, $D = 10^{-5}$ cm.^{2} sec.$^{-1}$, $c_1 = 2 \times 10^{-5}$ farad. cm.$^{-2}$, $C^0 = 10^{-6}$ mole cm.$^{-3}$, one deduces that β and γ are real when k_s is of the order of unity or larger. The case in which the latter condition is fulfilled will be first discussed.

It is seen from equation 18 that the potential–time relationship contains two types of functions of the generalized form $2T/\pi^{1/2}$ and $\exp\,(T^2)$ erfc (T) where T is either $\beta t^{1/2}$ or $\gamma t^{1/2}$. By calculating the ratio

$$\frac{\exp\,(T^2)\,\mathrm{erfc}\,(T)}{2T/\pi^{1/2}}$$

one can show that the terms containing the exponentials and error function complements in (18) are

smaller than one hundredth of the term in $T^{1/2}$ when $\beta t^{1/2}$ and $\gamma t^{1/2}$ are smaller than, say, 7. By using the smallest possible value of $\gamma (\beta > \gamma)$, one concludes that this approximation is valid for times longer than approximately 5×10^{-5} sec. One then can use the following simplified equation which is written without the introduction of any assumption about the concentrations or diffusion coefficients

$$E - E_e =$$
$$- \frac{RT i_t}{nF} \left\{ \begin{array}{c} \frac{2}{\pi^{1/2} nF} \left(\frac{1}{C_O^0 D_O^{1/2}} + \frac{1}{C_R^0 D_R^{1/2}} \right) t^{1/2} \\ - \frac{RT}{nF} \left[\frac{1}{nF} \left(\frac{1}{C_O^0 D_O^{1/2}} + \frac{1}{C_R^0 D_R^{1/2}} \right) \right]^2 c_1 \\ + \frac{1}{nF k_s C_O^{0(1-\alpha)} C_R^0 \alpha} \end{array} \right\} \quad (22)$$

Equation 22, as written for the particular case in which the double layer capacity c_1 is equal to zero, is identical with the equation derived in our previous papers[2] for that case. When $c_1 = 0$, there is a sudden potential variation at the beginning of electrolysis, but this is not the case when the double layer capacity is taken into account. It follows from (18) that $E - E_e = 0$ at $t = 0$, and that there is a progressive variation of potential as the electrolysis proceeds. This is indeed observed experimentally[3] (Fig. 1).
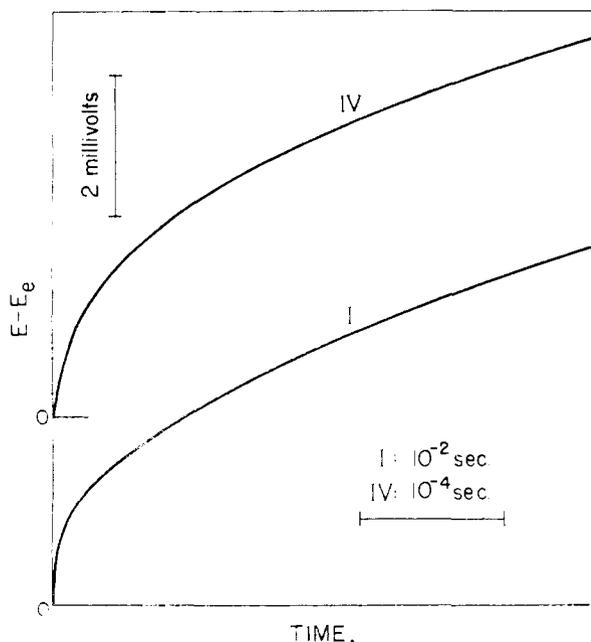

Fig. 1.—Tracings of potential–time curves for the deposition of Cd^{++} on cadmium amalgam. The number of each curve refers to the conditions listed in Table I.

