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Rectification by the Electrical Double Layer and Adsorption Kinetics

BY MITSUGI SENDA¹ AND PAUL DELAHAY

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Qualitative and quantitative treatments are given of non-faradaic rectification by the electrical double layer for specific adsorption of a neutral substance or an ionic species in presence of a large excess of supporting electrolyte. Control of the mean charge (\bar{q}) and/or mean potential (\bar{E}) is considered. Rectification at constant \bar{q} results in a shift of \bar{E} for an ideal polarized electrode and *vice-versa*. It is best to maintain \bar{E} constant and to supply the compensating charge by means of a double pulse method. A theory of this method is developed without assumption about the explicit form of the rate equation for adsorption kinetics. The charge variation due to rectification is expressed in terms of the elements of the equivalent circuit for the non-faradaic impedance and the latter are given as functions of thermodynamic and kinetic parameters for adsorption. The influence of frequency is analyzed, and it is shown how the general equation can be applied directly to the analysis of experimental results. Particular types of adsorption kinetics are also discussed. The method is applicable to frequencies ($f > 1$ Mc.) at which non-faradaic impedance measurements with a bridge are hardly feasible.

We consider an ideal polarized electrode on which an ionic species or a neutral substance is specifically adsorbed. The differential capacity of the double layer depends on the surface concentration of adsorbed species and consequently on adsorption kinetics. The corresponding non-faradaic impedance has been studied by a number of workers²⁻⁵ and has provided useful information on adsorption kinetics. It was concluded that adsorption of a number of organic substances on mercury is diffusion controlled up to frequencies at which bridge measurements can be made (below 500 Kc.). The kinetics of adsorption proper could also be studied for some substances and adsorption exchange rates were determined. Lorenz⁶ recently extended measurements up to approximately 1 Mc. by the use of a T-bridge. The double layer impedance is very low in comparison with the cell resistance at high frequencies, and it seems that another approach is necessary for investigation well beyond 1 Mc. Non-faradaic rectification provides such an approach as was recognized by Barker.⁷ This author studied rectification by the double layer in the absence of complications due to adsorption kinetics and for mass transfer. Theoretical analysis has not appeared thus far to our knowledge and is given here.

Qualitative Discussion

The charge on an ideal polarized electrode does not vary linearly with potential,⁸ and rectification results when the electrode potential varies periodically with time. This non-faradaic rectification will be discussed qualitatively in a manner which is inspired from a similar analysis of faradaic rectification.⁹

(1) Postdoctoral research associate, January 1960-March 1961; on leave from the Department of Agricultural Chemistry, Kyoto University, Kyoto, Japan.

(2) (a) A. N. Frumkin and V. I. Melik-Gaikazyan, *Doklady Akad. Nauk, SSSR*, **77**, 855 (1951); (b) V. I. Melik-Gaikazyan, *Zhur. Fiz. Khim.*, **28**, 560, 1184 (1952).

(3) T. Berzins and P. Delahay, *J. Phys. Chem.*, **59**, 906 (1955).

(4) (a) W. Lorenz and F. Mückel, *Z. Elektrochem.*, **60**, 507 (1956); (b) W. Lorenz, *ibid.*, **62**, 192 (1958).

(5) For a review see R. Parsons, Ch. 1 in Vol. I, "Advances in Electrochemistry and Electrochemical Engineering," P. Delahay ed., Interscience Publishers, Inc., New York, in course of publication.

(6) W. Lorenz, *Z. physik. Chem., N.F.*, **26**, 424 (1960).

(7) G. C. Barker, "Transactions of the Symposium on Electrode Processes, Philadelphia, 1959," E. Yeager, ed., John Wiley and Sons, Inc., New York, N. Y., in course of publication.

(8) D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

(9) P. Delahay, M. Senda and C. H. Weis, *J. Am. Chem. Soc.*, **83**, 312 (1961).

