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Elovich Adsorption Kinetics and the Heterogeneous Surface

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Earlier treatments of the rate of adsorption on a heterogeneous surface have given results which do not agree with the Elovich equation at very short times. It is shown that the familiar, simple model of a nonuniform surface does, in fact, lead to a rate equation in good agreement with the Elovich equation at very short as well as at very long times. The model gives a physical significance to the constant t_0 and, when t_0 is appreciable, leads to Elovich plots having two linear sections. Similar experimental plots can be found. The common assumption that the activation energy for chemisorption increases with the energy of adsorption is incompatible with the model when the energy of chemisorption decreases with coverage and is thus difficult to justify: The apparent justification to be found in earlier treatments of the simple model is shown to be unsound.

INTRODUCTION

The rate of adsorption of gases on solids is often satisfactorily represented by the expression

$$d\theta/dt = \alpha \exp(-\beta\theta), \qquad (1)$$

which is generally known as the Elovich equation (see Ref. *1*). Here, θ is proportional to the quantity adsorbed and the parameters α and β usually depend on temperature and pressure. Equation (1) may be integrated to give

$$\theta = (1/\beta) \ln (t + t_0) - C, \qquad (2)$$

where $t_0 = 1/\alpha\beta$ and C is a constant.* Another form which will be found useful is obtained by differentiation of (2) which gives

$$d\theta/dt = 1/\beta(t + t_0) \qquad (3)$$

Various authors (*2*, *3*, *4*) have derived expressions similar to Eq. (2) using a simple model of a nonuniform surface. In each case, the equation arrived at was of the form

$$\theta = k_1 \ln t + k_2, \qquad (4)$$

where k_1 and k_2 are constants. Equation (4) differs from (2) by the absence of t_0 from the time-dependent term, so that a finite initial rate, $1/\beta t_0$, is not obtained. Both Stone (*3*) and Kubokawa (*4*) conclude that the simple model is at fault. The present communication shows that the simple model leads, on the contrary, to an expression which behaves like the Elovich equation at very small as well as at very large times. In addition, the model gives a precise significance to t_0.

The choice of a function to represent the dependence of the activation energy of adsorption, E_a, on the energy of adsorption, H, will also be discussed. It is emphasized that the relation between E_a and H need not be known in order to derive (4). The choice of such a relation is imposed, however, if the effect of nonnegligible desorption rates is to be considered. When applied to the simple model (*2*, *3*, *4*), the choice made by Halsey (*5*) is difficult to reconcile with well-established observations. Another choice can be made which is in more general agreement with experiment.

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* It frequently happens that the process obeying Elovich kinetics appears to be superimposed on a relatively "instantaneous," limited, adsorption, so that the linear plot of θ against log $(t + t_0)$ does not extrapolate to $\theta = 0$ at $t = 0$. In such circumstances, however, one may still consider the Elovich equation to be satisfied, although not for the over-all process down to zero time. The pre-exponential factor $\alpha = 1/\beta t_0$ does not then give the initial rate of adsorption, but otherwise retains its significance with regard to the process obeying Elovich kinetics.

The Simple Model and Eq. (4)

Following Halsey (*5*), Porter and Tompkins (*2*), and Stone (*3*), the essential steps in the derivation of Eq. (4) are briefly given below, except that no dependence of E_a on H is specified. The term "simple model" refers to a surface on which a fixed number of adsorption sites are associated with a continuous distribution of activation energies of adsorption. The distribution function, N, is assumed to be constant ($dN/dE_a = 0$) and desorption rates are taken to be negligible. A set of sites is defined as all those sites associated with the same value of the activation energy, E (where the subscript is dropped, E_a is to be assumed). The rate of adsorption on any set of sites is then,

$$\frac{d\theta_E}{dt} = \int_0^1 \lambda P \exp\left(\frac{-E}{RT}\right) d\theta \qquad (5)$$

