hampered by the absence of quantitative knowledge of the other terms which affect ΔF for the unfolding process. The general theory, in the context of which our Δf_u terms have been placed, is useful as a framework for assessing the importance of hydrophobic interactions, but it is too crude to permit analysis of those aspects of protein denaturation which do not directly arise from hydrophobic interactions.

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[CONTRIBUTION FROM THE COATES CHEMICAL LABORATORY, LOUISIANA STATE UNIVERSITY, BATON ROUGE 3, LOUISIANA]

Rate Equation for Adsorption of a Neutral Substance at a Metal–Electrolyte Interface

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An equation is derived for the rate of adsorption of a neutral substance at a metal–electrolyte interface for processes obeying the logarithmic Temkin isotherm. A recent investigation in this Laboratory has indicated that this isotherm is obeyed over a rather wide range of concentrations by a number of organic substances of varied structure. Adsorption kinetics is characterized by an *exchange rate* v^0 which is expressed in terms of a *standard rate constant* $\boldsymbol{k}^0$, the activity of adsorbed species in solution a, the charge-dependent part ΔG^q of the standard free energy of adsorption ΔG^0, a *coverage parameter* (not the coverage) λ $(0 < \lambda < 1)$ and a *charge parameter* ρ $(0 < \rho < 1)$. Variations $\delta(\Delta G^q)$ with the charge density q on the electrode can be determined experimentally from the dependence of ΔG^0 on q. More conveniently $\delta(\Delta G^q)$ is obtained from the variations of the potential E with $\ln a$ at constant q. ($\partial E/\partial \ln a$ at constant q is the Esin and Markov coefficient.) The parameters λ and ρ are determined from $(\partial \ln v^0/\partial \ln a)$ at constant q and $(\partial \ln v^0/\partial \Delta G^q)$ at constant a. The adsorption rate is expressed in terms of v^0, the parameter b characterizing the isotherm, λ, ρ, the variation $\delta(\Delta G^q)$ of ΔG^q and the variation $\delta\Gamma$ of the surface concentration Γ which result from a change of q. Correction for mass transfer and for the double layer structure is indicated. The principle of a new *coulostatic* method for the measurement of v^0 is discussed, and correlation of the present theory with other methods for v^0 determination is outlined. The basic equation for adsorption rate reminds one of the Butler, Erdey-Gruz, Volmer equation for electrode kinetics; v^0 is the counterpart of the exchange current, and the charge parameter ρ is analogous to the transfer coefficient in electrode kinetics.

The thermodynamics of adsorption of a neutral substance at a metal–electrolyte interface, which is based on the Gibbs adsorption isotherm, is well understood but hardly anything is known about adsorption kinetics, except for purely diffusion controlled processes.[2,3] The kinetic problem is attacked here for adsorption of a neutral substance obeying the logarithmic Temkin isotherm,[4] and a basic equation is derived which expresses the rate of adsorption as a function of experimental quantities. This equation appears to be quite general as will be shown below and may serve as a basis for the development of adsorption kinetics at metal–electrolyte interfaces. The key ideas are: (i) In the thermodynamic analysis of adsorption at a metal–electrolyte interface, it is often convenient to choose the charge density q as the independent electrical variable rather than the electrode potential E.[5] The charge density q, rather than E, is the "natural" electrical parameter in the treatment of adsorption, whereas the opposite holds for electrode processes. (ii) It is inferred from recent work in this Laboratory that the logarithmic Temkin isotherm is approximately obeyed for a number of organic neutral substances of varied structure over a fairly wide concentration range. (iii) The equations given by Temkin[4] for the rates of adsorption and desorption of a gas on a solid apply (see below). (iv) The influence of the charge density on rates of adsorption and desorption can be expressed in terms of a charge parameter defined below and the charge-dependent part of the standard free energy of adsorption. This idea is novel, to our knowledge, and is the key to the following treatment. Any surface process subsequent to adsorption will be neglected or assumed to be sufficiently fast and consequently not rate-determining. A more general treatment of adsorption processes followed by a slow surface process is now being considered.

Rate Equation for the Adsorption–Desorption Process

Activities and Isotherm.—We represent the adsorption of a neutral substance O at a metal–electrolyte interface by

$$\mathrm{O} + \mathrm{S} = \mathrm{A} \qquad (1)$$

where S is a site and A is the adsorbed species. This formalism is inspired from the application of order-disorder theory to adsorption.[6] We assume that the equations derived by Temkin[4] for the rates of adsorption ($\overrightarrow{v}$) and desorption ($\overleftarrow{v}$) apply, and we first derive expressions for the activities of the species of eq. 1. We shall then verify that the logarithmic Temkin isotherm is obeyed. The

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[1] Postdoctoral fellow, 1960–1962.

[2] For a review, *cf.* R. Parsons, Chap. 1 in "Advances in Electrochemistry and Electrochemical Engineering," Vol. I, edited by P. Delahay, Interscience-Wiley, New York, N. Y., 1961, pp. 1–64.

[3] Adsorption kinetics with diffusion control has been worked out for linear and Langmuir isotherms. The main significance of this work resided in showing that diffusion-controlled adsorption can be slow. This point had been overlooked in a number of investigations, especially with the dropping mercury electrode.

[4] M. I. Temkin, *Zhur. fiz. Khim.*, **15**, 296 (1941); translation available. The logarithmic Temkin isotherm, often referred to as a "Temkin isotherm," is only a particular form of the more general equation derived by Temkin.