The analysis of equation 18 involves some difficulty when the quantities $\beta t^{1/2}$ and $\gamma t^{1/2}$ are complex because error functions of complex arguments are not tabulated. However, equation 18 can be transformed in a real form by the follow-

ing procedure: the error function is expanded in a uniformly convergent series, which, as was pointed out by Born,[9] can be separated into real and imaginary parts. By replacing the error functions in (18) by this series and by rearranging terms, one finds that the imaginaries cancel out, and that equation 18 is thus transformed in a real form. The resulting equation is too complicated for any practical purpose, but it can be shown that, if the absolute values of $\beta t^{1/2}$ and $\gamma t^{1/2}$ are larger than unity, the series resulting from expansion of the error functions are negligible with respect to the terms containing the square root of time. An equation identical to (22) is obtained, and this equation can thus be applied for any value of k_s.

Determination of Kinetic Parameters

It follows from equation 22 that a plot of $E - E_e$ against $t^{1/2}$ yields a straight line whose intercept at time $t = 0$ depends on two terms containing the rate constant k_s and the differential capacity c_1. Hence, the rate constant k_s can be determined from experimental data provided that the term in k_s is not negligible in comparison with the term in c_1. By assuming that the term containing the rate constant should not be less than one tenth of the capacity term, and by taking the following representative values, $n = 2$, $T = 300°K.$, $D_O = D_R = 10^{-5}$ cm.^{2} sec.$^{-1}$, $c_1 = 2 \times 10^{-5}$ farad. cm.$^{-2}$, $C_O = C_R = 10^{-5}$ moles. cm.$^{-5}$, one deduces from (22) that values of k_s up to 100 cm. sec.$^{-1}$ could easily be determined.

It is convenient to evaluate the rate constant k_s from

$$(E - E_e)_{t_i^{1/2}} = - \frac{RT}{nF} \frac{i_t}{i}$$
$$= - \frac{RT}{n^2 F^2} \frac{i_t}{k_s C_O^{0(1-\alpha)} C_R^0 \alpha} \quad (23)$$

at $t_i^{1/2}$ given by

$$t_i^{1/2} = \frac{\pi^{1/2}}{2} \frac{RT}{n^2 F^2} \left(\frac{1}{C_O^0 D_O^{1/2}} + \frac{1}{C_R^0 D_R^{1/2}} \right) c_1 \quad (24)$$

Since the slope of the linear plot of $E - E_e$ against $t^{1/2}$ is

$$\delta = \frac{2}{\pi^{1/2}} i_t \frac{RT}{n^2 F^2} \left(\frac{1}{C_O^0 D_O^{1/2}} + \frac{1}{C_R^0 D_R^{1/2}} \right) \quad (25)$$

the combination (23) and (25) yields the following very simple expression for $t_i^{1/2}$

$$t_i^{1/2} = \frac{\pi c_1 \delta}{4 i_t} \quad (26)$$

An example of plot of $E - E_e$ against $t^{1/2}$ is shown in Fig. 2 for the reduction of cadmium ions on cadmium amalgam under the conditions listed in Table I.

TABLE I

DATA[a] FOR THE SYSTEM $Cd^{++}/Cd(Hg)$

Expt.	$C^0_{cd^{++}}$ $\times 10^{-7}$ mole cm.$^{-3}$	δ $\times 10^{-3}$ v. sec.$^{-1/2}$	$t_i^{1/2}$ $\times 10^{-3}$ sec.$^{1/2}$	$(E - E_e)t_i^{1/2}$, mv.	i_0 $\times 10^{-2}$, amp. cm.$^{-2}$	k_s $\times 10^{-2}$ cm. sec.$^{-1}$
I	10	0.242	0.716	−0.40	3.03	4.48
II	5.0	0.490	1.45	−0.70	1.73	4.56
III	2.5	0.990	2.90	−1.20	1.01	4.43
IV	1.0	2.41	7.11	−2.45	0.494	4.41

Av. 4.47

[a] Supporting electrolyte, 1 M sodium sulfate; current density 9.30 $\times 10^{-4}$ amp. cm.$^{-2}$; cadmium concentration in amalgam, 0.6 mole % (4.0×10^{-4} mole cm.$^{-3}$); temperature, 25 $\pm$ 0.1°; double layer differential capacity, 3.5 $\times 10^{-5}$ farad. cm.$^{-2}$.