$$= A(1 - \theta_E) \qquad (6)$$

where

$$A = \lambda P \exp(-E/RT) \qquad (7)$$

and λ and P, the pressure, are constant. Integration of (6) gives,

$$\theta_E = 1 - \exp(-At) \qquad (8)$$

The coverage θ, over the entire surface, is given by the sum over all sets,

$$\theta = N \int_{E_1}^{E_2} \theta_E dE \qquad (9)$$

where E_1 and E_2 are the limits of the distribution of activation energies. Integration of (9) is simplified by assuming that the sets of sites are successively filled ($\theta_E \approx 1$) in order of increasing values of E, no set beginning to fill before the preceding set is saturated (in contrast to the correct procedure where all sets are allowed to fill simultaneously at different rates). With the above assumption, Eq. (9) becomes simply*

$$\theta = N \int_{E_1}^{E} dE = N(E - E_1) \qquad (10)$$

In order to obtain E as a function of time (*2*, *3*, *5*), each set of sites is assumed to fill instantaneously at a time given by $t = 1/A$, from which $E = RT \ln \lambda Pt$. Substitution in Eq. (10) gives

$$\theta = N(RT \ln \lambda Pt - E_1) \qquad (11)$$

Equation (11) is of the form of Eq. (4) and differs from the Elovich expression, (2), by the absence of t_0 from the logarithmic term. Stone (*3*) and Kubokawa (*4*) conclude that the absence of t_0 results from the neglect of desorption by the simple model. It can be shown, however, that such is not the case. Equation (11) leads to an infinite rate of adsorption as $t \rightarrow 0$, whereas the Elovich equation gives the finite value $1/\beta t_0$. According to the simple model, on the other hand, the initial rate on any set of sites has a finite value A, so that the initial rate over the entire surface must be finite as well. Thus (11) is inconsistent with the model and the discrepancy must arise from the approximate method of integration.

An Exact Rate Equation for the Simple Model

An exact expression for the over-all rate of adsorption may be obtained by the method of Kubokawa (*4*), who would not have arrived at the equivalent of (4) had the correct limits been used in his final integration. The method avoids the arbitrary site-filling procedure used to simplify the integration of (9). For the rate of adsorption over all sets, Kubokawa writes

$$\frac{d\theta}{dt} = N \int \left(\frac{d\theta_E}{dt}\right) dE$$

$$= N \int \left(\frac{d\theta_E}{dt}\right)\left(\frac{dE}{dA}\right) dA \qquad (12)$$

By differentiation of (8), one obtains

$$(d\theta_E/dt) = A \exp(-At)$$

and from (7),

$$(dE/dA) = -RT/A$$

Substitution in (12) then gives

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* Note that Eq. (10) can be rearranged to $E = E_1 + (1/N)\theta$, which is often assumed *a priori*. The site-filling procedure assumed above, combined with the constant distribution function, provides a particular mechanism whereby a linear increase of E with coverage may be obtained. Brunauer, Love, and Keenan (*6*) substituted such an expression directly into (5). The result reduces to Eq. (1) for $\theta \ll 1$.

$$\frac{d\theta}{dt} = -NRT \int_{A_1}^{A_2} \exp(-At)dA \quad (13)$$

When the distribution of activation energy has the finite limits E_1 and E_2 (where $E_1 < E_2$), the solution of Eq. (13) is

$$d\theta/dt = (NRT/t)[\exp(-A_2t) - \exp(-A_1t)] \quad (14)$$

where A_1 and A_2 are the values of A corresponding to E_1 and E_2. The variation of θ with time can be obtained from (14) by integration, but the result is too cumbersome for practical use. When the limit E_2 is very large, A_2 approaches zero and (14) reduces to the relatively simple expression

$$d\theta/dt = (1/\beta' t)[1 - \exp(-t/t'_0)] \quad (15)$$

where $\beta' = 1/NRT$ and $t'_0 = 1/A_1$.