Two types of control will be considered: control of the mean charge \bar{q} or the mean potential \bar{E} and control of the alternating component of the charge or potential. Simple cases correspond to either \bar{q} or \bar{E} constant. If the alternating current density for the charging of the double layer is a harmonic-free sinusoidal function of time (A.C. control), the potential-time variations include harmonics. Conversely, the current-time variations include harmonics for harmonic-free sinusoidal variations of potential (A.V. control.)

Rectification at Constant Mean Charge.—Variations of E for A.C. control include, in this case, the fundamental harmonic at the frequency f and the $2f$ -harmonic (Fig. 1A). The latter results in a shift $\delta_0 E$ of \bar{E} . This shift can, in principle, be observed as follows: the ideal polarized electrode is coupled with a reference electrode and is charged at a given potential (an ideal polarized electrode would remain indefinitely at this potential); the cell is connected to an A.C. signal generator by means of a capacitor having a very low capacity in comparison with the double layer capacity, and the alternating current is controlled as a harmonic-free sinusoidal function of time; application of the A.C. signal causes the rectification voltage $\delta_0 E$ to appear.

When there is A.V. control (Fig. 1B) and \bar{q} is constant, the non-linearity of the \bar{q} - \bar{E} relationship results in a varying component of the charge at the frequency $2f$. This component is compensated on a time average by a charge of equal magnitude and opposite sign since \bar{q} must remain constant. This requires a shift $\delta_0 E$ of the mean potential. The rectification voltage is the same as for A.C. control because of the reciprocity between Fig. 1A and 1B.

The mean potential can be maintained constant provided the necessary charge is supplied by an outside source when the A.C. signal is applied. This result is achieved by simultaneous application of the A.C. signal and a rectangular current pulse of short duration (perhaps 10 microsec.). The pulse height is determined by trial and error until $\delta_0 E$, as measured with a cathode-ray oscilloscope, is equal to zero and independent of the duration of application of the A.C. signal. Application of this *double pulse method* to faradaic rectification was described in a previous paper from this Laboratory.¹⁰

(10) M. Senda, H. Imai and P. Delahay, *J. Phys. Chem.*, **63**, 1253 (1961).

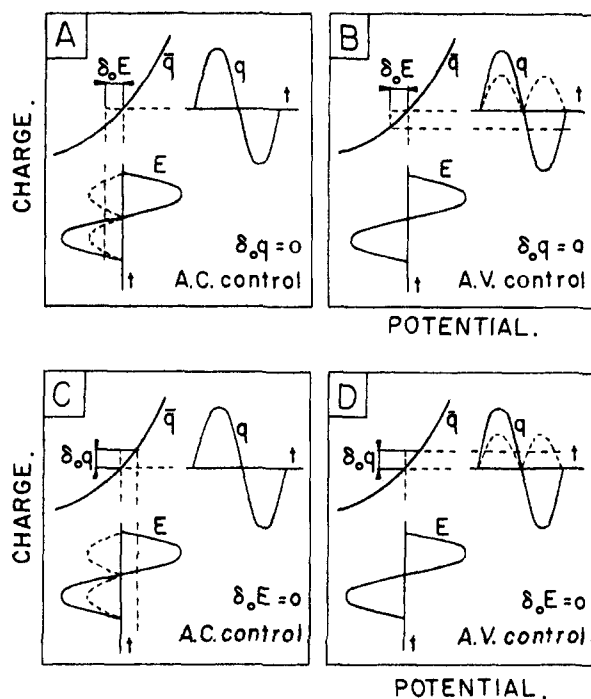


Fig. 1.—Non-faradaic rectification in the absence of complication due to mass transfer.

Rectification at Constant Mean Potential.—A.C. control in this case produces a $2f$ -component of E which must be compensated since \bar{E} is constant (Fig. 1C). There results a change $\delta_0 q$ in the mean charge and a transient current for the double layer charging. This *rectification current* can be observed when the cell with the ideal polarized electrode is connected to a potentiometer so that \bar{E} is kept constant. Application of the A.C. signal then results in a charging current which dies out progressively. In actuality, the charging current-time variations depend on the circuit resistance.

