

ADVANCES IN CATALYSIS

AND RELATED SUBJECTS

VOLUME 21

EDITED BY

D. D. ELEY

HERMAN PINES

PAUL B. WEISZ

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THE BIG KINETIC NETWORK

AN EDITORIAL PREFACE

Here and there, in one form or another, we hear calls for re-evaluation of nearly every human activity and "advance." In keeping with the statistical nature of the human assemblage, the questioning takes all forms, from the kind to the belligerent, from the divine to the ridiculous. They all are intrinsic ingredients of the dynamics of human evolution. Yet, they all seek to alter the complex kinetics of the process of human activity to achieve better overall results. Suddenly, we find ourselves touched by a feeling of familiarity of concepts . . .

. . . The concentration of living gazelles is determined by their rate of production (a function of the concentration of many reactants, the concentration of gazelles itself, etc.) and by the rate of their disappearance (a function of the concentrations of tigers, men, certain viral and bacterial species, etc.). . . . The products the gazelle creates, including itself, it returns to the ecological box, where they in turn become reactants in the kinetic equations of other species . . . The entire network of coupled kinetic processes is endothermic with energy derived partly thermally, partly photochemically from the sun . . . transients or new reactants introduced into a steady-state kinetic network result in the modification of many species concentrations . . . many kinetic sequences, especially exothermic ones, can undergo dramatic instabilities . . . catalysts play vital-roles in all rate processes . . .

We are all familiar with the comforting situation in kinetics when a reactant is present "in excess" and consequently drops out as a factor of concern; equally happy is the circumstance where a product of reaction is carried away or diluted sufficiently in the available reaction space so that its concentration causes no noticeable back-reaction, inhibition, or poisoning.

Man rose above animal by drawing upon *additional* reactants, i.e., reactants other than the near-steady-state species of the living ecological network and the sun's current energy flux. Now, nearing the year 2000 (by one of the available time scales) he is learning that some of his added reactants ("resources") are not or will not be "in excess." Furthermore,

his reaction space is now proving sufficiently small to result in noticeable and disturbing concentrations for some products. Appreciable new effects now appear in the ecological network of rate processes.

Having thus lifted himself above animal existence—he must now analyze his influence on the complex ecological rate network, and to practice his added rate-processes *highly selectively* to avoid undesirable or tragic consequences which, unfortunately are not self-evident in any highly interactive kinetic matrix.

Unfortunately, human overreaction to a newly recognized disturbance is the rule rather than exception. Then, quick measures, designed as remedies for or escapes from the disturbance created become themselves *new* factors introduced into the ecological system whose total consequences are often even *more* poorly understood. The introduction of (at least some of) the psychochemically active molecules into the life system presents an interesting, extreme example; only “perhaps” however, and that is the point.

We are reminded of the fascinating role of catalytic selectivity in human behavior by J. R. Smythies’ discussion* of the possible generation of schizophrenia as a result of a slight aberration in catalytic selectivity in a methoxylation reaction, as illustrated by the creation of a molecule manyfold more hallucinogenic than mescaline when methoxylation occurs in the para- as compared to the meta-position of amphetamines.

Just as catalytic selectivity is vital to all inner life processes of the individual, it stands at a focal point of importance in the total interaction of the entirety of man with his environment: It is involved in reducing the amount of the resources consumed; it destroys traces of polluting exhaust gases. We can foresee that catalysis will get involved in other constructive roles; providing recycling pathways of materials; the creation of alternate products that are ecologically acceptable; and participation in future utilization of alternate energy sources including the sun. Many challenges for catalysis lie ahead, for an indefinite, if not infinite span of time.

This volume of the *Advances in Catalysis* adds an infinitesimal, yet by our scale of knowledge, sizeable increment of knowledge. It is largely devoted to elementary kinetic processes on catalysts.