(8) A distortion of potential-time curves resulting from the double layer capacity is also observed in the case of totally irreversible processes. No abrupt change of potential is observed at time $t = 0$, although the simplified treatment, in which the double layer capacity is neglected, predicts such a change (see P. Delahay and T. Berzins, THIS JOURNAL, **75**, 2486 (1953).

(9) M. Born, "Optik," reprinted by Edwards Brothers, Ann Arbor, Michigan, 1943, p. 483.
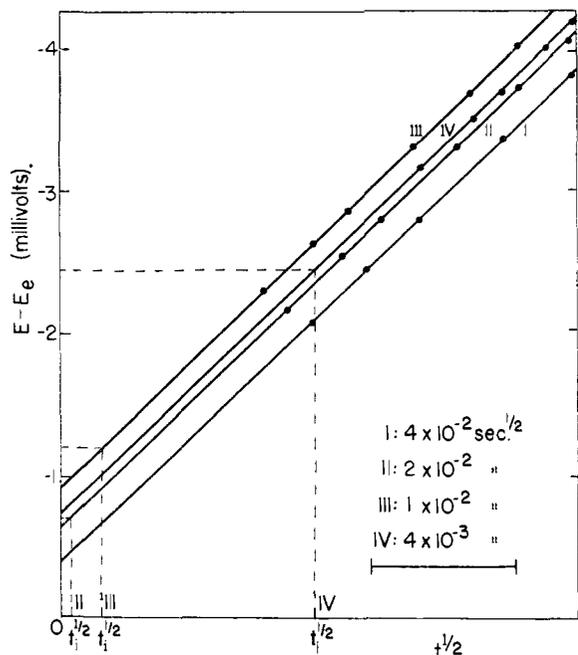
Fig. 2.—Plot of $E - E_e$ against $t^{1/2}$ for the system $Cd^{++}/$ Cd(Hg). See data in Table I.

Unless the concentrations C_O^0 and C_R^0 are equal, the value of the intercept given by (23) contains the transfer coefficient α. Conversely, when $C_O^0 = C_R^0$ the knowledge of α is not required in calculation of k_s. The following method for determining α, which was used by Gerischer[10] in his studies on electrolysis with alternating current, can be applied: the exchange current is determined for varying concentrations of one reactant, the concentration of the other reactant being kept constant, and the logarithm of the exchange current density is plotted against logarithm of the varying concentration. A straight line whose slope is either α or $1 - \alpha$ is obtained, as one can readily see from the definition of the exchange current density by equation 5. It was verified on the basis of the data in Table I that such a linear relationship is indeed obtained experimentally.

The transfer coefficient can also be determined, as was pointed out in our previous paper,[2] by plotting the quantity

$$\ln \frac{\left[1 - \left(\frac{t}{\tau_c}\right)^{1/2}\right] - \left[1 + \left(\frac{t}{\tau_a}\right)^{1/2}\right] \exp\left[\frac{nF}{RT}(E - E_e)\right]}{i_t}$$

against $E - E_e$, where the τ's are the transition times for the cathodic and anodic processes, respectively. The slope of the resulting line is $\alpha nF/RT$, and the transfer coefficient is thus readily obtained. The precision of this method is not very good because of errors made during the recording of potential–time curves with a cathode ray oscilloscope. This drawback is not encountered in the preparation of plots such as those in Fig. 2 because variations of potential are then much smaller than in the case of the above logarithmic plot.