A.V. control at constant \bar{E} causes a $2f$ -component of the charge to appear (Fig. 1D). The latter is equivalent to a change $\delta_0 q$ in the mean charge which is the same as in Fig. 1C because of the reciprocity between Fig. 1C and 1D. The corresponding rectification current is observed for the same experimental conditions as for Fig. 1C.

In conclusion, the type of control of the alternating component is immaterial when changes in the mean component of the charge or the potential are considered. When \bar{q} is constant, there appears a rectification voltage $\delta_0 E$ which is equal to zero in the double pulse method. When \bar{E} is constant, a rectification current is observed.

Variations of Mean Components of the Charge, Potential and Surface Concentration.—We shall consider non-faradaic rectification for an ideal polarized electrode on which an ionic species or a neutral substance is specifically adsorbed, and we shall correlate adsorption kinetics with rectification. The basis of the analysis is similar to that in previous work on the non-faradaic impedance (Lorenz^{4b} in particular), but second-order terms are now considered for the charge on the electrode. The ap-

proach is similar to that in a previous paper⁹ from this Laboratory on faradaic rectification.

The charge on the electrode $q = q(E, \Gamma)$ is a function of the electrode potential E and the surface concentration Γ of adsorbed substance. One has

$$\delta_p q = (\partial q / \partial E) \delta_p E + (\partial q / \partial \Gamma) \delta_p \Gamma + \delta_p^2 q \quad (1)$$

where $\delta_p^2 q$ represents the second-order terms, namely

$$\delta_p^2 q \approx \frac{1}{2} \left[\left(\frac{\partial^2 q}{\partial E^2} \right) (\delta_1 E)_p^2 + \left(\frac{\partial^2 q}{\partial \Gamma^2} \right) (\delta_1 \Gamma)_p^2 \right] + \left(\frac{\partial^2 q}{\partial E \partial \Gamma} \right) (\delta_1 E \delta_1 \Gamma)_p \quad (2)$$

There $p = 0, 1$ and 2 corresponds, respectively, to the mean value, the fundamental harmonic and the second harmonic. Higher harmonics are neglected since δE is supposed to be small. One has $\delta_p^2 q = 0$ for $p = 1$, *i.e.*, for linearization. Equation 2 is approximate because the p -values of $(\delta_1 E)^2$ and $(\delta_1 \Gamma)^2$ are taken rather than the p -values of $(\delta E)^2$ and $(\delta \Gamma)^2$. All derivatives are taken at equilibrium in eq. 1 and 2. The terms $(\partial q / \partial E) \delta_p E + (\partial q / \partial \Gamma) \delta_p \Gamma$, as written for the fundamental harmonic ($p = 1$), correspond to the linearized non-faradaic impedance. The term $\delta_p^2 q$, as written for $p = 0$, accounts for rectification and gives the change in the mean charge of the electrode upon application of the A.C. signal. Steady-state for supply of matter by semi-infinite linear diffusion is reached for the alternating current provided $(\omega t)^{1/2} \gg 1$ where $\omega = 2\pi f$ (f frequency) and t is the time elapsed since the application of the A.C. signal.

In the simplest possible case $\partial q / \partial \Gamma = 0$, as for instance for the supporting electrolyte alone. One then has at constant mean charge ($\delta_0 q = 0$), $(dq/dE) \delta_0 E + \delta_0^2 q = 0$. Further, $(\delta_1 E)_0^2 = V_A^2/2$, V_A being the amplitude of the alternating voltage applied to the double layer. Since dq/dE is the differential capacity c_1 of the double layer one has, as was shown by Barker⁷

$$\delta_0 E = - \frac{V_A^2}{4} \frac{1}{c_1} \frac{dc_1}{dE} \quad (3)$$

Conversely, the charge variation at constant mean potential is $\delta_0 q = \delta_0^2 q$, *i.e.*