[5] R. Parsons, *Trans. Faraday Soc.*, **51**, 1518 (1955).

[6] For a review, *cf.*, *e.g.*, J. M. Honig, *J. Chem. Educ.*, **38**, 538 (1961).

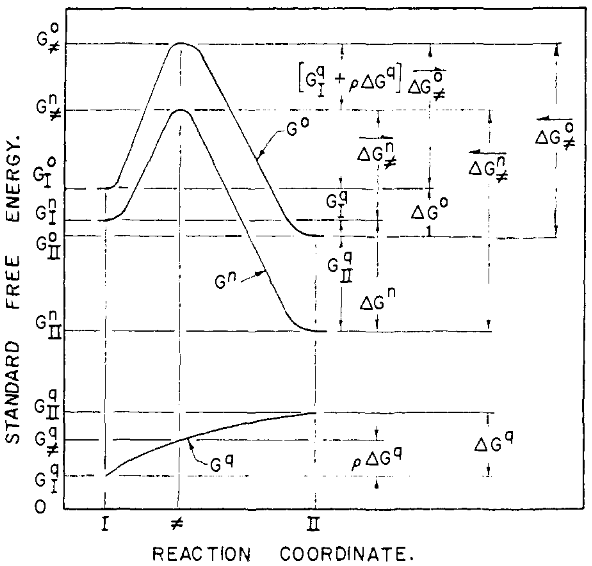

Fig. 1.—Standard free energies against reaction coordinate.

basic equations given by Temkin are (eqs. 15, 48, 68 and 69 in ref. 4), with the notations used below

$$b\Gamma = h(q) + RT \ln a_O \qquad (2)$$

$$\vec{v} = \vec{k}\, a_O \exp[-(\lambda b/RT)\Gamma] \qquad (3)$$

$$\overleftarrow{v} = \overleftarrow{k} \exp\{[(1 - \lambda)b/RT]\Gamma\} \qquad (4)$$

where Γ is the surface concentration[7]; a_O the activity of O in solution; b a characteristic parameter for the isotherm; $h(q)$ a quantity which is a function of the charge density alone at constant temperature and pressure (this function will be defined further below); $\vec{k}$ and $\overleftarrow{k}$ are rate constants for adsorption and desorption, respectively; $0 < \lambda < 1$ is what we shall call the *coverage parameter*[8] (not to be confused with the coverage itself!); R and T are as usual. Equation 2 is the logarithmic Temkin isotherm as written by Parsons.[9] Equations 3 and 4 express the dependence of the rates of adsorption and desorption on coverage. We can postulate with the formalism of eq. 1 that $\vec{v}$ is proportional to the product of the activities of O and S and $\overleftarrow{v}$ is proportional to the activity of A. Thus

$$a_S = \exp[-(\lambda b/RT)\Gamma] \qquad (5)$$

$$a_A = \exp\{[(1 - \lambda)b/RT]\Gamma\} \qquad (6)$$

It must be shown that eqs. 5 and 6 yield the logarithmic Temkin isotherm. We have at equilibrium

$$\mu_O + \mu_S = \mu_A \qquad (7)$$

where the μ's are the chemical potentials. Further

$$\mu_O = \mu_O{}^0 + RT \ln a_O \qquad (8)$$

$$\mu_S = (\mu_S{}^n + \mu_S{}^q) + RT \ln a_S \qquad (9)$$

$$\mu_A = (\mu_A{}^n + \mu_A{}^q) + RT \ln a_A \qquad (10)$$

where the μ^n's are the charge-independent parts of the standard chemical potentials of S and A, and the μ^q's are the charge-dependent parts of these potentials. It follows by combination of eqs. 7 to 10 that

$$\begin{aligned} b\Gamma &= (\Delta G^n + \Delta G^q) + RT \ln a_O \qquad (11)\\ &= -\Delta G^0 + RT \ln a_O \end{aligned}$$

where $-\Delta G^n = \mu_O{}^0 + \mu_S{}^n - \mu_A{}^n$ and $-\Delta G^q = \mu_S{}^q - \mu_A{}^q$. Equation 11 is the logarithmic Temkin isotherm, as written in terms of the standard free energy of adsorption ΔG^0 or its parts ΔG^n and ΔG^q. Note that ΔG^0 as well as *variations* of ΔG^q with q can be obtained experimentally. It follows from eqs. 2 and 11 that $h(q) = -\Delta G^0$, and the symbol $h(q)$ need not be retained below.

Adsorption Exchange Rate.—Kinetics of adsorption will be treated by a method analogous to that used for electrode processes in the derivation of the current and exchange current.[10] We shall neglect first complications arising from mass transfer of the adsorbed species in solution. We designate the initial state of the system undergoing reaction 1 by I, the final state by II, and the transition state by the symbol $\neq$. The standard free energies are

$$G_I{}^0 = \mu_O{}^0 + \mu_S{}^n + \mu_S{}^q \qquad (12)$$

$$G_{II}{}^0 = \mu_A{}^n + \mu_A{}^q \qquad (13)$$

$$G_{\neq}{}^0 = \mu_{\neq}{}^n + \mu_{\neq}{}^q \qquad (14)$$

where $\mu_{\neq}{}^n$ and $\mu_{\neq}{}^q$ are the charge-independent and charge-dependent parts of $G^0{}_{\neq}$, respectively. The standard free energy of activation for the forward reaction (adsorption) is

$$\begin{aligned} \Delta\vec{G}_{\neq}{}^0 &= G_{\neq}{}^0 - G_I{}^0 \qquad (15)\\ &= (\mu_{\neq}{}^n - \mu_O{}^0 - \mu_S{}^n) + (\mu_{\neq}{}^q - \mu_S{}^q)\\ &= \Delta\vec{G}_{\neq}{}^n + (\mu_{\neq}{}^q - \mu_S{}^q) \end{aligned}$$

