[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY]

Voltage-step Method for the Kinetic Study of Fast Electrode Reactions

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A method is described for the kinetic study of fast electrode reactions in which a voltage impulse represented by a step function is applied to a cell composed of the working and the unpolarized reference electrodes. The resulting current–time curve is recorded by means of a cathode-ray oscilloscope. The exchange current is calculated from a plot of current against square root of time. This plot is linear for sufficiently short times and a voltage step not exceeding 2–5 mv. The transfer coefficient is obtained from a log–log plot of exchange current against concentration of one reactant, the concentrations of the other reactants being kept constant. The selection of conditions in which the charging or discharging of the double layer can be neglected is discussed. Results for the cadmium amalgam electrode are comparable with data obtained by other authors by a.c. electrolysis and the current-step method. Comparison with other relaxation methods for the kinetic study of fast electrode reactions is made.

Introduction

Three *relaxation methods* have been developed for the study of fast electrode reactions, namely, the potential-step method[2] (potentiostatic method), electrolysis with superimposed alternating voltage[3] (Randles, Ershler, Gerischer) and the current-step method.[4] A modified and simplified form of the potential-step method is described here. The principle is as follows.

The working electrode whose kinetics is studied is coupled with an unpolarized electrode, and the voltage corresponding to equilibrium at the working electrode is applied to the cell. The voltage applied to the cell is then varied by a small increment not exceeding 2 to 5 mv. and the resulting current–time curve is recorded with a cathode-ray oscilloscope. The kinetic parameters for the electrode reaction are deduced from the current–time variations for different concentrations of one reactant, the concentration of the other reactants remaining constant.

In this method, the voltage across the cell during electrolysis is constant but the potential of the working electrode changes because of variations of ohmic drop. The method differs in this respect from the potential-step method of Gerischer and Vielstich[2] in which the potential of the working electrode is kept constant.

Current–Time Relationship

The current–time relationship is derived from the current–potential characteristic of the electrode reaction, due allowance being made for the variations of the potential and the concentrations of reactants during electrolysis. The current–potential equation for an electrode process symbolized by the reaction O + *n*e = R can be written in the form[5]

$$i = i_0A \left\{ \frac{C_\mathrm{O}}{C_\mathrm{O}{}^0} \exp\left[- \frac{\alpha nF(E - E_\mathrm{e})}{RT} \right] - \frac{C_\mathrm{R}}{C_\mathrm{R}{}^0} \left[\frac{(1 - \alpha)nF(E - E_\mathrm{e})}{RT} \right] \right\} \qquad (1)$$

where

$$i_0 = nFk_\mathrm{s}\, C_\mathrm{O}{}^{0(1 - \alpha)}\, C_\mathrm{R}{}^{0\alpha} \qquad (2)$$

is the *exchange current* per unit area and the notations are as follows: i the current (positive for a net cathodic reaction) for an electrode of area A; C_O and C_R the concentrations of O and R at the electrode surface; the C^0's the bulk concentrations; α the transfer coefficient; E the potential (European convention); E_e the equilibrium potential for the concentrations $C_\mathrm{O}{}^0$ and $C_\mathrm{R}{}^0$; k_s the rate constant characterizing the electrode process at the standard potential for the couple O + *n*e = R; F the faraday; R the gas constant and T the absolute temperature.

The exponentials in (1) can be expanded and, if $(E - E_\mathrm{e}) \leqslant RT/\alpha nF$, *i.e.*, in general $(E - E_\mathrm{e}) \leqslant$ 2–5 mv. at room temperature, only the first two terms in the expansion need be retained. Thus

$$i = i_0A \left[\frac{C_\mathrm{O}}{C_\mathrm{O}{}^0} - \frac{C_\mathrm{R}}{C_\mathrm{R}{}^0} - \frac{nF(E - E_\mathrm{e})}{RT} \right] \qquad (3)$$

Furthermore

$$E - E_\mathrm{e} - iR_\mathrm{t} = V \qquad (4)$$

where V is the total voltage *variation*, and R_t is the total resistance of the cell and the calibrated resistance (connected to oscilloscope) in series with the cell. The quantity V is positive when $E > E_\mathrm{e}$ and *vice versa*.