Values of the rate constant k_s calculated for the

(10) H. Gerischer, Z. Elektrochem., **57**, 604 (1953).

data of Fig. 2 are listed in Table I, and the average value, $k_s = 4.5 \times 10^{-2}$ cm. sec.$^{-1}$, is in excellent agreement with the value, $k_s = 4.2 \times 10^{-2}$ cm. sec.$^{-1}$, obtained by Gerischer[10] by electrolysis with superimposed alternating voltage. The values of the transfer coefficient $\alpha = 0.21$ obtained from the plot of log i_0 against log $C_{Cd^{++}}^0$ and the value $\alpha = 0.23$ deduced by the other method discussed above are in good agreement with Gerischer's value[10] of 0.17 ± 0.03.

Experimental

Cell.—The cell (Fig. 3), which was similar to the one used by Gerischer[11] in his studies of electrolysis with superimposed alternating voltage, was essentially composed of two amalgam electrodes of identical composition. A hanging amalgam drop was the working electrode, and the other electrode was an amalgam pool having an area about 200 times larger than the drop. The amalgam was let to flow at a constant rate through an ordinary polarographic capillary, and the amalgam drops were caught in the groove on a small glass spoon attached to the capillary with such an inclination that the drops rolled slowly down the groove. The capillary, which was held in a closely fitting glass sleeve, could be rotated about its axis in such a fashion that the drops rolling along the groove touched the tip of a small gold-plated platinum wire serving as terminal of the working electrode. This platinum wire was sealed in a glass tube and only its tip, about 0.1 mm. long, was left uncovered. The wire was coated with gold because mercury does not adhere to platinum. The hanging drop was renewed by collecting additional drops until the limit of adhesion was exceeded and the drop was dislodged. A new drop of very reproducible size was then replaced on the platinum tip. The obvious advantage of the hanging drop over the dropping electrode in this type of study is the elimination of a device for synchronization of the dropping electrode with the recording of potential–time curves.
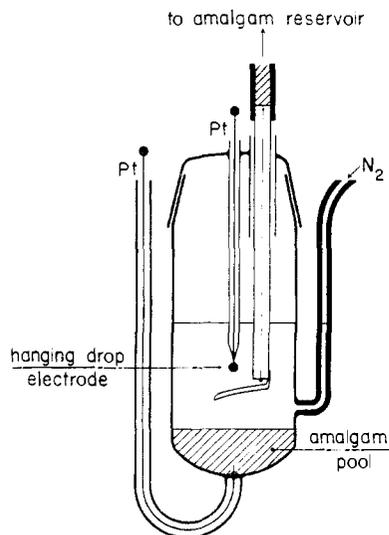

Fig. 3.—Cell with hanging mercury drop.

The size of the amalgam drop was determined by collecting a known number of drops and by weighing them according to standard polarographic techniques. The amalgam was prepared by dissolving in mercury a known weight of finely divided pure cadmium metal in a nitrogen atmosphere.

Solutions were freed from dissolved oxygen before electrolysis by bubbling nitrogen through them according to polarographic practice. This gas was also passed through the cell before each measurement to eliminate any gradient of concentration.

Compensation of Ohmic Drop.—The ohmic drop in the cell, which was much larger than the potential changes in

(11) H. Gerischer, Z. physik. Chem., **202**, 302 (1953).