We postulate that the charge dependent part of the standard free energy of activation is a monotonic function of the reaction coordinate. This assumption is similar to the one made in electrode kinetics whereby it is postulated that the potential dependent part of the standard free energy of activation is a monotonic function of the reaction coordinate (*cf.* ref. 10). Thus (Fig. 1)

$$\mu_{\neq}{}^q - \mu_S{}^q = \rho(\mu_A{}^q - \mu_S{}^q) \qquad (16)$$

where ρ $(0 < \rho < 1)$ is what we shall call, the *charge parameter*. Thus the charge parameter ρ in adsorption kinetics is the analog of the transfer coefficient α in electrode kinetics. One deduces from eqs. 15 and 16

$$\overrightarrow{\Delta G}_{\neq}{}^0 = \overrightarrow{\Delta G}_{\neq}{}^n + \rho(\mu_A{}^q - \mu_S{}^q) \qquad (17)$$

and, likewise, for the backward process (desorption)

$$\begin{aligned} \overleftarrow{\Delta G}_{\neq}{}^0 &= G_{\neq}{}^0 - G_{II}{}^0 \qquad (18)\\ &= (\mu_{\neq}{}^n - \mu_A{}^n) + (\mu_{\neq}{}^q - \mu_A{}^q)\\ &= \overleftarrow{\Delta G}_{\neq}{}^n - (1 - \rho)(\mu_A{}^q - \mu_S{}^q) \end{aligned}$$

Since $\Delta G^q = \mu_S{}^q - \mu_A{}^q$ (see eq. 11), eqs. 15 and 18 become

$$\overrightarrow{\Delta G}_{\neq}{}^0 = \overrightarrow{\Delta G}_{\neq}{}^n + \rho\Delta G^q \qquad (19)$$

$$\overleftarrow{\Delta G}_{\neq}{}^0 = \overleftarrow{\Delta G}_{\neq}{}^n - (1 - \rho)\Delta G^q \qquad (20)$$

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[7] The surface concentration, that is the total surface excess minus the contribution from the diffuse double layer, should be nearly equal to the total surface excess for a neutral substance since the interaction of such a substance with the electrical field in the *diffuse* double layer is probably quite low for a neutral species.

[8] The parameter λ is denoted by α in Temkin's work.[4] We use λ to avoid confusion with the transfer coefficient in electrode kinetics.

[9] R. Parsons, *Proc. 4th Conf. Electrochem.*, Vol. I, English translation, Consultants Bureau, New York, N. Y., 1961, p. 18. Note that $b = B^2$, where B is the parameter used by Parsons.

[10] See particularly the approach of R. Parsons, *Trans. Faraday Soc.*, **47**, 1332 (1951).

The rate constants are, on the assumption that the transmission coefficients are equal to 1

$$\begin{aligned}\overrightarrow{k} &= (kT/h)\exp(-\Delta\overrightarrow{G}_{\neq}{}^{0}/RT) \qquad (21)\\ &= (kT/h)\exp(-\Delta\overrightarrow{G}_{\neq}{}^{n}/RT)\exp(-\rho\Delta G^{q}/RT)\\ &= k_f\exp(-\rho\Delta G^{q}/RT)\end{aligned}$$

$$\begin{aligned}\overleftarrow{k} &= (kT/h)\exp(-\Delta\overleftarrow{G}_{\neq}{}^{0}/RT) \qquad (22)\\ &= (kT/h)\exp(-\Delta\overleftarrow{G}_{\neq}{}^{n}/RT)\exp[(1-\rho)\Delta G^{q}/RT]\\ &= k_b\exp[(1-\rho)\Delta G^{q}/RT]\end{aligned}$$

where k is the Boltzmann constant; h the Planck constant; and k_f and k_b are rate constants which are independent of the charge density on the electrode. The rates of adsorption ($\overrightarrow{v}$) and desorption ($\overleftarrow{v}$) are[11]

$$\begin{aligned}\overrightarrow{v} &= \overrightarrow{k}a_{O}a_{S}\\ &= k_f a_{O}\exp[-(\lambda b/RT)\Gamma]\exp[-\rho\Delta G^{q}/RT] \qquad (23)\end{aligned}$$

$$\begin{aligned}\overleftarrow{v} &= \overleftarrow{k}a_{A}\\ &= k_b\exp\{[(1-\lambda)b/RT]\Gamma\}\exp[(1-\rho)\Delta G^{q}/RT] \qquad (24)\end{aligned}$$

At equilibrium $\overrightarrow{v} = \overleftarrow{v} = v^0$, where v^0 is the *adsorption exchange rate*[12] (by analogy with the exchange current in electrode kinetics). After introduction of Γ, as given by the isotherm (eq. 11), in eq. 23 or 24 one obtains

$$v^0 = k^0 a_{O}{}^{1-\lambda}\exp[(\lambda-\rho)\Delta G^{q}/RT] \qquad (25)$$

where k^0 (in cm. sec.$^{-1}$) is the adsorption standard rate constant given by

$$\begin{aligned}k^0 &= k_f\exp(\lambda\Delta G^{n}/RT)\\ &= k_b\exp\{[-(1-\lambda)\Delta G^{n}/RT]\} \qquad (26)\end{aligned}$$

Equation 25 is fundamental, we believe, for the understanding of the kinetics of adsorption processes obeying a logarithmic Temkin isotherm. It should be noted that v^0, λ and ρ can be determined experimentally but that k^0 and ΔG^q cannot (see below). Only *variations* of ΔG^q with q can be determined.