$$\delta_0 q = \frac{V_A^2}{4} \frac{dc_1}{dE} \quad (4)$$

This result was already reported by Barker.⁷

We now consider the more general case in which $\partial q / \partial \Gamma \neq 0$. When the mean potential is constant ($\delta_0 E = 0$), as would be for the ideal case of a cell circuit with zero resistance (r , as defined for current densities) one has $\delta_0 q = \delta_0^2 q$ since $\delta_0 \Gamma = 0$ under such conditions (see Appendix). Actually, $r \neq 0$ and $\delta_0 E \neq 0$. The charging current is equal to the current which would flow if a voltage-step equal to $-\delta_0 E$ were applied to the cell circuit across the resistance r . At time $t = 0$ one has: $\delta_0 q = 0$, $\delta_0 \Gamma = 0$ and $\delta_0 E = -\delta_0^2 q / (\partial q / \partial E)$. For $t > 0$ (t finite), $\delta_0 \Gamma \neq 0$ and mass transfer of the constituents of the double layer must be considered. As $t \rightarrow \infty$, $\delta_0 E \rightarrow 0$ and $\delta_0 q \rightarrow \delta_0^2 q$. One has in the simple case corresponding to $\partial q / \partial \Gamma = 0$ (*cf.* eq. 4)

$$\frac{d\delta_0 q}{dt} = \frac{\delta_0^2 q}{r(\partial q / \partial E)} \exp \left[- \frac{t}{r(\partial q / \partial E)} \right] \quad (5)$$

$$\delta_0 q = \delta_0^2 q \{ 1 - \exp[-t/r(\partial q / \partial E)] \} \quad (6)$$

When $\delta_0 q = 0$ for $t \geq 0$, $\delta_0 \Gamma = 0$ for $t = 0$ and $\delta_0 E = -\delta_0^2 q / (\partial q / \partial E)$. For $t \rightarrow \infty$, one has

$$\delta_0 E = - \frac{\delta_0^2 q}{(\partial q / \partial E) + (\partial q / \partial \Gamma)(\partial \Gamma / \partial E)} \quad (7)$$

$$\delta_0 \Gamma = (\partial \Gamma / \partial E)(\delta_0 E)_{t \rightarrow \infty}$$

and consequently $\delta_0 E$ and $\delta_0 \Gamma$ depend on mass transfer of the double layer constituents.

In the double pulse method, $\delta q = \delta_0^* q$, $\delta_0 \Gamma = 0$ and $\delta_0 E = 0$ for $t \geq 0$. The charge $\delta_0^* q$ is supplied from an outside source at $t = 0$ for all practical purposes by the use of a short rectangular current pulse and $\delta_0 E$ is maintained at zero despite the finite resistance of the cell circuit.

In practice, two types of measurements are possible: (a) comparison of the charging current resulting from rectification with the charging current for a voltage step equal to $-\delta_0 E$ (Barker⁷); (b) the double pulse method.

Non-Faradaic Impedance.—The term $\delta_0^* q$ of eq. 1 will be evaluated in terms of the elements of the equivalent circuit of the non-faradaic impedance just as the faradaic rectification voltage was previously expressed in terms of the components of the faradaic impedance.⁹ The current density variation for the first harmonic is (cf. eq. 1)

$$\delta_1 I = j\omega(\partial q/\partial E)\delta_1 E + j\omega(\partial q/\partial \Gamma)\delta_1 \Gamma \quad (9)$$

where j is the operator $(-1)^{1/2}$ and $\delta_1 \Gamma$ depends on adsorption kinetics. As $\omega \rightarrow \infty$, $\delta_1 \Gamma \rightarrow 0$ since variations of potential are too rapid for adsorption to follow. If z_ω is the non-faradaic impedance for $\omega \rightarrow \infty$, the impedance at the frequency ω is composed of z_ω in parallel with the impedance z_ω corresponding to the term in $\delta_1 \Gamma$ of eq. 9. The impedance z_ω will be evaluated by consideration of adsorption kinetics.