DISCUSSION

Although (15) does not have the form of (3), the two equations behave in a very similar way so that the simple model, under certain circumstances, can account for Elovich kinetics. The limit of (15) as $t \rightarrow 0$ is $1/\beta' t'_0$, whereas that of (3) is $1/\beta t_0$. For $t \gg t_0$, on the other hand, the approximations $d\theta/dt = 1/\beta' t$ and $1/\beta t$ are valid. At intermediate times, (15) gives slightly larger rates than (3) when the constants of both equations have the same values. Slightly different values for t_0 and t'_0, however, will make the two nearly coincide when very short times are neglected, as in practice they often are. In such cases, kinetic data which obey (15) will give an acceptable straight line when θ is plotted against log $(t + t_0)$, in accordance with the integrated Elovich equation, (2). Specifically, when t'_0 is not more than three or four times greater than the time at which the first measurement is made, data which obey (15) will give a satisfactory Elovich plot using $t_0 \approx t'_0/2$. This is demonstrated by Curve A of Fig. 1, for which the data were obtained by graphical integration of Eq. (15), using arbitrary values of the constants. When t'_0 is considerably greater than the time of the first measurement, more acceptable plots are obtained by taking $t_0 = t'_0$. The resulting curve (B, Fig. 1) has two linear sections, that

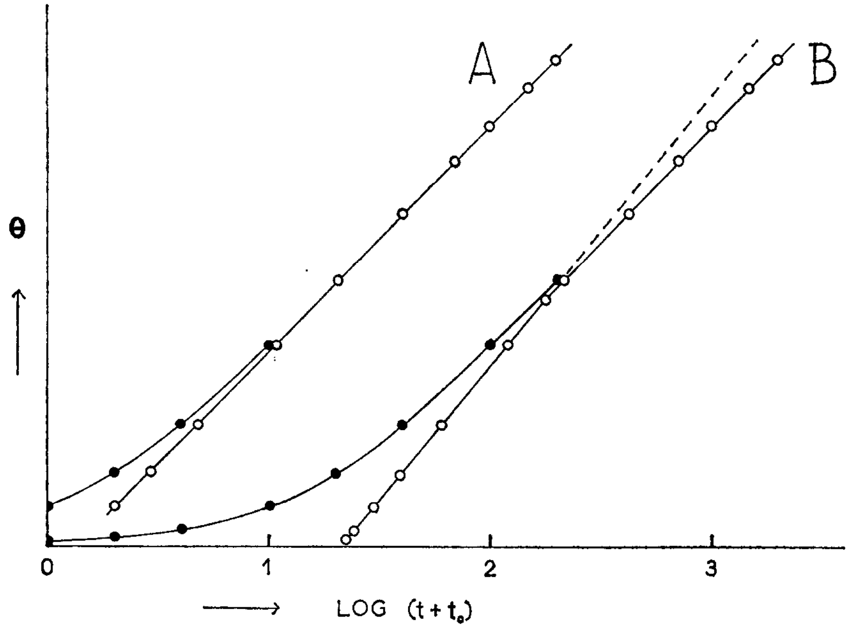

FIG. 1. Elovich plots (coverage, θ, against $t + t_0$) of data calculated by means of Eq. (15). Curve A: calculated with $t'_0 = 2$; ●, plotted with $t_0 = 0$; ○, plotted with $t_0 = t'_0/2 = 1$. Curve B: calculated with $t'_0 = 20$; ●, plotted with $t_0 = 0$; ○, plotted with $t_0 = t'_0 = 20$.

of smaller slope appearing at higher times. The ratio of the two slopes (about 1.2) is independent of the values of the constants. The second linear section almost disappears when $E_2 - E_1$ is less than about $5RT$, a negative curvature then being observed. The curves of Fig. 1 show that t_0 is related to t'_0, the inverse of the initial rate on the set of sites associated with the smallest activation energy.