Rate Equation.—We consider a perturbation caused by a variation $\delta(\Delta G^q)$ of ΔG^q, i.e. by the corresponding change in the charge density of the electrode. Thus

$$\delta(\Delta G^q) = \Delta G^q - \Delta G_i{}^q \qquad (27)$$

where $\Delta G_i{}^q$ is the initial value of ΔG^q. $\delta(\Delta G^q)$ is a known function of time. If we introduce

$$\delta\Gamma = \Gamma - \Gamma_i \qquad (28)$$

Γ_1 being the initial value of Γ, the net adsorption rate is

$$\begin{aligned}v &= \mathrm{d}\Gamma/\mathrm{d}t \qquad (29)\\ &= \mathrm{d}\delta\Gamma/\mathrm{d}t\\ &= v^0\\ &\left\{\begin{array}{l}\exp[-(\lambda b/RT)\delta\Gamma\}\exp[-(\rho/RT)\delta(\Delta G^q)]\\ -\exp[((1-\lambda)b/RT)\delta\Gamma]\exp[((1-\rho)/RT)\delta(\Delta G^q)]\end{array}\right\}\end{aligned}$$

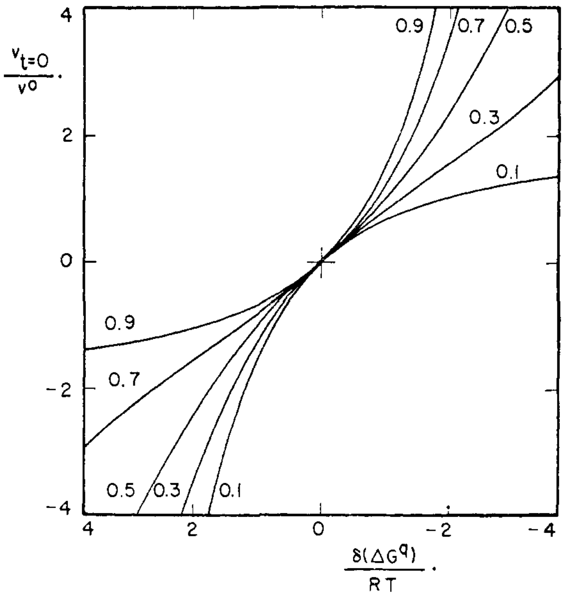

Fig. 2.—Variations of $v_{t=0}/v^0$ with $\delta(\Delta G^q)/RT$ according to eq. 30 for different values of the charge parameter ρ. Net adsorption rates are positive, and net desorption rates negative.

For instance, if ΔG^q varies according to a step function, $\delta(\Delta G^q)$ is equal to a constant, and the net adsorption rate at time $t = 0$ is

$$v_{t=0} = v^0\{\exp[-(\rho/RT)\delta(\Delta G^q)] - \exp[((1-\rho)/RT)\delta(\Delta G^q)]\} \qquad (30)$$

Note that the term in Γ drops out in eq. 30 since $\delta\Gamma = 0$ at $t = 0$. The rate v for $t > 0$ decreases continuously and Γ approaches the equilibrium value corresponding to $\Delta G^q + \delta(\Delta G^q)$ for $t \rightarrow \infty$.

Equation 30 recalls the Butler, Erdey-Gruz, Volmer equation for electrode kinetics,[13] and a plot of $v_{t=0}/v^0$ against $\delta(\Delta G)^q$ (Fig. 2) is similar to a plot of $I/I_a{}^0$ against the overvoltage[14] η (I, current density, $I_a{}^0$, apparent exchange current density). The two diagrams, however, correspond to very different experimental conditions. The electrode potential E for given activities of reactants and products is uniquely determined for the plot $I/I_a{}^0$ against η since $\eta = E - E_e$, E_e being the equilibrium potential. This is not the case for the plot of $v_{t=0}/v^0$ against $\delta(\Delta G^q)$ since $\Delta G_i{}^q$ in eq. 27 is for any value of the charge density q on the electrode.[15] Moreover, the current density is independent of time in the absence of complications resulting from non steady-state mass transfer and/or variations

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[11] The dimensions of $\overrightarrow{k}$ and $\overleftarrow{k}$ are mol. cm.$^{-2}$ sec.$^{-1}$ because the concentration $C_{\neq}$ of the activated complex for a heterogeneous process is expressed in mol. cm.$^{-2}$ Thus $\overrightarrow{v} = (kT/h)C_{\neq}$ is in mol. cm.$^{-2}$ sec.$^{-1}$ Now, $C_{\neq} = (K_{\neq}a_{O}a_{S})/f_{\neq}$, where $K_{\neq}$ is the *thermodynamic* equilibrium constant for the equilibrium between the reactants and the activated complex, and $f_{\neq}$ is the activity coefficient of the activated complex. Thus, $\overrightarrow{v} = (kT/h)(K_{\neq}/f_{\neq})a_{O}a_{S}$. We note that $a_{O}a_{S}$ and $K_{\neq}$ are dimensionless since activities are defined as ratios of fugacities. Therefore, the units of $\overrightarrow{v}$ are the units of $(kT/h)(K_{\neq}/f_{\neq})$. Further, it follows from eq. 21 that $\overrightarrow{k} = (kT/h)(K_{\neq}/f_{\neq})$. Since the units of $f_{\neq}$ are mol.$^{-1}$ cm.^{2}, the units of $\overrightarrow{k}$ and $\overrightarrow{v}$ are mol. cm.$^{-2}$ sec.$^{-1}$. The same reasoning holds for $\overleftarrow{v}$ and $\overleftarrow{k}$. The same argument holds for the units of the rate constant and reaction velocities for charge transfer processes in electrode kinetics.