The flux ϕ_a for adsorption is a function of the potential E , the volume concentration C^* of adsorbed substance at the electrode surface and the surface concentration Γ . Hence

$$\delta_1 \phi_a = (\partial \phi_a/\partial E)\delta_1 E + (\partial \phi_a/\partial C^*)\delta_1 C^* + (\partial \phi_a/\partial \Gamma)\delta_1 \Gamma \quad (10)$$

on the assumption that only the first derivatives are considered in the expansion. Non-linearity could also be considered just as for the charge (cf. eq. 1 and 2), but this will not be done for the sake of simplicity. This simplification is justified since $\delta_1 E$ is supposed to be sufficiently small.

As in another paper,¹¹ we correlate variations of C^* and ϕ_a for the fundamental frequency by

$$\delta_1 C^* = (h_r - jh_x)\delta_1 \phi_a \quad (11)$$

where an anodic current corresponds to a positive flux and h is a function whose explicit form is solely determined by the mass transfer process. For instance, $h_r = h_x = (2\omega D)^{-1/2}$ (D diffusion coefficient of adsorbed species) for semi-infinite linear diffusion.¹² Since adsorption and mass transfer are the only processes involving the adsorbed substance (no loss in a charge transfer reaction), one has

$$-\delta_1 \Gamma = (1/j\omega)\delta_1 \phi_a \quad (12)$$

where $\omega = 2\pi f$, f being the frequency. By combining eq. 10, 11 and 12 one obtains

$$\delta_1 \Gamma = \frac{1}{\omega} \frac{1}{\left(\frac{\partial q}{\partial \Gamma}\right)} \times \frac{1}{(x^d + x^*) + j(r^d + r^*)} \delta_1 E \quad (13)$$

where

$$r^d = - \{1/[(\partial q/\partial \Gamma)(\partial C^*/\partial E)]\} h_r \quad (14)$$

$$x^d = - \{1/[(\partial q/\partial \Gamma)(\partial C^*/\partial E)]\} h_x \quad (15)$$

(11) M. Senda and P. Delabay, *J. Phys. Chem.*, **65**, 1580 (1961).

(12) This value of h_r and h_x is derived by application of Duhamel's theorem for a sinusoidal flux. Cf., e.g., H. S. Carslaw and J. C. Jaeger, "Conduction of Heat in Solids," Oxford University Press, London, 1947, p. 57, eq. 9.

$$r^* = \{1/[(\partial q/\partial \Gamma)(\partial C^*/\partial E)]\} [1/(\partial \phi_a/\partial C^*)] \quad (16)$$

$$x^* = - \{1/[(\partial q/\partial \Gamma)(\partial C^*/\partial E)]\} (1/\omega)(\partial C^*/\partial \Gamma) \quad (17)$$

all derivatives being taken at equilibrium. The frequency dependent component z_ω of the non-faradaic impedance (see discussion of eq. 9) is directly obtained from eq. 9 and 13. Thus

$$1/z_\omega = 1/(r_s - jx_s) \quad (18)$$

where

$$r_s = r^d + r^* \quad (19)$$

$$x_s = x^d + x^* \quad (20)$$

The impedance z_ω thus corresponds to the series combination of r_s and x_s . Conversely, determination of r_s and x_s (after correction of the non-faradaic impedance for z_ω (cf. eq. 9)) should allow study of adsorption kinetics.^{4,6,13}