It includes a discussion (May) of low energy electron diffraction as an

* “Beyond Reductionism” (A. Koestler and J. R. Smythies, eds.). Pages 349–352. Macmillan, New York, 1970.

evolving technique in the examination of the structure and dynamics of sorbed atoms on surfaces. The sorptive interaction of carbon monoxide molecules with tungsten and other metals is exhaustively reviewed (Ford) and serves as an illustrative model of adsorption phenomena. The curious Elovich equation that describes variations of rate with surface coverage in a diversity of systems, is discussed (by Aharoni and Tompkins in terms of structural surface properties and interactive parameters. The discussion of elementary processes in sorptive and diffusion processes of molecules is carried (by Riekert) to the intracrystalline world of zeolites where the concepts of two-dimensional surface and of three-dimensional space merge and necessitate a review of descriptive approaches.

We also have the pleasure of including an analysis and discussion by C. Wagner that relates overall behavior of catalytic systems to atomic intermediates on (and in) catalytic solids and to experimentally observable parameters. It is a treatment that illustrates the richness of results that can be derived from basically simple and well accepted physical chemical concepts.

P. B. WEISZ

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Kinetics of Adsorption and Desorption and the Elovich Equation

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The Elovich equation

$$dq/dt = a \exp(b - q), \quad (1)$$

where q is the amount adsorbed at time t , and a , b are constants, has wide applicability in representing rates of adsorption and with obvious modification (and to a lesser extent) to rates of desorption. Although not exempt from criticism (1-3), it appears (4, 5, 13) to have more general validity than other equations that have been proposed. It was first formulated to describe the kinetics of oxidation processes (6) and later developed for adsorption kinetics by Elovich, Roginskii, and Zeldovich, and their collaborators (7-12). Most of the experimental systems to which this equation has been applied are listed in Table II. The applicability of Eq. (1) is usually tested by using the integrated form (13),

$$q = (2.3/b) \log ab + (2.3/b) \log[t + (1/ab)], \quad (2)$$

assuming, as lower limits of integration, $q = 0$, $t = 0$. For large values of t (i.e., $t \gg 1/ab$), the plot of q against $\log t$ is linear, and values of a and b may be derived from its slope ($2.3/b$) and intercept $[(2.3/b) \log(ab)]$; these values may then be used to construct the plot of q against $\log[t + (1/ab)]$, and thereby to extend the linearity to smaller t values and theoretically to $t = 0$. In the literature (12-18), various alternative procedures for testing Eq. (1) and for calculating the parameters have been used.

I. Deviations from Equation (1) at Small t

Equation (2), when applied to many systems, e.g., H_2 adsorption on ZnO , Cr_2O_3 , $ZnO \cdot Cr_2O_3$, $ZnO \cdot MoO_3$, gives a plot convex to the $\log(t + 1/ab)$ axis at low values of t .¹ One common explanation is that an initial instantaneous adsorption q_0 precedes the rate process; the lower limits of integration then become $t = 0$, $q = q_0$, and

$$q = (2.3/b) \log(ab) + (2.3/b) \log(t + t_0), \quad (3)$$

¹ For literature references to particular systems, see Table II on page 44.

where

$$t_0 = (1/ab) \exp bq_0. \quad (4)$$

The choice of the values of t_0 in Eq. (3) is then made *empirically* in order to obtain the best linearity of the plot of q against $\log(t + t_0)$; in contrast, in Eq. (2), t_0 is restricted *solely* to the value $1/ab$ and q_0 is zero. It is implicit in Eq. (3) that the rate dq/dt is a function of the *total* amount of gas adsorbed, irrespective of whether some adsorption has taken place "instantaneously" before the rate process commences. Equation (3) does *not* apply when the initial uptake and the subsequent slow process are assumed to be two separate and independent processes. The approximate value of q_0 in Eq. (3) may be obtained by a linear extrapolation of the q against $\log(t + t_0)$ plot to $t = 0$; subtraction of this value from q (the total amount adsorbed) gives the amount q' taken up in the slow process after any time t . If an instantaneous adsorption has, indeed, taken place, then the plot of q' against $\log[t + (1/ab)]$ should preserve its linearity to $t = 0$. For H_2 on $2MnO \cdot CrO_3$, Taylor and Thon (13) confirmed that the initial adsorption was not governed by the exponential law [Eq. (1)]. In contrast, for H_2 on $ZnO \cdot CrO_3$, the magnitude of t_0 was virtually zero, despite an observed initial, massive, rapid adsorption; they therefore concluded that this initial adsorption was linked continuously to the subsequent slow process that had started with an initial, abnormally high velocity. Thus, two different stages of the same process occur on the same set of sites, but the energy distribution of the sites changes from a rapidly varying function at low activation energies to a constant distribution over the higher energy sites. The Elovich process is then valid only at some time $t_m > 0$, when b in Eq. (1) first attains a constant minimum value; in the interval $0 < t < t_m$, b decreases, i.e., the slope $dq/d \log[t + 1/ab]$ increases with time. An alternative concept of two separate rate processes proceeding on two different sets of sites at greatly different velocities means that the total amount of adsorption q should not be inserted to test the Elovich equation.