[12] This term was introduced, to our knowledge, by T. Berzins and P. Delahay, *J. Phys. Chem.*, **59**, 906 (1955).

[13] (a) For a detailed treatment, see K. J. Vetter, "Elektrochemische Kinetik," Springer-Verlag, Berlin, 1961. (b) For a survey, see, *e.g.*, P. Delahay in ref. 2, pp. 233–318.

[14] The $I/I_a{}^0$ against η plot corresponding to Fig. 2 is given by H. Gerischer and W. Vielstich, *Z. physik. Chem.* (Frankfurt), **3**, 16 (1955).

[15] It is assumed that the logarithmic Temkin isotherm is valid for any value of q or E being considered.

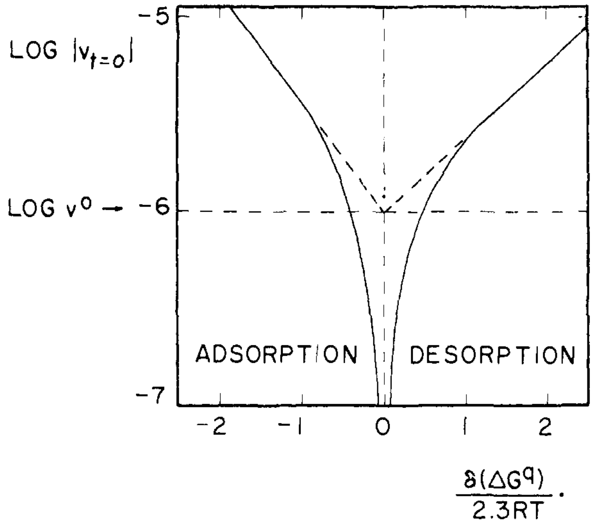

Fig. 3.—Adsorption analogy of a Tafel plot: theoretical plot for $v^0 = 10^{-6}$ mol. cm.$^{-2}$ sec.$^{-1}$ and $\rho = 0.6$.

of electrode properties, etc., and equilibrium is never reached for $\eta \neq 0$. Conversely, $v_{t=0}$ is only for time $t = 0$, and adsorption equilibrium is ultimately reached.

As in the case of electrode processes one can consider two limiting cases:

(i) When $\delta(\Delta G^q) << -RT/(1-\rho)$, the second exponential in eq. 30 can be neglected in comparison with the first; when $\delta\,(\Delta G)^q \gg RT/\rho$, the first exponential is negligible in comparison with the second. Consequently, a plot of ln $v_{t=0}$ against $\delta(\Delta G^q)$ for either of these conditions is linear (Fig. 3), i.e., one has in adsorption kinetics the analog of Tafel lines is electrode kinetics. The extrapolated lines intersect at a point whose abscissa corresponds to $\delta(\Delta G^q) = 0$ and whose ordinate is ln v_0. Experimental determination of these lines may be quite impossible when $v°$ is high and adsorption is essentially diffusion controlled, even for very short times, for the rather large values of $\delta(\Delta G^q)$ which are required. Extrapolation of rates to time $t = 0$ is then very uncertain or impossible. Further, variations of potential corresponding to $\delta(\Delta G^q)$ may be so large as to cause the electrode to operate under conditions in which it is no longer an ideal polarized electrode.

(ii) For small departure from equilibrium, eq. 29 can be linearized in the form

$$v_{\eta\rightarrow 0} = -(v^0/RT)[b\delta\Gamma + \delta(\Delta G^q)] \qquad (31)$$

Hence, at $t = 0$, $v_{t=0}$ for $\eta \rightarrow 0$ is proportional to $\delta(\Delta G^q)$, just as the current density I in electrode kinetics is proportional to η for $I \rightarrow 0$.

Determination of the Coverage Parameter λ and Charge Parameter ρ.—It follows from eq. 25 that

$$(\partial \ln v^0/\partial \ln a_O)_q = 1 - \lambda \qquad (32)$$

$$RT\,(\partial \ln v^0/\partial \Delta G^q)_{a_O} = \lambda - \rho \qquad (33)$$

and λ and ρ are readily obtained provided v^0 can be measured as a function of ΔG^q, i.e., as a function of the charge density q on the electrode. The procedure corresponding to eq. 32 is similar to the one applied in electrode kinetics[13] for the determination of transfer coefficients.