The series circuit ($r_s - c_s$) which is equivalent to z_ω can be converted to the parallel circuit ($r_p - c_p$) already considered by Lorenz.^{4b} The corresponding phase angle θ is such that

$$\tan \theta = x_s/r_s = 1/\omega c_s r_s \quad (21)$$

$$= r_p/x_p = \omega c_p r_p$$

It follows from eq. 14 to 20 that

$$\tan \theta = \frac{1 + (1/h_x)(1/\omega)/(\partial \Gamma/\partial C^*)}{(h_r/h_x) + (1/h_x)[-1/(\partial \phi_a/\partial C^*)]} \quad (22)$$

or, for semi-infinite linear diffusion as mass transfer process

$$\tan \theta = \frac{1 + (A/\omega^{1/2})}{1 + B\omega^{1/2}} \quad (23)$$

with

$$A = (2D)^{1/2}/(\partial \Gamma/\partial C^*) \quad (24)$$

$$B = -(2D)^{1/2}/(\partial \phi_a/\partial C^*) \quad (25)$$

Equation 23 was already obtained by Lorenz.^{4b} There is diffusion control when $r^* \ll r^d$, i.e. for $B\omega^{1/2} \ll 1$ and control by slow adsorption when $B\omega^{1/2} \gg 1$. Further, there is very strong adsorption for $A/\omega^{1/2} \ll 1$ and weak adsorption for $A/\omega^{1/2} \gg 1$. These are relative terms since the conditions for which they apply depend on ω . Four extreme cases can be distinguished:

Diffusion control, very strong adsorption: $\tan \theta \approx 1$
 Diffusion control, very weak adsorption: $\tan \theta \approx A/\omega^{1/2}$
 Adsorption control, very strong adsorption: $\tan \theta \approx 1/B\omega^{1/2}$
 Adsorption control, very weak adsorption: $\tan \theta \approx (A/B)(1/\omega)$

Since $\omega = 2\pi f$, one has $B\omega^{1/2} \gg 1$ or $B\omega^{1/2} \ll 1$, for $-(\partial \phi_a/\partial C^*) < 10^{-4} f^{1/2}$ (control for slow adsorption) or $-(\partial \phi_a/\partial C^*) > f^{1/2}$ (diffusion control), respectively, all quantities being expressed in c.g.s. units. Likewise, one has $A/\omega^{1/2} \gg 1$ or $A/\omega^{1/2} \ll 1$ for $(\partial \Gamma/\partial C^*) < 2 \times 10^{-6} f^{-1/2}$ (very weak adsorption) or $(\partial \Gamma/\partial C^*) > 2 \times 10^{-1} f^{-1/2}$ (very strong adsorption). These numerical limits give orders of magnitude of the frequency to be used. Some numerical data are available in the papers of Lorenz, et al.^{4,6,13}

Non-Faradaic Rectification.—The change in mean charge $\delta_0^* q$ which is measured by the double pulse method will be expressed in terms of the elements of the non-faradaic impedance. The quantities $(\delta_1 E)_0^2$, $(\delta_1 \Gamma)_0^2$ and $(\delta_1 E \delta_1 \Gamma)_0^2$ appearing in eq. 2, as written for $p = 0$, are for $\delta_1 E = V_A \exp(j\omega t)$

$$(\delta_1 E)_0^2 = (1/2) V_A^2 \quad (26)$$

$$(\delta_1 \Gamma)_0^2 = \frac{1}{2} V_A^2 \frac{1}{[(\partial E/\partial \Gamma)]^2 r_s^2 + x_s^2} \quad (27)$$

(13) (a) W. Lorenz and E. O. Schmalz, *Z. Elektrochem.*, **62**, 301 (1958); (b) W. Lorenz, F. Möckel and W. Müller, *Z. physik. Chem.*, N.F., **25**, 145 (1960); (c) W. Lorenz and W. Müller, *ibid.*, **25**, 161 (1960).