the early stages of electrolysis, was compensated with the bridge of Fig. 4. The cell CE containing only the supporting electrolyte (amalgam electrodes replaced by identical mercury electrodes) was placed in one of the arms of the bridge, and the adjustable resistance R_3, in a series with the variable capacitor C_1, served as the equivalent circuit of the cell. The bridge was fed at a few millivolts[12] by an oscillator at 1,000 cycles per second. The elements R_3 and C_1 were adjusted with $R_1 = R_2$ until balance was obtained. The balance indicator was the cathode-ray oscilloscope used in the recording of potential–times curves. The differential capacity of the double layer for the working amalgam electrode was measured by a similar method. In the latter case, the amalgam drop was replaced by a mercury drop of the same area which was immersed in the supporting electrolyte alone in a cell connected by a bridge to the cell containing the cadmium amalgam and the supporting electrolyte plus cadmium ions $(2.5 \times 10^{-4}$ molar). The value of c_1, which depended on the potential of the mercury drop, varied slightly with the cadmium ion concentration, but this variation could be neglected in view of the limited range of concentrations which was covered (see Table I).
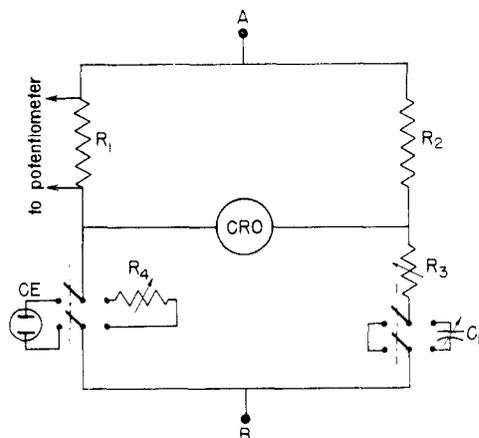

Fig. 4.—Schematic diagram of bridge for compensation of ohmic drop.

The capacitor C_1 was removed from the circuit and the cell replaced by a variable resistance R_4 which was adjusted to balance again the bridge. The balanced bridge was connected in AB to the constant current generator described below, and the current through R_4 (i.e., through the cell) was determined by measuring the ohmic drop in the resistance R_1 with a student potentiometer. A constant current distribution was maintained in the bridge during the recording of potential–time curves by selecting R_1 in such a manner that the voltage drop across this resistance exceeded more than 100 times the cell e.m.f. developed during electrolysis.

Current Impulse Generator.—The current impulse generator was essentially the same as the instrument used in previous investigations on constant current electrolysis in this laboratory except that an electronic rather than a mechanical switch was used to minimize transients at the beginning of electrolysis. The bridge AB was connected (Fig. 5) to a constant voltage power supply having an output of 300 volts. Transients in the power supply were virtually eliminated by the condenser C_2 having a capacity of 100 microfarads. The thyratron T_1 was triggered by the diode circuit of Fig. 5[13] which shortened transients resulting from the firing of the thyratron to less than a microsecond. Extinguishing of the thyratron was accomplished by opening of the plate circuit.

When currents lower than the minimum discharge current (approximately 1 milliampere for thyratron 2050) were desired, an additional resistor R_6 was inserted as indicated in Fig. 5.

(12) A voltage of small amplitude has to be applied to the bridge to obtain good balance because the double layer capacity changes with potential.

(13) W. C. Elmore and M. Sands, "Electronics—Experimental Techniques," McGraw-Hill Book Co., New York, N. Y., 1949, pp. 95–105.
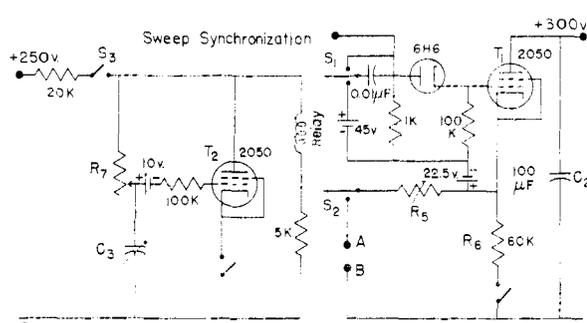

Fig. 5.—Schematic circuit of generator of current impulses: R_5, adjustable from 5000 ohms to 3 megohms in 10 steps; R_7, 2 megohms in 0.1 megohm steps; C_3, 0.1 to 1 microfarad in 0.1 microfarad steps; for other data see diagram and text.

