In the acidic buffer, the current density and kinetic parameters were found to vary with time, as might have been anticipated from the fact that iodide, the reduction product of iodate, reacts with iodate to form iodine at *p*H 3.2. A catalytic cycle, involving iodine as an intermediate, is therefore operative. Moderate stirring caused a decrease in current at a given potential, due to partial removal of iodide. In the alkaline buffer, the current density was essentially independent of time. However, in the presence of camphor, time variations were noted. Also, when enough potassium iodide was added to the borate buffer to make the iodide concentration 0.10 *M*, variations of current density with time were noted both in the presence and absence of camphor.

Several linear portions were found in each plot of log $i_c/nFAC_{ox}$ *versus* electrode potential. The effect of camphor was to increase markedly the apparent value of n_a and to decrease the value of k^0. From the present results it does not appear possible to assign a single value of n_a, and therefore a single-rate determining reduction step over a wide range of potentials.

URBANA, ILLINOIS

[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY, AND THE OAK RIDGE INSTITUTE OF NUCLEAR STUDIES]

Adsorption Kinetics with Diffusion Control—The Plane and the Expanding Sphere

BY PAUL DELAHAY AND CHARLES T. FIKE

RECEIVED DECEMBER 9, 1957

Adsorption kinetics with control by diffusion toward a plane and an expanding sphere (dropping mercury electrode) are discussed from computer solutions of the corresponding boundary value problems. The kinetics are characterized by two quantities: D/Γ_m and C^0/a, D being the diffusion coefficient of the adsorbate, Γ_m the surface concentration for full coverage, C^0 the bulk concentration of adsorbate, and a the adsorbate volume concentration for full coverage when the isotherm is identified with its tangent at $C^0 = 0$ (linearized isotherm). It is shown that adsorption equilibrium is practically reached within less than 1 sec. when $C^0 \geq 10a$ (an order of magnitude for values of D and Γ_m generally encountered). The process is somewhat slower for the expanding sphere than for the plane. Coverage for a given C^0 varies fairly linearly with $t^{1/2}$ at the beginning of the adsorption process.

Adsorption kinetics with diffusion control were discussed in previous papers[1] for the simplified cases of either a linearized isotherm or a large volume concentration of adsorbate. It was concluded from theory and experiment that adsorption equilibrium (with respect to the bulk concentration) for concentrations in the segment of the isotherm which can reasonably be linearized is practically reached only after 15–30 minutes. Significant implications in electrochemical kinetics, polarography, surface tension measurements were discussed. Implications in radiotracer techniques also should be mentioned.

An analytical solution for the complete isotherm was not reported and, in fact, would be very difficult to obtain.[2] However, it was possible to carry out calculations for the complete isotherm with the ORACLE computer at Oak Ridge for diffusion at a plane and an expanding sphere (dropping mercury electrode). These results are summarized below.

Adsorption on a Plane

Influence of Concentration.—In this case which was previously stated[1a] we consider adsorption on a plane with control by semi-infinite linear diffusion. Conditions for a surface initially free of adsorbate are

$$C = C^0 \text{ for } x > 0 \text{ and } t = 0$$

$$C \longrightarrow C^0 \text{ for } x \longrightarrow \infty \text{ and } t \geq 0$$

$$\frac{D}{\Gamma_m} \int_0^t \left(\frac{\partial C}{\partial x}\right)_{x=0} \mathrm{d}t = \frac{C_{x=0}/a}{1 + C_{x=0}/a} \qquad (1)$$

where x is the distance from the interface solid–solution, t the time elapsed since the beginning of the adsorption process, C the volume concentration of adsorbate, C^0 the volume concentration of adsorbate in the bulk of solution (maintained constant for $x \rightarrow \infty$), D the diffusion coefficient of adsorbate (assumed to be independent of C), Γ_m the surface concentration of adsorbate for full coverage and a the parameter of the Langmuir isotherm. Note that a is the concentration for which the surface concentration Γ is equal to Γ_m when the isotherm is identified with its tangent at $C^0 = 0$ (linearized isotherm)

The influence of the quantities C^0/a and D/Γ_m which characterize adsorption kinetics in this case will be studied separately. Results will be expressed as the ratio Γ_t/Γ_e of the surface concentration Γ_t at time t to the surface concentration Γ_e when equilibrium is reached ($\Gamma_t/\Gamma_e \rightarrow 1$ for $t \rightarrow \infty$).

Variations of Γ_t/Γ_e with time for different bulk concentrations are shown in Fig. 1 for the value $D/\Gamma_m = 10^4$ cm.^{4} sec.$^{-1}$ mol.$^{-1}$. This value is quite representative: $D = 5 \times 10^{-6}$ cm.^{2} sec.$^{-1}$; $\Gamma_m = 5 \times 10^{-10}$ mole cm.$^{-2}$, *i.e.*, a coverage of approximately 30 sq. ångströms per molecule.