$$(\delta, r^3 E)_0^2 = \frac{1}{2} V_A^2 \frac{1}{(\partial E / \partial \Gamma)} \frac{x^* x_s}{(r_s^2 + x_s^2)} \quad (28)$$

$$\delta_0^2 q = \frac{V_A^2}{2} \left[\frac{1}{2} \left(\frac{\partial^2 q}{\partial E^2} \right) + (\lambda_1 + \lambda_2) \frac{(x^*)^2}{r_s^2 + x_s^2} + \lambda_3 \frac{x^* x^d}{r_s^2 + x_s^2} \right] \quad (29)$$

where

$$\lambda_1 = \frac{1}{2} \left(\frac{\partial^2 q}{\partial \Gamma^2} \right) / \left(\frac{\partial E}{\partial \Gamma} \right)^2 \quad (30)$$

$$\lambda_2 = \left(\frac{\partial^2 q}{\partial E \partial \Gamma} \right) / \left(\frac{\partial E}{\partial \Gamma} \right) \quad (31)$$

$$\frac{(x^*)^2}{r_s^2 + x_s^2} = \frac{[A/\omega^{1/2}]^2}{[1 + B\omega^{1/2}]^2 + [1 + (A/\omega^{1/2})]^2} \quad (32)$$

$$\frac{x^* x_s}{r_s^2 + x_s^2} = \frac{(A/\omega^{1/2})}{(1 + B\omega^{1/2})^2 + [1 + (A/\omega^{1/2})]^2} \quad (33)$$

The amplitude of the voltage V_A applied to the non-faradaic impedance is $V_A = I_A |z|$, where I_A is the amplitude of the current and z is the total non-faradaic impedance (cf. discussion of eq. 9). V_A is not measurable, in practice, at the frequencies used in rectification studies because z is negligibly small in comparison with the total cell resistance. I_A , however, can be measured easily.

The derivatives in eq. 29 to 31 are taken at equilibrium and are thermodynamic quantities which can be determined from electrocapillary curves obtained for different volume concentrations of the adsorbed substance. Likewise, A is a thermodynamic quantity which can be obtained by the same method. The only unknown in the analysis of the experimental dependence of $\delta_0^2 q$ on frequency is the kinetic parameter B (eq. 25), and this parameter thus can be obtained.

It is seen from eq. 29 that $\delta_0^2 q \rightarrow (V_A^2/4)(\partial^2 q/\partial E^2)$ for $\omega \rightarrow \infty$, i.e., eq. 4 is applicable, as it should, since there is no effect of mass transfer. Some simplified forms of eq. 29 will be given for the case in which $\lambda_2 \gg \lambda_1$. This condition is not unrealistic in a number of practical instances.¹⁴ The term in $(\lambda_1 + \lambda_2)$ or λ_2 then can be neglected when $A/\omega^{1/2} \ll 1$ (very strong adsorption) or $A/\omega^{1/2} \gg 1$ (very weak adsorption), respectively. One has: $B\omega^{1/2} \gg 1$ and $A/\omega^{1/2} \ll 1$ (adsorption control)

$$\frac{x^* x^d}{r_s^2 + x_s^2} \approx \frac{A}{B_2 \omega^{1/2}} \quad (34)$$

$B\omega^{1/2} \gg 1$ and $A/\omega^{1/2} \gg 1$ (adsorption control)

$$\frac{(x^*)^2}{r_s^2 + x_s^2} = \frac{1}{1 + \left(\frac{B}{A} \omega \right)^2} \quad (35)$$

$B\omega^{1/2} \ll 1$ and $A/\omega^{1/2} \ll 1$ (diffusion control)

$$\frac{x^* x^d}{r_s^2 + x_s^2} \approx \frac{A}{2\omega^{1/2}} \quad (36)$$

$B\omega^{1/2} \ll 1$ and $A/\omega^{1/2} \gg 1$ (diffusion control)

$$\frac{(x^*)^2}{r_s^2 + x_s^2} \approx 1 \quad (37)$$

The above results are general and do not depend on any particular form of the rate equation for adsorption kinetics. A particular case is treated in Appendix as an example, namely, that corresponding to adsorption kinetics according to Brunauer, Love and Keenan.¹⁵

(14) Cf. e.g., M. Breiter and P. Delahay, *J. Am. Chem. Soc.*, **81**, 2938 (1959).