The combination of (3) and (4) in which C_O and C_R are functions of time is the current–time relationship for a given voltage variation. The explicit form of this relationship depends on the functions C_O and C_R and, consequently, on the mass transfer process by which O and R are brought to and removed from the electrode. The concentrations will be calculated by assuming that a large excess of supporting electrolyte (in comparison with $C_\mathrm{O}{}^0$ and $C_\mathrm{R}{}^0$) is present and that conditions of semi-infinite linear diffusion prevail. The latter assumption is valid even for spherical or cylindric electrodes provided that the radius of curvature of the electrode is not too small (perhaps not less than 0.01 to 0.1 cm.) and the electrolysis is of short duration. These conditions can easily be fulfilled.

The concentrations $C_\mathrm{O}(x,t)$ and $C_\mathrm{R}(x,t)$ are then solutions of Fick's equation, as written for substances O and R, for the following conditions: $C_\mathrm{O}(x,t) = C_\mathrm{O}{}^0$ and $C_\mathrm{R}(x,t) = C_\mathrm{R}{}^0$ at $x \geqslant 0$ and $t = 0$, x being the distance from the electrode, and t the time elapsed after the voltage variation; $C_\mathrm{O}(x,t) \rightarrow C_\mathrm{O}{}^0$ and $C_\mathrm{R}(x,t) \rightarrow C_\mathrm{O}{}^0$ for $t \geqslant 0$ and $x \rightarrow \infty$; and i, as calculated from (3) and (4), is such that $i = nFAD_\mathrm{O}[\partial C_\mathrm{O}(x,t)/\partial x]_{x=0} = -nFAD_\mathrm{R}[\partial C_\mathrm{R}(x,t)/\partial x]_{x=0}$, the D's being the diffusion coefficients of O and R.

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

[3] For a survey see, for instance, P. Delahay, "New Instrumental Methods in Electrochemistry," Interscience Publishers, Inc., New York, N. Y., 1954, pp. 146–178.

[4] T. Berzins and P. Delahay, THIS JOURNAL, **77**, 6448 (1955).

[5] H. Gerischer, *Z. Elektrochem.*, **55**, 98 (1951); see also ref. 4.

The solution of this boundary value problem, as obtained by the Laplace transformation, is

$$i = \frac{i_0 A V}{i_0 A R_t + RT/nF} \exp(\lambda^2 t) \operatorname{erfc}(\lambda t^{1/2}) \qquad (5)$$

with

$$\lambda = \frac{i_0}{nF} \frac{RT/nF}{i_0 A R_t + RT/nF} \left[\frac{1}{D_O^{1/2} C_O^0} + \frac{1}{D_R^{1/2} C_R^0} \right] \qquad (6)$$

and where the notation "erfc" represents the complement of the error function.

Since the function $\phi = \exp(\lambda^2 t)\operatorname{erfc}(\lambda t^{1/2})$ decreases with increasing values of t, the current decreases continuously during electrolysis. At $t = 0$, $\phi = 1$, and one verifies that the current has the value obtained by combining (3) and (4) and by noting that $C_O = C_O^0$ and $C_R = C_R^0$ for $t = 0$; the current is then entirely controlled by the kinetics of the electrochemical reaction. Conversely, for sufficiently long times the current is entirely diffusion controlled. This can be shown readily by expanding the error function in (5) for arguments larger than unity. An order of magnitude of time τ at which diffusion becomes prevalent can be determined by setting for instance $\lambda\tau^{1/2} = 1$, *i.e.*, $\tau = 1/\lambda^2$.

Finally, eqs. 5 and 6—as written for $R_t = 0$—reduce to the result for the potential-step method derived by Gerischer and Vielstich.[2] The latter result itself is a modified form of the current–potential–time for irreversible processes in polarography and related methods[6] (Smutek, Evans and Hush, Kambara and Tachi, Delahay).