Elovich plots showing several linear regions have frequently been reported (*1*). Of particular interest here are the results of Cimino *et al.* (*7*) for hydrogen adsorption on ZnO, since their Elovich plots bear a remarkable resemblance to the calculated Curve B of Fig. 1. The present author, incidentally, has obtained curves of type B for the adsorption of another reducing gas (CO) on ZnO, although these were obtained with a constant-volume apparatus and a pressure which was allowed to fall to about 10% of its initial value. Unfortunately, no solution of the rate equation for constant-volume systems is available, so that one cannot conclude with certainty that the simple model is unable to account for such behavior to within the accuracy of the measurements. It is, of course, possible that the rate is very insensitive to the ambient pressure, as has been shown for a number of systems (*1*). The simple model, however, makes no provision for such a possibility.

It is sometimes of interest to have a qualitative understanding of the behavior of the simple model when desorption rates are not entirely negligible. For this purpose, noting that the activation energy of desorption is given by $E_d = E_a + H$, it is useful to know the relation between E_a and the energy of adsorption, H, so that E_d may be expressed as a function of E_a. When dealing with the kinetics of adsorption on a heterogeneous surface, it appears to be customary (*2*, *3*, *4*), following Halsey (*5*), to choose the relation $E_a = rH$ (where $r < 1$ is constant). Since E_a, however, must also increase as θ increases, the simple model thus leads to adsorption energies which increase with coverage, the adsorbate being immobile. As is well known (8), such a variation of H with θ is in contradiction with nearly all calorimetric measurements. Indeed, it is usually assumed (*8*, *9*) that the decrease of H with coverage brings about the increase of E_a, so that a relation such as $E_a = E_2 - rH$, for example, might be proposed (*13*).

It must be noted that the above objections to the use of $E_a = rH$ are not applicable to the analysis of Halsey (*5*), which does not neglect desorption and does not contradict calorimetric data provided that the total heat evolved at a given pressure is plotted against coverage for a series of increasing pressures. Such behavior is assured by allowing the lower limit of the occupied region of the H distribution to decrease with increasing pressure.* In addition, Halsey justifies the assumption $E_a = rH$ to the extent that it leads to the prediction of rapid desorption followed by slower readsorption when the temperature of the nonequilibrium system is suddenly increased, in agreement with the observations of Taylor and Liang (*11*). Other workers [see ref. (*2*)], however, have studied systems where adsorption occurs without preliminary desorption, so that the assumption of Halsey cannot be universally true. The absence of rapid desorption on thermal cycling is consistent, rather, with the assumption $E_a = E_2 - rH$, whereupon E_d for all occupied sites is greater than E_a for all sites remaining to be filled.

Apparent justification for the application of $E_a = rH$ to the simple model is to be found in the analyses of Stone (*3*) and Kubokawa (*4*), but can be shown to be illusory. If $E_a = rH$, then the activation energy for desorption is relatively small when E_a is small, so that the error introduced in (11) by the neglect of desorption will be relatively more important at smaller

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* At any given pressure, however, the model implies that sites of larger H are last to be occupied, so that $(dH/d\theta)_P$ should increase with time, i.e., $d\theta/dt$ should fall more rapidly than dH/dt. No calorimetric evidence for such an effect appears to be available, although $d\theta/dt$ has been shown to fall more rapidly than the rate of change of conductivity when O_2 is adsorbed on NiO (*10*). Such an effect could be related to a variation of E_a with H, but is more readily taken to indicate the occurrence of two types of bonding (*8*, *10*).

times. Stone was thus led to conclude that the appearance of t_0 in the logarithmic term of (2) is a correction for this effect, providing an indirect justification of the assumption $E_a = rH$, as well as giving physical significance to t_0. As has been shown, however, the simple model accounts for t_0 independently of desorption or any assumed relation between E_a and H. Kubokawa, on the other hand, having assumed that E_a increases with H, argues that appreciable desorption rates will thereby cause β to decrease at higher values of P, in agreement with many observations. The argument assumes, however, that higher P is synonymous with higher θ, whereas the experimental example given by Kubokawa (H_2 on ZnO) shows that β varies with P even over the same range of coverage. One may therefore conclude that the observed variation of β with P does not justify the assumed variation of E_a with H.