Influence of Mass Transfer.—It was assumed above that the activity of substance O at the electrode, a_O, is eq. 25 is equal to the bulk activity a_O. We now treat the case in which $a_O \neq a_O^0$ ($a_O < a_O^0$ for net adsorption, $a_O > a_O^0$ for net desorption). The derivation, which is similar to that of eq. 29, yields

$$v = v_i^0 \left\{ \begin{array}{l} (a_O/a_O^0)\exp[-(\lambda b/RT)\delta\Gamma]\exp[-(\rho/RT)\delta(\Delta G^q)] \\ -\exp[((1-\lambda)b/RT)\delta\Gamma]\exp[((1-\rho)/RT)\delta(\Delta G^q)] \end{array} \right\} \qquad (34)$$

where the exchange rate v_i^0 is written for the initial value of v^0 corresponding to ΔG_i^q, that is (cf. eq. 25)

$$v_i^0 = k^0(a_O^0)^{(1-\lambda)}\exp[(\lambda-\rho)\Delta G_i^q/RT \qquad (35)$$

The activity a_O in eq. 34 is a function of time which depends on the variations of $\delta(\Delta G^q)$ with time and the conditions of mass transfer. Equation 30 for $t = 0$ still applies since $a_O = a_O^0$ at $t = 0$. The linearized form of eq. 34 is

$$v_{\eta\rightarrow 0} = v_i^0\{(\delta a_O/a_O^0) - (1/RT)[b\delta\Gamma + \delta(\Delta G^q)]\} \qquad (36)$$

where $\delta a_O = a_O - a_O^0$. Equation 36 should be particularly useful in the analysis of experimental methods for the determination of exchange rates because of its mathematical simplicity in comparison with eq. 34.

Correction for the Effect of the Diffuse Double Layer.—It was assumed that the activity a_O in the *preadsorption state*[16] is either equal to the bulk activity a_O^0 or can be correlated to a_O^0 by consideration of mass transfer. This is only approximate because molecules of the adsorbed species O interact with the electrical field in the *diffuse* double layer. Correction can be made[17] provided the field strength is known. As a first approximation, one can assume that the presence of O in solution does not alter significantly the field strength calculated from the Gouy–Chapman theory for the plane corresponding to the preadsorption state. The correction is a simple one with such an assumption (and an assumption about the position of the preadsorption state) and will not be discussed further. This correction is analogous to the Frumkin correction in electrode kinetics,[18] but is probably much less significant than the latter correction in most instances.

Rate Equation for the Adsorption-Desorption Process as a Function of the Charge on the Electrode and the Electrode Potential

We now consider the correlation between ΔG^q and variations of the charge density q on the electrode. It follows from eq. 11 for the isotherm, that variations of ΔG^q with q are known provided the variations of ΔG^0 with q can be determined. It suffices, therefore, to determine Γ and b for different charge densities and extrapolate the value of $b\Gamma$ to the value of a_O selected for the standard state or to any constant value of a_O. This procedure is purely thermodynamic in nature, and only requires the application of the Gibbs adsorption isotherm. One has for an ideal polarized electrode at constant temperature and pressure and for a constant electrolyte composition[19]

$$q = -(\partial\gamma/\partial E)_{a_O} \qquad (37)$$

$$\Gamma = -(1/RT)(\partial\gamma/\partial \ln a_O)_E \qquad (38)$$

where E is the potential as measured against a reference electrode reversible to a cation or anion in solution, and γ is the interfacial tension for the electrode-electrolyte interface. One first ascertains

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(16) We use this expression by analogy with "Preelectrode State" introduced by Parsons.[2]

(17) E. A. Guggenheim, "Thermodynamics, an Advanced Treatment for Chemists and Physicists," 3rd ed., North-Holland Publishing Co., Amsterdam, 1957, *cf.* Chapter 11.

(18) For a review, *cf.*, *e.g.*, R. Parsons in ref. 2.

(19) For a review, see, *e.g.*, R. Parsons in "Modern Aspects of Electrochemistry," J. O'M. Bockris, editor, Butterworths, London, 1954, pp. 103–179. For a general and rigorous derivation, *cf.* R. Parsons and M. A. V. Devanathan, *Trans. Faraday Soc.*, **49**, 404 (1953).

that the logarithmic Temkin isotherm is obeyed from a plot of Γ against ln a, and then deduces the variations of ΔG^q with q from a plot of ΔG^0 against q. Such calculations can be greatly speeded up by the use of a computer (I.B.M. digital computer, model 1620) and cubic interpolation of the data on γ as was found in this Laboratory.[20] The computer method also appears to yield more accurate data than graphic differentiation.

The variations of the charge-dependent part, ΔG^q, of ΔG^0 with q can also be determined in a simpler way by consideration of the *Esin and Markov coefficient*,[21] $g \equiv (\partial E/\partial \ln a)_q$, at constant charge and constant electrolyte composition. It was pointed out by Parsons[22] that, if the Temkin isotherm is obeyed, the plot of E against ln a_O is linear at constant charge, *i.e.*, the Esin and Markov coefficient for a given charge is independent of the activity a_O. The preparation of such a plot does not require the determination of Γ by eq. 38 and requires only application of eq. 37. If the coefficient g at constant q varies with a_O, the logarithmic Temkin isotherm, and consequently the above kinetic treatment, does not apply. Linearity of the plot of g against ln a at constant q, however, does not necessarily imply that the logarithmic Temkin isotherm is applicable. Indeed, it was shown recently in this Laboratory[23] that the logarithmic Temkin isotherm is a sufficient, but not necessary, condition for the Esin and Markov coefficient g at constant q to be independent of the activity a_O. In principle, an infinite number of isotherms satisfying certain conditions yield a constant g at constant q and further, none of the isotherms[24] listed by Parsons,[9] other than the logarithmic Temkin isotherm, correspond to a constant g at constant q. In summary: (i) if a plot of E against ln a_O is linear, the logarithmic Temkin isotherm may or may not be valid; (ii) if the plot of E against ln a_O is not linear, one of the common isotherms[24] may or may not be obeyed; (iii) if the plot of E against ln a_O is linear and the logarithmic Temkin isotherm is not obeyed, none of the common isotherms[24] apply.