II. Discontinuities in the Elovich Plot

In some systems, e.g., H_2 on ZnO , $ZnO \cdot CrO_3$, $ZnO \cdot MoO_3$, $NiMgO$, WS_2 ; H_2 on Pt , Pd , Rh , Ir ; O_2 on NiO and Ag , the plot of q against $\log(t + t_0)$ has been closely approximated by two or more linear segments, with different values of a and b over limited ranges of t and so

give rise to discontinuities. Such discontinuities can often be detected in the primary plot of q against t and hence do *not* arise solely as a result of applying the Elovich equation (64). Later segments at the plot of q against $\log(t + t_0)$ may have higher slopes (lower values of b) e.g., H_2 on ZnO, $ZnO \cdot Cr_2O_3$, WS_2 , etc., or there may be an irregular sequence of b values in plots where more than two linear segments are obtained, e.g., H_2 on Pd, Ir, Rh, Pt, ZnO; O_2 on Ag. The number of segments, their relative slopes, and time of appearance may vary with the nature of the adsorbate and adsorbent, and even with different samples of the same adsorbent (39, 40), and also with the pressure and temperature. In some systems, the slopes of the various segments vary in the same direction but not to the same extent with temperature (5), and the log time corresponding to their intersection decreases roughly linearly as the temperature is increased; in other systems, e.g., H_2 on Pd, Rh, more complex behavior is evident. Attempts (5) to explain the presence of discontinuities in terms of surface heterogeneity, anisotropy, formation of surface complexes, etc., have proved unsuccessful. It is probable that such discontinuities are, in fact, caused by the presence of contaminants (see Section XX), and Low's rejection (5) of this explanation is, in our view, erroneous.

III. Effect of Pressure on the Magnitudes of a and b

According to Eq. (1), the rate of adsorption decreases exponentially as the amount adsorbed increases, hence it is difficult to detect experimentally the effects of pressure in a constant-volume system even over a large pressure decrease. For example, Taylor and Thon (13) concluded that dq/dt depends on the initial, but not on the ambient, pressure. Pressure effects are best tested by abruptly changing the pressure during the course of adsorption. Pressure dependences

$$x = \frac{d \log(dq/dt)}{d \log p}$$

have been obtained with $x = \frac{1}{2}$ (dissociative chemisorption), e.g., O_2 on Ge (38), H_2 on Ni (19, 95), and $x = 1$ (nondissociative adsorption), e.g., N_2 on Fe (23) and also with $x > 1$. Other peculiar effects have also been recorded, e.g., the slow introduction of hydrogen onto ZnO causes a considerable increase of the rate of adsorption compared with that

obtained subsequent to rapid additions of gas (96). However, although there are systems to which the following conclusions do not apply, in general a increases and b decreases slightly (or remains constant) with increase of pressure. In some systems, e.g., H_2 on Ni, Pt, Ru, Ir, Rh, Pd, Fe, ZnO, $ZnO \cdot Cr_2O_3$, $\ln a$ has been found to increase and b to decrease proportionally to the increase in the initial pressure. In other systems, different effects are obtained in low- and high-pressure regimes, or at high and low temperatures, particularly with respect to the values of a (16), suggesting that these a values (which are obtained by lengthy extrapolation) have little physical significance.