An activation energy which increases with H is also a feature of the Porter and Tompkins model (*2*), where the rate-determining process is not the primary act of chemisorption but that of migration from one chemisorption site to another. This mechanism, although later discarded by its authors on experimental grounds (*12*), is still cited (*9*) and it would perhaps not be out of place here to draw attention to its theoretical weaknesses. The Porter and Tompkins derivation of Eq. (*4*) replaces E_a by E_m, the activation energy for migration between chemisorption sites. In order that E_m may increase with coverage, a linear distribution of adsorption energies is assumed and a site-filling procedure is adopted such that sets are successively occupied in the order of increasing H by migration from one set to another. Such a procedure implies that the adsorbate may enter the chemisorbed "phase" only from the lower end of the H distribution. It is necessary, in addition, to suppose that the energy of activation for diffusion from the occupied site A to the vacant site B increases rather markedly as H_B increases. The justification for such an assumption, however, is far from self-evident. Further difficulties arise from the related requirement that direct entry from the gas phase (or a very mobile adsorbed state) be prohibited except at the lower end of the H distribution. To account for the above feature it is necessary to assume, for example, that the height of the barrier to direct entry (E_a), like that of the diffusion barrier (E_m), increases rapidly with H. Since E_a, in addition, must always be considerably larger than E_m, except at the point of entry, the former is required to increase with H even more rapidly than does E_m, which must itself increase rather markedly in order to account for the site-filling procedure. The diffusion model thus appears relatively unattractive in view of the nature of the assumptions involved. This is particularly so when one considers that a variation of E_a with H somewhat less extreme than that mentioned above suffices by itself (*3*, *5*) to permit the derivation of (4). In spite of the above criticism, however, the diffusion model would evidently merit attention in the event of Elovich kinetics being observed with a system where independent evidence for diffusion of the chemisorbed species was also available.

REFERENCES

1. LOW, M. J. D., *Chem. Rev.* **60**, 267 (1960).

2. PORTER, A. S., AND TOMPKINS, F. C., *Proc. Roy. Soc.* (*London*) **A217**, 529 (1953).

3. STONE, F. S., *in* "Chemistry of the Solid State" (W. E. Garner, ed.), p. 367. Butterworths, London, 1955.

4. KUBOKAWA, Y., *Bull. Chem. Soc. Japan* **33**, 734 (1960).

5. HALSEY, G. D., *J. Phys. Coll. Chem.* **55**, 21 (1951).

6. BRUNAUER, S., LOVE, K. S., AND KEENAN, R. G., *J. Am. Chem. Soc.* **64**, 751 (1942).

7. CIMINO, A., MOLINARI, E., AND CIPOLLINI, E., *Actes Congr. Intern. Catalyse, 2e, Paris, 1960,* **2**, 263 (1961).

8. DE BOER, J. H., *Advan. Catalysis* **8**, 18 (1956).

9. ASHMORE, P. G. "Catalysis and Inhibition of Chemical Reactions," p. 165. Butterworths, London, 1963.

10. KUCHYNKA, K., AND KLIER, K., *Collection Czech. Chem. Commun.* **28**, 148 (1963).

11. TAYLOR, H. S., AND LIANG, S. C., *J. Am. Chem. Soc.* **69**, 1306 (1947).

12. GUNDRY, P. M., AND TOMPKINS, F. C., *Trans. Faraday Soc.* **52**, 1609 (1956).

13. SCHOLTEN, J. J. F., ZWEITERING, P., KONVALINKA, J. A., AND DE BOER, J. H., *Trans. Faraday Soc.* **55**, 2166 (1959).