We assume that the logarithmic Temkin isotherm is obeyed and consider the plot of the Esin and Markov coefficient g with the charge density on the electrode. It was found by Mr. T. H. Tidwell in this Laboratory that such a plot varies with the nature of the substance. For instance, g *versus* q may be linear over a rather wide range of q's or g may be independent of q; etc. It follows from the relation derived by Parsons[22]

$$g \equiv (\partial E/\partial \ln a_O)_q = (RT/b)(\mathrm{d}\Delta G^0/\mathrm{d}q) \quad (39)$$

that (*cf.* eq. 11)

$$[\delta(\Delta G^q)]_{q_i}^{q} = \frac{b}{TR}\int_{q_i}^{q} g\,\mathrm{d}q \quad (40)$$

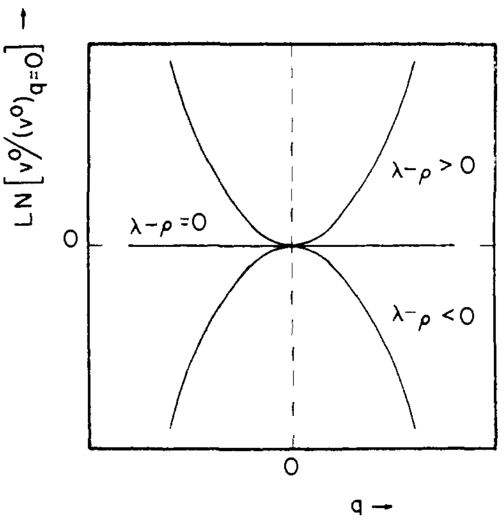

Fig. 4.—Schematic variations of the logarithm of the exchange rate v^0 with the charge density q for an Esin and Markov coefficient varying linearly with q and for $\lambda - \rho \gtrless 0$ (*cf.* eq. 25 and 41).

The quantity $\delta(\Delta G^q)$ needed in the kinetic equations is directly computed by integration of the Esin and Markov coefficient from the initial charge q_i to q. In particular, $\delta(\Delta G^q)$ varies linearly with q when g is independent of q, and $\delta(\Delta G^q)$ varies with q^2 when g varies linearly with q.

The exchange rate v^0 can be correlated with q by combination of eqs. 25 and 40. Thus

$$v^0 = k^0 a_O^{(1-\lambda)} \exp\left\{[(\lambda - \rho)/RT](b/RT)\int_{q_i}^{q} g\,\mathrm{d}q\right\} \quad (41)$$

For instance, if g varies linearly with q, a plot of ln v^0 against q is parabolic for $\lambda \neq \rho$ and has an extremum at $q = 0$ (Fig. 4) The exchange rate is independent of q when $\lambda = \rho$ regardless of the dependence of g on q. The dependence of v^0 on q may be used judiciously in the selection of q for which v^0 is measured, especially when exchange rates are high and may exceed the upper limit of measurable v^0's for certain limits of q.

It should be emphasized that v^0 is a measurable quantity but that k^0 and ΔG^q cannot be measured and only variations of ΔG^q with charge density can be determined experimentally. For this reason it is convenient to write eq. 41 as

$$v^0 = k_r^0 a_O^{1-\lambda} \exp\left\{[(\lambda - \rho)/RT](b/RT)\int_0^{q} g\,\mathrm{d}q\right\} \quad (42)$$

where k_r^0 is the *rational*[25] *standard rate constant* defined by

$$k_r^0 = k^0 \exp[(\lambda - \rho)\Delta G^{q=0}/RT] \quad (43)$$

Likewise, v^0 at $q = 0$ might be called the *rational exchange rate.*

Coulostatic and Other Methods of Measurement of Exchange Rates

Coulostatic Method with Step Variations of the Charge.—The rate could, in principle, be measured by the techniques used in ordinary adsorption studies (tracers, etc.) but, for fast adsorption, it should prove convenient to correlate v to electrical variables characterizing operation of the electrode.

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(20) D. M. Mohilner and P. R. Mohilner, unpublished investigation.

(21) The expression "Esin and Markov effect" was coined by D. C. Grahame, *Ann. Rev. Phys. Chem.*, **6**, 337 (1955), to denote the shift of the point of zero charge with varying bulk concentration of adsorbed species. For generalization and details, see Parsons.[22]

(22) R. Parsons, "Proceedings of the 2nd International Congress on Surface Activity," Vol. 3, Butterworths, London, 1957, pp. 38–44.

(23) D. M. Mohilner and P. Delahay, unpublished investigation.

(24) These isotherms are: linear (Henry's law), Freundlich, Langmuir, Volmer, Amagat, square root, virial, van der Waals, Frumkin, Temkin.

(25) By analogy with the rational potential, *i.e.*, the potential referred to the point of zero charge; *cf.*, D. C. Grahame, *Chem. Revs.*, **41**, 441 (1947).