Recording of Potential–Time Curves.—By closing the double pole double throw relay S_1S_2, which was adjusted in such a manner as to close S_2 slightly before S_1, the bridge circuit AB containing the electrolytic cell was connected to the constant current generator and the triggering signal from a 45 volt battery was applied to the control grid of thyratron T_1. The same signal also triggered the horizontal sweep of the recording oscilloscope. The relay S_1S_2 was actuated by closing switch S_3 manually. The cell was disconnected after a definite time before secondary electrode reactions (decomposition of supporting electrolyte) could occur with the resulting contamination of the working electrode. This was accomplished by connecting thyratron T_2 in parallel with the relay coil. The thyratron T_2 became conductive after a definite interval, which was adjusted by varying R_7 and C_3, and the electrolysis circuit was thus opened.

The voltage across the electrolytic cell was recorded (Fig. 4) with a calibrated cathode-ray oscilloscope (Tektronix model 531 with differential preamplifier 53D-54D) having a maximum sensitivity of one millivolt per centimeter. Oscillograms were photographed on 35 mm. film, and readings were made from enlarged images.

Appendix

The transforms of the relative concentrations defined by equations 13 are

$$\bar{\psi}_0 = M \exp\left(- s^{1/2}x/D_0^{1/2}\right) \quad (27)$$

$$\bar{\psi}_R = N \exp\left(- s^{1/2}x/D_R^{1/2}\right) \quad (28)$$

where M and N are integration constants whose values are determined by satisfying the transforms of the boundary condition (14) and a similar condition in terms of ψ_R. Thus

$$M = \frac{nF}{RT} \lambda_0 D_0^{1/2} \frac{\bar{E}(s)}{s^{1/2} + \lambda_0 D_0^{1/2} + \lambda_R D_R^{1/2}} \quad (29)$$

$$N = - \frac{nF}{RT} \lambda_R D_R^{1/2} \frac{\bar{E}(s)}{s^{1/2} + \lambda_0 D_0^{1/2} + \lambda_R D_R^{1/2}} \quad (30)$$

where $\bar{E}(s)$ is the Laplace transform of $E - E_e$.

By calculating now $(\partial \psi_0/\partial x)_{x=0}$ and expressing this function in terms of the Laplace transform of the faradaic current one obtains the following current-potential relationship

$$\bar{\imath}_f = - \frac{nF}{RT} i_0 \left[\bar{E}(s) - \frac{a\bar{E}(s)}{s^{1/2} + a}\right] \quad (31)$$

where

$$a = \frac{i_0}{nF} \left(\frac{1}{D_0^{1/2}C_0^0} + \frac{1}{D_R^{1/2}C_R^0}\right) \quad (32)$$

The transform of the capacity current, as deduced from (6), is

$$\bar{\imath}_c(s) = - c_1 s\bar{E}(s) + c_1(E - E_e)_{t \to +0} \quad (33)$$

where, in this case, $(E - E_e)_{t \to +0} \to 0$ for $t \to +0$.

One deduces from (7), (31) and (33) the following equation in $\bar{E}(s)$

$$\frac{i_t}{s} = -c_1 s E(s) - \frac{nF}{RT} i_0 \left[\bar{E}(s) - \frac{a\bar{E}(s)}{s^{1/2} + a} \right] \quad (34)$$

from which the Laplace transform of the potential can be easily obtained. Thus

$$\bar{E}(s) = -\frac{i_t}{c_1} \frac{s^{1/2} + a}{s^{3/2}(s + a s^{1/2} + b)} \quad (35)$$

with

$$b = \frac{nF}{RT} \frac{i_0}{c_1} \quad (36)$$

By factorization of the denominator in (35) and application of the theory of partial fractions, one can write equation 35 in the form

$$\bar{E}(s) = -\frac{i_t}{c_1} \frac{1}{\gamma - \beta} \left[\frac{1}{s(s^{1/2} + \beta)} - \frac{1}{s(s^{1/2} + \gamma)} + \frac{a}{s^{3/2}(s^{1/2} + \beta)} - \frac{a}{s^{3/2}(s^{1/2} + \gamma)} \right] \quad (37)$$

where β is defined by equation 19 and γ is defined by the same equation as (19) but with a minus sign in front of the bracket in the right-hand member.