The following conclusions can be drawn from Fig. 1. (a) The rate of attainment of equilibrium coverage (with respect to the bulk concentration) increases with concentration. (b) At very low concentrations, variations of Γ_t/Γ_e with time are hardly dependent on the bulk concentration of adsorbate.[3] It was pointed out previously[1a] that Γ_t/Γ_e, at any time, is independent of the bulk con-

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(1) (a) P. Delahay and I. Trachtenberg, THIS JOURNAL, **79**, 2355 (1957); (b) **80**, 2094 (1958). A detailed bibliography is given in these papers.

(2) Dr. E. J. Pellicciaro of the University of Delaware investigated this problem at Oak Ridge during the Summer of 1957.

(3) Computations were not made for C^0/a <0.01 because major changes in coding would have been required.

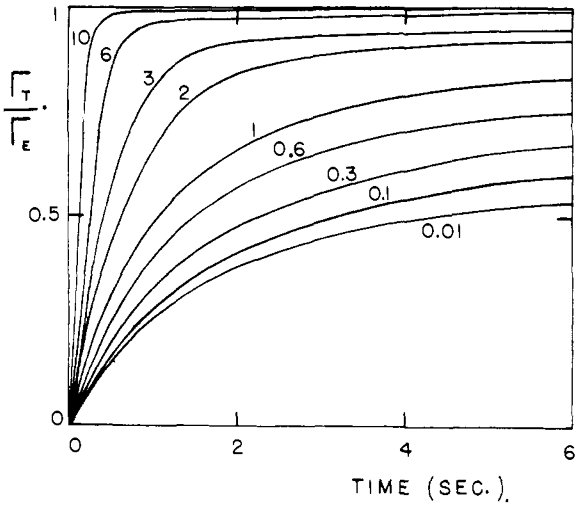

Fig. 1.—Variations of Γ_t/Γ_e with time for adsorption on a plane and for different concentrations of adsorbate (expressed as the ratio C^0/a). Γ_t surface concentration at time t, Γ_e equilibrium surface concentration for C^0. Curves calculated for $D/\Gamma_m = 10^4$ cm.^{4} sec.$^{-1}$ mole.$^{-1}$.

centration for the linearized isotherm. For instance, if the concentration is doubled the diffusion rate is doubled but the equilibrium surface concentration is also multiplied by two. (c) Even when the bulk concentration corresponds to the "flat" part of the isotherm, equilibrium with respect to the bulk concentration is not reached very quickly (within 1 sec. for $C^0/a = 10$) except for very large C^0's.

Influence of the Factor D/Γ_m.—The two quantities D and Γ_m in the ratio D/Γ_m of equation 1 do not vary over a very wide range at least if macromolecules are excluded. The rate of equilibrium attainment, however, is quite sensitive to variations of D/Γ_m (Fig. 2).

Adsorption on an Expanding Sphere (Dropping Mercury Electrode)

The mathematical problem for this case was previously stated.[1a] Thus, Fick's equation as modified by Ilkovic[4] for the expanding sphere

$$\partial C/\partial t = D\partial^2 C/\partial x^2 + (2/3)(x/t)\partial C/dx \qquad (2)$$

must be solved. The initial and boundary conditions are the same as for the plane except that equation 1 is now replaced by

$$\frac{D}{\Gamma_m}\frac{1}{t^{2/3}}\int_0^t t^{2/3}\left(\frac{\partial C}{\partial x}\right)_{x=0} \mathrm{d}t = \frac{C_{x=0}/a}{1 + C_{x=0}/a} \qquad (3)$$

where $t^{2/3}$ accounts for the area variation of the spherical interface.

Variations of Γ_t/Γ_e with time for the expanding sphere and for conditions otherwise identical to those of Fig. 1 are shown in Fig. 3. Values of Γ_t/Γ_e for the expanding sphere are somewhat smaller than the corresponding values for the plane because of expansion of the interface. As a practical rule, equilibrium is reached with respect to the bulk concentration only when $C^0 \geq 10a$ ($D/\Gamma_m = 10^4$ cm.^{4} sec.$^{-1}$ mole^{-1}), *e.g.*, for concentrations in the plateau of