Determination of i_0, k_s and α

If $\lambda t^{1/2} \ll 1$ one has $\exp(\lambda^2 t) \approx 1$ and erfc $(\lambda t^{1/2}) \approx 1 - (2\lambda/\pi^{1/2})t^{1/2}$, and there follows from (5)

$$i = \frac{i_0 A V}{i_0 A R_t + RT/nF} \left(1 - \frac{2\lambda}{\pi^{1/2}} t^{1/2}\right) \qquad (7)$$

The plot of i against $t^{1/2}$ is linear and its slope yields the value of the quantity λ given by (6). The intercept of this line at $t = 0$ readily yields the exchange current i_0. The transfer coefficient α is obtained by determining i_0 for different concentrations of either O or R, one concentration being kept constant. A plot of log i_0 against the logarithm of the varying concentration then is a straight line whose slope yields[7] α (see eq. 2).

The method was applied to the cadmium amalgam electrode in 0.5 M sodium sulfate at 20°. Results presented as the plot of log i_0 against log $C_{Cd^{++}}$ are shown in Fig. 1 together with data for the same electrode as obtained by a.c. electrolysis[7] and the current-step method.[4] Data by the voltage-step method yield the values $k_s = 2.6 \times 10^{-2}$ cm. sec.$^{-1}$ and $\alpha = 0.25$ which are in fairly good agreement with the results obtained by other authors: $k_s = 4.2 \times 10^{-2}$ cm. sec.$^{-1}$ and $\alpha = 0.17$ by a.c. electrolysis; $k_s = 4.5 \times 10^{-2}$ cm. sec.$^{-1}$ and $\alpha = 0.22$ by the current-step method. The main source of discrepancy is the strong dependence of the kinetic parameters on traces of impurities in solution. Better agreement would probably have been obtained by the application of the three methods to the same solution for identical conditions of exposure of the electrode (contamination).

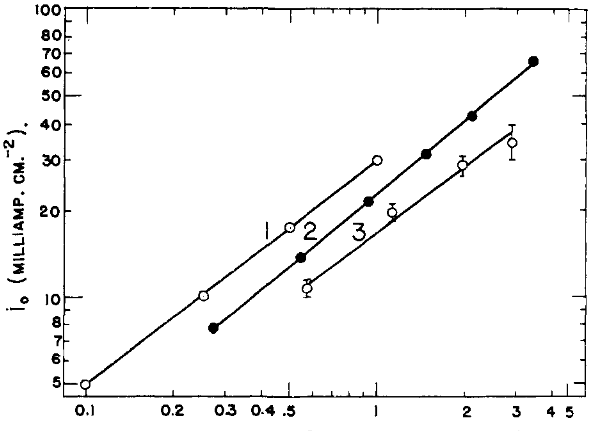

Fig. 1.—Plot for the determination of α: 1, current-step method; 2, a.c. electrolysis; 3, voltage-step method.

In the preparation of the plot i *vs.* $t^{1/2}$ current should not be read at very short times when the charging or discharging of the double layer interferes. The current for the latter process is $i_c = (V/R_t) \exp(-t/R_t c_d)$ where the differential capacity c_d is constant over the interval of potential V. Obviously t should be so large that $i_c \ll i$ where i is given by (7). Taking to simplify matters i at $t = 0$ and $R_t = 0$, one deduces

$$\exp(-t/R_t c_d) \ll i_0 A R_t/(RT/nF) \qquad (8)$$

Representative values in (8) are, for instance, $R_t = 30$ ohms, $c_d = 1$ microfarad (mercury drop electrode), $A = 2 \times 10^{-2}$ cm.^{2}, $i_0 = 10^{-2}$ amp. cm.$^{-2}$ (see Fig. 1), and $n = 2$. Hence, $t \geqslant 5 \times 10^{-5}$ sec. One should also have $\lambda t^{1/2} \ll 1$, or ($D = 10^{-5}$ cm.^{2} sec.$^{-1}$, $C_0 = C_R = 10^{-6}$ mole cm.$^{-3}$) for the above case $t < 2 \times 10^{-3}$ sec. The limits t for which the plot of i *vs.* $t^{1/2}$ can be utilized to calculate i_0 are thus easy to determine.