(15) (a) S. Brunauer, K. S. Love and R. G. Keenan, *ibid.*, **64**, 751 (1942); (b) see also T. L. Hill, *Advances in Catalysis*, **4**, 211 (1952).

Conclusion

Non-faradaic rectification allows the quantitative study of kinetics for adsorption of neutral substances or ions in presence of a large excess of a supporting electrolyte.¹⁶ No explicit form of the rate equation for adsorption kinetics need be postulated and kinetics is characterized by the partial derivative of the rate with respect to the concentration at constant potential and coverage. Interpretation in terms of a particular type of adsorption kinetics is also possible. The method has the advantage over the non-faradaic impedance method to allow determinations at frequencies far too high for bridge measurements. Experimental study is now in progress.

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Appendix

Variations of $\delta_0 \Gamma$ for $\delta_0 E = 0$.—By definition of the flux one has

$$\delta_0 \Gamma = - \int_0^t \delta \phi_a dt \quad (38)$$

Further

$$\delta C^* = \frac{1}{(\pi D)^{1/2}} \int_0^t \frac{\delta \phi_a}{(t-u)^{1/2}} du \quad (39)$$

Hence, in view of eq. 10

$$\delta \phi_a = - \frac{\partial \phi_a}{\partial \Gamma} \int_0^t \delta \phi_a dt + \frac{1}{(\pi D)^{1/2}} \left(\frac{\partial \phi_a}{\partial C^*} \right) \int_0^t \frac{\delta \phi_a}{(t-u)^{1/2}} du \quad (40)$$

It can be shown by Laplace transformation that the only solution of eq. 40 is $\delta \phi_a = 0$. Hence, $\delta \Gamma = 0$.

Adsorption Kinetics According to Brunauer, Love and Keenan.—One has¹⁵

$$\phi_a = k_d \sigma \exp \left[- \frac{W_d^0 - \beta_d \sigma}{RT} \right] - k_a C^* (1 - \sigma) \exp \left[- \frac{W_a^0 + \beta_a \sigma}{RT} \right] \quad (41)$$

where k_d and k_a are rate constants, σ is the coverage ($\sigma = \Gamma/\Gamma_m$, Γ_m maximum surface concentration), W_d^0 and W_a^0 are activation energies for adsorption and desorption for $\sigma = 0$, respectively. The energies W_d^0 and W_a^0 are dependent on the electrode potential.¹⁶ It is postulated in eq. 41 that energies of activation for adsorption and desorption are linear functions of the coverage. One has at equilibrium¹⁷

$$\sigma = \rho C^* / (1 + \rho C^*) \quad (42)$$

where

$$\rho = (k_a/k_d) \exp \{ [(W_d^0 - W_a^0) - (\beta_d + \beta_a)\sigma] / RT \} \quad (43)$$

If θ_a^0 is the adsorption exchange rate at equilibrium, the partial derivatives at equilibrium are

$$\frac{\partial \phi_a}{\partial E} = - \frac{\phi_a^0}{RT} \frac{\partial}{\partial E} (W_d^0 - W_a^0) \quad (44)$$

$$\frac{\partial \phi_a}{\partial \Gamma} = \phi_a^0 \left[\frac{1}{\Gamma_m} \left(\frac{1}{\sigma} + \frac{1}{1-\sigma} \right) + \frac{1}{\Gamma_m} \frac{1}{RT} (\beta_d + \beta_a) \right] \quad (45)$$

$$\frac{\partial \phi_a}{\partial C^*} = - \frac{\phi_a^0}{C^*} \quad (46)$$

Simpler forms corresponding to the Langmuir isotherms are directly obtained from the above equations for $\beta_a = \beta_d = 0$.

(16) J. A. V. Butler, *Proc. Roy. Soc. (London)*, **A122**, 399 (1929).

(17) Equation 42 reduces to a Temkin isotherm when σ is in the vicinity of 0.5.