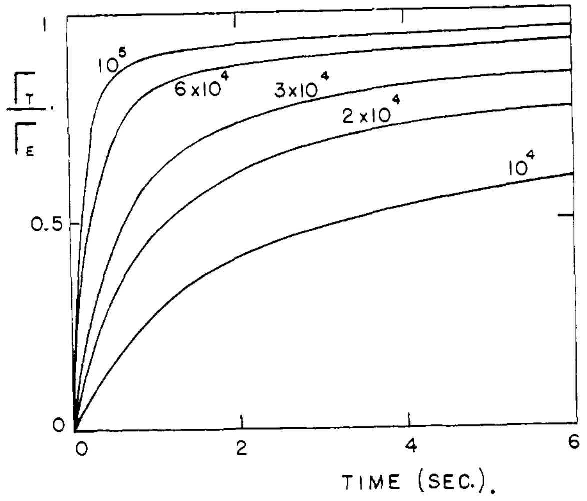

Fig. 2.—Same diagram as in Fig. 1 but for a given volume concentration, $C^0 = 0.1a$, and different values of D/Γ_m (in cm.^{4} sec.$^{-1}$ mole^{-1}).

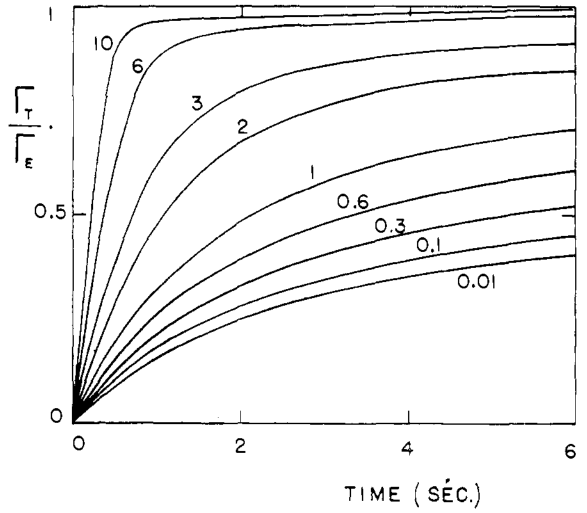

Fig. 3.—Same diagram as in Fig. 1 but for the expanding sphere.

the isotherm. This limit, of course, represents only an order of magnitude. (For instance, one could have $C^0 > a$ in some cases.) This conclusion is of significance in electrochemical studies with the dropping mercury electrode, particularly in measurements of the double layer differential capacity for solutions containing an adsorbed organic substance. An experimental criterion for attainment of equilibrium is the independence of the differential capacity per unit area of drop time as was shown previously.[1b] However, application of this criterion requires quite precise measurements of the differential capacity on account of the slow increase of Γ_t/Γ_e with time for $t > 5$ sec. (Fig. 3). Somewhat more favorable conditions are achieved with long drop times[5] (10–15 sec.). The hanging mercury drop is perhaps more advantageous than the dropping mercury electrode in such studies, especially when the solution is stirred mechanically before measurements—but not during measure-

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(4) D. Ilkovic, *J. chim. phys.*, **35**, 129 (1938). This is a modification of Fick's equation for linear diffusion as adapted to a moving boundary.

(5) H. A. Laitinen, private communication.

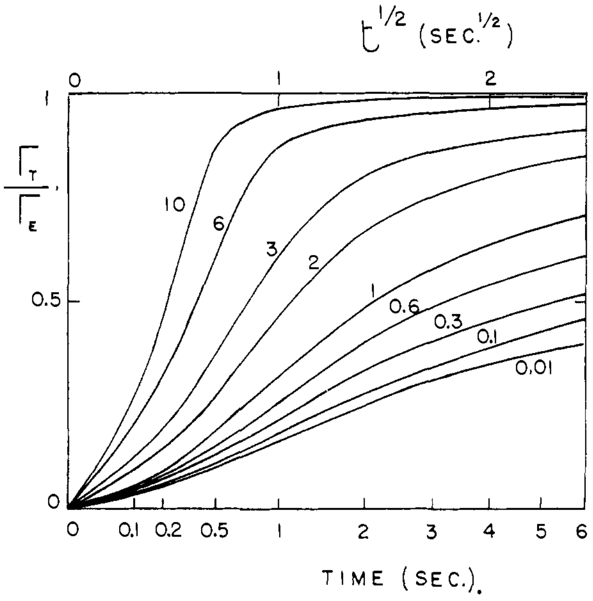

Fig. 4.—Variations of Γ_t/Γ_e with $t_{1/2}$ for the data of Fig. 3.

ments to avoid oscillations of the drop—to speed up attainment of equilibrium.[1a]

Influence of the Sphericity.—The sphericity of the solid-solution interface is not considered in equation 2. This simplification is quite permissible when the diffusion layer thickness is very small in comparison with the radius of curvature of the mercury drop, *e.g.*, for drop times shorter than 2–4 seconds. For longer drop times equilibrium should be approached somewhat more rapidly than the results deduced from equation 2 indicate, but not to the point of invalidating the foregoing conclusions. From comparison of the Ilkovic equation for polarographic diffusion currents with modified forms of this equation in which sphericity is considered, one concludes that the increase in diffusion rate resulting from sphericity does not exceed 5–10% for drop times as large as 10–15 seconds. The increase in adsorption rates caused by sphericity is probably of the same order of magnitude. Detailed calculations were not performed because we were primarily interested in the order of magnitude of diffusion rates at the dropping mercury electrode.