The chief advantage of this method over the potentiostatic method is the simplicity of the apparatus. Furthermore, no reference electrode is needed and the difficulties attending the use of a Luggin–Haber capillary are eliminated.[8] The main disadvantage of the voltage-step method, in comparison with the potentiostatic method, is the relatively long time required for the charging or discharging of the double layer. This time is appreciably shorter in the potentiostatic method, and consequently the condition $\lambda t^{1/2} \ll 1$ is more easily satisfied for large values of i_0 than in the voltage-step method. Values of the rate constant k_s (see eq. 2) as large as 0.1 cm. sec.$^{-1}$—an order of magnitude—can be determined by this method whereas values of k_s larger by perhaps one order of magnitude can be obtained by the potentiostatic method. Finally, the mathematical analysis of the voltage-step method requires for the sake of simplicity that the potential step does not exceed 2–5 mv. This restriction need not be imposed in the potentiostatic method. The accuracy of the two methods should be comparable; the main sources of error are electrode contamination and errors in the oscillographic recording.

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(6) At least for diffusion toward a plane electrode.

(7) H. Gerischer, *Z. Elektrochem.*, **57**, 605 (1953); see also ref. 4.

(8) R. Piontelli, *ibid.*, **59**, 778 (1955); this author designed and studied in detail a Luggin–Haber capillary for plane electrodes and for which errors on potentials are greatly minimized.

Experimental

A cell with hanging cadmium amalgam drop[9] was utilized. The drop falling from a dropping amalgam electrode was collected in a small glass spoon and then, by rotation of the spoon, suspended on a gold-plated platinum tip. This method of collecting drops was found much easier to apply than the one in which drops are collected in a spoon attached to the capillary dropping amalgam electrode as recommended by Gerischer. A large pool of cadmium amalgam served as reference electrode. The amalgam was prepared by dissolution of fine cadmium turnings in mercury in a nitrogen atmosphere. The same amalgam was used for the pool and the hanging drop electrode.

The cell was connected to two resistances R_1 and R_2 in series. The calibrated and adjustable resistance R_1 was connected to a Tektronix cathode-ray oscilloscope model 531 with 53D preamplifier. Resistance R_2 (a few ohms; not critical) across which the voltage increment of 2–5 mv. was set up was connected to a 1.5 volt battery with a suitable resistance in series. Resistance R_2 was normally short-circuited by a *good* switch, which upon opening thus caused the voltage applied to the cell to vary by a few mv. Toggle switches were not adequate because vibrations in the switch caused transients, whereas switches with blades did not have this defect.

The preparation of solution, the deaeration by nitrogen, and the recording of current-time curves followed conventional practice.

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[9] H. Gerischer, *Z. physik. Chem.*, **202**, 302 (1953); see also ref. 4.

[CONTRIBUTION FROM THE CHEMICAL ENGINEERING DIVISION, ARGONNE NATIONAL LABORATORY]

The Kinetics of the Reaction of Fluorine with Iodine Pentafluoride to Form Iodine Heptafluoride[1]

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The kinetics of the vapor phase reaction of fluorine with iodine pentafluoride to form iodine heptafluoride has been studied from 55.6 to 95°. The rate of the reaction was found to be second order with respect to the reactant pressures. The rate constants showed an Arrhenius temperature dependence, with an activation energy of 14 kcal. per mole. The reaction was homogeneous, suggesting that the rate-determining step is a bimolecular collision.

The preparation of iodine pentafluoride[2a] and iodine heptafluoride[2b] had been described by Ruff. The authors suggested that the reaction of iodine pentafluoride and fluorine, in the temperature region of 100 to 270°, resulted in an equilibrium mixture of the pentafluoride and the heptafluoride. Experimental limitations prevented them from observing whether complete conversion of the pentafluoride was possible.