The inverse transform of (37) is derived by application of the convolution integral.[14] Thus, by noting that the inverse transform of $1/s$ and $1/s^{3/2}$ are 1 and $2(t/\pi)^{1/2}$, respectively, and that the inverse transform of $(s^{1/2} + \beta)^{-1}$ is

$$\frac{1}{(\pi t)^{1/2}} - \beta \exp(\beta^2 t) \, \mathrm{erfc}(\beta t^{1/2})$$

one has

$$E - E_e =$$
$$-\frac{i_t}{c_1(\gamma - \beta)} \left[\begin{array}{l} \gamma \int_0^t \exp(\beta^2 \theta) \, \mathrm{erfc}(\beta \theta^{1/2}) \, d\theta \\ - \beta \int_0^t \exp(\gamma^2 \theta) \, \mathrm{erfc}(\gamma \theta^{1/2}) d\theta \end{array} \right] \quad (38)$$

The integrals in (38) can be readily evaluated by integration by parts, and equation 18 is thus obtained.

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The Mechanism of the Thermal Decomposition of Methyl Ethyl Ketone

By Chas. E. Waring and Marshall Spector[1]

The thermal decomposition of gaseous methyl ethyl ketone has been investigated in the presence of various inhibitors. Nitric oxide was found to catalyze the decomposition while propylene reduced the rate to a limiting value. The amount of inhibition in the presence of propylene was found to be dependent upon the partial pressure of ketone, indicating that the chain propagating step must be bimolecular. A chain mechanism is proposed that is in accord with the experimental facts.

Introduction

A previous paper[2] has reported that the rate of the thermal decomposition of methyl ethyl ketone, like that of acetone,[3] was markedly catalyzed, rather than inhibited, by the addition of nitric oxide. At low partial pressures of NO (ca. 5 mm.) a slight inhibition was detectable in the initial stage of the MeEtCO reaction, indicating that free radicals were, perhaps, produced to some extent. However, since the magnitude of the inhibition was so small or, at least, masked by the strong catalytic effects, it seemed reasonable to assume that chain processes did not play an important role in the reaction. Consequently, the authors postulated a rearrangement mechanism for the decomposition that was in agreement with the reaction products.

More recently[4] it has been shown that the rate of diethyl ketone, unlike that of acetone and methyl ethyl ketone, is reduced to a limiting value by the addition of small amounts of NO. This limiting rate was reproducible and no catalytic effect was observed out to 20 mm. partial pressure

of inhibitor. This unexpected result raised the question as to the difference between the mechanism of decomposition of diethyl ketone and the two lower members of the series. In view of their behavior toward nitric oxide, one is tempted to postulate that the decomposition of acetone and methyl ethyl ketone proceed through a rearrangement rather than a free radical mechanism. However, Smith and Hinshelwood[5] have shown that propylene inhibits the acetone decomposition, thus indicating the presence of free radicals.

As a first step in resolving these differences, it was thought worthwhile to reinvestigate the decomposition of methyl ethyl ketone in the presence of various inhibitors and to evaluate the decomposition mechanism proposed by the previous authors[2] in the light of our results.

Experimental

A. Material.—Technical grade methyl ethyl ketone was fractionated through a four-foot vacuum-jacketed, helices-packed column having a ten-to-one reflux ratio. The fraction distilling over at a constant temperature of 78.9° was collected and stored in a cool, dark place over anhydrous potassium carbonate, a drying agent found by Lochte[6] to have no tendency to cause internal condensation. The measured index of refraction at 23° was 1.3762, which compared favorably with the literature value of 1.3765 at the

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