Comparison with a Very Approximate Treatment.—A *very approximate* calculation of Γ_t/Γ_e can be made when $C^0 \gg a$ as was shown by several authors (see ref. 1a for bibliography). Thus, the flux for the diffusion current for an electrode process, as calculated by Ilkovic,[4] is substituted for $D(\partial C/\partial x)_{x=0}$ in eq. 3; and it then follows very simply that Γ_t/Γ_e varies linearly with $t^{1/2}$. It is seen from Fig. 4 that departure from this simple relationship is not too pronounced for values of Γ_t/Γ_e somewhat smaller than unity. Even when the condition $C^0 \gg a$ is not fulfilled, Γ_t/Γ_e still varies fairly linearly with $t^{1/2}$. It readily can be shown that this result is to be expected for adsorption for the linearized isotherm.[6] The foregoing conclusions also hold for adsorption on a plane.

Acknowledgments.—The support of the Office of Naval Research is gladly acknowledged. This problem was initially discussed with Dr. T. W. Hildebrandt before his departure from Oak Ridge.

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(6) Expand the error function in equation 5 of ref. 1a for small arguments and retain only the first two terms.

Baton Rouge, Louisiana

[Contribution from The Weizmann Institute of Science]

Kinetics of Hydrogen Exchange between Hydrogen Peroxide and Water Studied by Proton Magnetic Resonance[1,2]

By M. Anbar, A. Loewenstein and S. Meiboom

Received December 16, 1957

The kinetics of hydrogen exchange between H_2O_2 and water have been investigated using the PMR method in the pH range of 2.5 to 6.5. The reaction was found to be both acid and base catalyzed. In the acid region, $p\text{H} < 4.5$, the reaction involves H_3O^+ and H_2O_2, while in the basic region it was found to involve HO_2^-, H_2O_2 and H_2O. The reaction constants are 1.6×10^7 l. mole^{-1} sec.$^{-1}$, and 7.3×10^7 l.^{2} mole^{-2} sec.$^{-1}$, respectively.

Introduction

The rate of exchange of hydrogen atoms bonded to oxygen is generally too fast to be measured by isotope labelling methods. Erlenmeyer and Gartner[3] found, by deuterium labelling, that hydrogen exchanges quickly and completely between hydrogen peroxide and water. Attempts to measure the rates of hydrogen exchange between two oxygen atoms (mainly between alcohols and water) are reported by Swain and Labes.[4]

In this paper we report measurements, by the PMR technique, of the rate of proton exchange between H_2O_2 and H_2O as function of pH and of H_2O_2 concentration. At sufficiently slow exchange rates the PMR spectrum of aqueous H_2O_2 solutions is expected to consist of two lines, corresponding to the protons in the H_2O_2 and H_2O, respectively. With increasing exchange rate, the two lines broaden and eventually merge into a single broad line which narrows on further increase of rate.[5,6]

In the H_2O_2–H_2O system, at room temperature, it was actually found that the exchange rate is never slow enough for the two lines to be separated, and a single line was always observed. However, the width of this line was found to be strongly dependent on the pH and on the H_2O_2 concentration of the solution.

The half-widths of the lines were used to evaluate the exchange rate, using the basic theory given by

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(1) This research has been sponsored in part by the Air Force Office of Scientific Research of the Air Research and Development Command, U.S.A.F., through its European Office under Contract No. AF61 (052)-03.

(2) Taken in part from a thesis presented by A. Loewenstein to the Hebrew University, Jerusalem, in partial fulfillment of the requirements to the Ph.D. degree.

(3) H. Erlenmeyer and H. Gartner, *Helv. Chim. Acta*, **17**, 970 (1934).

(4) C. G. Swain and M. M. Labes, This Journal, **79**, 1084 (1957), ref. 4.

(5) H. S. Gutowsky and A. Saika, *J. Chem. Phys.*, **21**, 1688 (1953).

(6) E. Grunwald, A. Loewenstein and S. Meiboom, *ibid.*, **27**, 630 (1957); A. Loewenstein and S. Meiboom, *ibid.*, **27**, 1067 (1957).