This investigation was undertaken to establish the stoichiometry and kinetics of the reaction, and to obtain some insight of the mechanism involved.

Experimental

Materials.—Iodine pentafluoride was prepared by the direct combination of fluorine and reagent grade resublimed iodine in a reaction vessel at 0°, at which temperature very little iodine heptafluoride was formed. The reaction vessel was cooled to the temperature of liquid nitrogen and the excess fluorine was distilled off at a pressure less than $10\ \mu$. After the vessel had been warmed to 0°, traces of iodine heptafluoride and fluorine were removed by a partial distillation of the iodine pentafluoride from the reaction vessel. The purity of the iodine pentafluoride was indicated by a constant vapor pressure (269.8 ± 0.8 mm.) at 75° before and after distillation of half its volume from the reaction vessel. As indicated in the experimental data, the apparent molecular weight given by gas density measurements was close to the formula weight. The vapor pressure of the iodine pentafluoride was found to be 116.4 mm. at 55°, which is in substantial agreement with the value of 119.9 and 120.0 mm. reported by Ruff[2a] and Rogers,[3] respectively.

Commercial high-purity fluorine gas was used after it had been assayed for purity by the method of Aoyama and Kanda.[4] This method, which employs the quantitative reaction of fluorine with mercury, indicated a purity in excess of 99% by volume. It was also shown to contain less than 0.5% of impurities by its quantitative reaction with bromine.[5]

Apparatus.—The apparatus consisted of a manifold made from welded $^3/_8$-inch nickel tubing, a cylindrical 575.8-ml. nickel reaction vessel, and a similar 573-ml. storage and metering vessel. The vessels were attached to the manifold by $^3/_4$-inch flare connectors, which were sealed with Teflon gaskets. A 25-ml. Fluorothene (polychlorotrifluoroethylene) tube, which contained the iodine pentafluoride, was similarly joined to the manifold. The components were separated by Hoke No. 1197 bellows-type valves, which are made of Monel with Teflon seats.

Pressure transmitters, which are described later, were attached directly to the reaction and metering vessels. The apparatus was contained in a forced-air thermostated box, and joined to an external nickel manifold which was equipped with liquid nitrogen cold traps, a high vacuum pump, and gas supplies of fluorine and helium.

The pressures in the system were measured with well-type mercury manometers, employing Booth–Cromer pressure transmitters[6] with self-balancing relays. Thin nickel diaphragms, which serve as sensing elements in this instrument, separated the vapor in the system from the mercury manometer balancing system, which contained only nitrogen. Very low pressures were measured with a thermocouple gage tube attached to the manifold in the constant temperature box.

The temperatures of the vapor in the apparatus were obtained from copper–constantan thermocouples inserted so as to be in contact with the bottom of nickel thermocouple wells in the reaction and metering vessels. A Rubicon Type B potentiometer was used, and the thermocouples were calibrated to 0.01° with a standard platinum resistance thermometer, employing a Leeds and Northrup G-2 Mueller bridge.

The time was measured with an electric timer which could be read to 0.01 minute.

Procedure.—The rate of the reaction was obtained from the change in total pressure, with time, after known partial pressures of the reactants were mixed in the reaction vessel.

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[1] Work performed under the auspices of the U. S. Atomic Energy Commission.

[2] (a) O. Ruff and A. Braida, *Z. anorg. allgem. Chem.*, **220**, 43 (1934); (b) O. Ruff and R. Keim, *ibid.*, **193**, 176 (1930).

[3] M. Rogers, *et al.*, THIS JOURNAL, **76**, 4843 (1954).

[4] S. Aoyama and E. Kanda, *Bull. Chem. Soc. Japan*, **12**, 409 (1937).

[5] J. Fischer, R. C. Vogel and J. Bingle, THIS JOURNAL, **78**, 902 (1956).

[6] S. Cromer, "The Electronic Pressure Transmitter and Self-Balancing Relay," SAM Laboratories, Columbia University, MDDC-803, 1947.