We consider a *coulostatic method* in which the charge on the electrode is a step function of time, and we assume that, for $t > 0$, the resistance of the circuit elements connected to the cell is so large that the drift of potential is negligible in the absence of complications due to adsorption. The variations of potential of the unpolarized electrode include: (a) a step variation and (b) a time-varying component due to variations of Γ with time as Γ varies progressively from Γ_i to the new equilibrium value corresponding to the charge $q + \delta q$. Hence, the total change of potential from its initial value before the change δq is

$$\delta E = (\partial E/\partial q)_\Gamma\, \delta q + (\partial E/\partial \Gamma)_q\, \delta\Gamma \qquad (44)$$

The quantities $(\delta E/\delta q)_\Gamma$ and $(\delta E/\delta\Gamma)_q$ can be taken for the values of Γ and q before application of the charge δq provided δq is sufficiently small. The variation $\delta\Gamma$ in eq. 44 is obtained by solving, for $\delta(\Delta G^q)$ equal to a constant, either eq. 31 in the absence of mass transfer considerations or eq. 36 with mass transfer. Mass transfer will be neglected here.[26] Thus

$$\delta\Gamma = -\,[\delta(\Delta G^q)/b]\{1 - \exp[-(v^0 b/RT)t]\} \qquad (45)$$

$$\delta E = (\partial E/\partial q)_\Gamma \partial q - (\partial E/\partial\Gamma)_q[\delta(\Delta G^q)/b]\{1 - \exp[-(v^0 b/RT)t]\} \qquad (46)$$

The potential varies exponentially with time, and v^0 can be deduced from the slope of the plot of $\log|\mathrm{d}\delta E/\mathrm{d}t|$ against t. The value of $(\partial E/\partial\Gamma)_q$ is not needed for application of this procedure, nor is it necessary to know $\delta(\Delta G^q)$. This may simplify matters considerably.

In practice, the charge δq is supplied to the electrode in a time τ which must be so short that $\delta\Gamma$, over the interval τ, is negligible in comparison with $\delta\Gamma$ for $t \rightarrow \infty$. Hence (*cf.* eq. 45)

$$\tau << RT/v^0 b \qquad (47)$$

and τ must be of the order of microsec. or even shorter for fast processes. For instance, for $b = 10^{13}$ mol.$^{-1}$ cm.^{2} cal. as an order of magnitude, one has $v^0\,\tau << 10^{-10}$ mol. cm.$^{-2}$, *i. e.*, $v^0\,\tau < 10^{-12}$ mol. cm.$^{-2}$; if $\tau = 10^{-7}$ sec., $v^0 < 10^{-5}$ mol. cm.$^{-2}$ sec.$^{-1}$. This limit for v^0 corresponds to a rather fast process. An instrument for the measurement of adsorption exchange rates by the coulostatic method (**coulostat**) is being developed in this Laboratory.

It is believed that this method is new[27] and that it also should prove useful in the study of electrode processes and in electroanalytical determinations of traces. Work on the latter two applications is also in progress.[28] (Conditions are really not coulostatic in the latter applications since the double layer discharges through the resistance corresponding to the electrode reaction.)

Non Faradaic Impedance and Rectification.—Measurements of the impedance of an ideal polarized electrode on which a neutral substance is adsorbed allow determination of v^0. The theory was worked out by several authors and, in particular, by Lorenz[29] in its most satisfying form. Lorenz did not assume a specific dependence of v^0 and v on experimental parameters, as embodied in eqs. 25 and 34 but he expressed the adsorption rate as a complete differential of E, C_O and Γ and proceeded to correlate v^0 with the electrode impedance. His treatment can easily be linked with the present theory.

Rectification by the double layer can also be applied, and a theory extending that of Lorenz to include rectification was developed in this Laboratory.[30] The comments made about the impedance also apply, but the interpretation is more complex. Further work on this subject is being considered.

Conclusion.—It appears possible from the theory developed here to correlate adsorption kinetics of a neutral substance at a metal–electrolyte interface with experimental parameters for adsorption obeying the logarithmic Temkin isotherm. The treatment reminds one of the Butler, Erdey-Gruz, Volmer theory for electrode processes. This work also led to the development of a new coulostatic method for the study of adsorption kinetics with a step variation of the charge. Since present knowledge of adsorption kinetics at metal–electrolyte interfaces is essentially non-existent, it is hoped that the present work may pave the way for further work.[31] Information of general interest for adsorption studies should result.

Several extensions of this theory are quite apparent and are now being examined: extension to complete Temkin isotherm, kinetics of simultaneous adsorption of two (or several) neutral substances on an ideal polarized electrode, adsorption of a neutral substance coupled with a homogeneous or surface chemical reaction, adsorption of ions, and adsorption coupled with a charge transfer reaction, analysis of kinetics for processes obeying other isotherms than the logarithmic Temkin isotherm.

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(26) The corresponding problem with mass transfer controlled by semi-infinite linear diffusion was also solved (P. Delahay, unpublished investigation).

(27) It should be noted that A. Obrucheva developed a method in which a solution of an adsorbed salt is added to the electrolyte in contact with an ideal polarized electrode, and the resulting change of potential is measured. This method is not adapted to fast adsorption processes, in contrast with the method described above. *Cf.*, A. Obrucheva, *Doklady Akad. Nauk S.S.S.R.*, **120**, 1072 (1958); *Zhur. fiz. Khim.*, **32**, 2155 (1958). See also A. N. Frumkin, "Transactions of the Symposium on Electrode Processes," E. Yeager, editor, John Wiley and Sons, New York, N. Y., 1961, pp. 1–12.

(28) P. Delahay and A. Aramata, unpublished work.

(29) W. Lorenz, *Z. Elektrochem.*, **62**, 192 (1958).

(30) M. Senda and P. Delahay, *J. Am. Chem. Soc.*, **83**, 3763 (1961).

(31) The essential results were reported in a communication to the editor, P. Delahay and D. M. Mohilner, *J. Phys. Chem.*, in course of publication.