IV. Effect of Temperature on a and b Values

Normally, with increase of temperature, a increases and b decreases (13); in some systems, e.g., H_2 on Ni, Ru, Ir, Pd, Ph; $ZnO \cdot Cr_2O_3$, WS_2 , more precise relationships have been obtained, e.g., both b and $\ln a$ being proportional to the reciprocal of the temperature (5). The presence of discontinuities in the Elovich plots, however, often obscure such dependences. Nevertheless, even in their absence, complex changes are often evident, e.g., a temperature increase may cause b to pass through maximum or minimum values as for H_2 on ZnO, $ZnO \cdot MoO_3$; O_2 on ZnO, or the variation of a with T may be changed by altering the ambient pressure.

In general, therefore, despite the usefulness of the Elovich equation as a method of representing data on rates of adsorption, not only the variation of the two important parameters a , and b with pressure and temperature, but also the presence of discontinuities, require that any acceptable theoretical model should, at least qualitatively, explain these results. Therefore, we first discuss the various theoretical interpretations of this equation.

V. Theoretical Interpretations of the Elovich Equation

Most derivations are based on an isothermal rate equation of the form

$$dq/dt = K(p)n \exp(-E/RT), \quad (5)$$

where, at constant temperature, $K(p)$ is a pressure-dependent constant comprising the collision frequency $[(p/2\pi mkT)^{1/2}]$ of the gaseous adsorbate molecules with unit area of adsorbent surface and a condensation

coefficient; n is the number of sites available for adsorption and E is the activation energy for adsorption and may be a function of q , or be independent of coverage, depending on the model adopted.

VI. Models Based on Site Number Variation

Equation (1) may be derived by assuming that the number of sites available for adsorption decreases exponentially with the number on which adsorption has already taken place, i.e., with extent of adsorption q : Thus

$$n_q = n_0 \exp(-bq); \quad (6)$$

n_0 is the number of sites available at $t = 0$, and b is a constant independent of T and p ; n_q is the number of sites still free after an amount q of adsorbate has been adsorbed. Thus, a in Eq. (1) is $K(p)n_0 \exp(-E/RT)$, and the activation energy for adsorption E is assumed to be independent of coverage. To impart physical significance to this model, the differential form of Eq. (6) may be combined with Eq. (1),

$$dn/dt = -n_0 b \exp(-bq) dq/dt = n_0 ab [\exp(-bq)]^2, \quad (7)$$

so that

$$dn/dt = (ab/n_0)n^2. \quad (8)$$

Equation (8) describes by a second-order process, the rate of "removal" or destruction of bare sites as a function of the number present on the surface, i.e., the normal concept that the total number of free-plus-covered sites on the surface is constant during the adsorption process is abandoned. In order to obtain the Elovich expression, a simultaneous first-order creation of sites by the act of adsorption must be also assumed.

Since the act of adsorption eliminates more sites than by actual occupancy, bare sites are in short supply and the rate of adsorption is therefore governed by the availability of sites. As an example of a specific model to conform with these requirements, we cite that proposed by Cimino *et al.* (76) for the adsorption of hydrogen on ZnO. They argue that, since both Zn^{2+} and O^{2-} ions have closed electron shells, no orbitals are available to form a surface bond for chemisorption. However, free electrons may be thermally excited from the valence band (or

from impurity levels); this excitation corresponds to the creation of "Zn³⁺ ions" as the active centers for chemisorption. When a molecule of hydrogen is adsorbed, some of the energy liberated in the act of chemisorption may be utilized to excite an electron from the valence band to form a Zn³⁺ ion. This Zn³⁺ ion, or positive hole, either chemisorbs a gas molecule and, in the process, generates another active center, or the free electron combines with one of the positive holes simultaneously formed in the excitation process and both are annihilated. Thus, there is a first-order creation of active "sites" and, since the number of positive holes is always equal to that of the free electrons, a second-order destruction of them, i.e.,

$$dq/dt = k(p)n, \quad \text{and} \quad -dn/dt = kn^2/n_0. \quad (9)$$

Combination of these equations [cf. Eq. (8)] then leads to Eq. (6), and, hence, to the Elovich equation (1).

Similar models had been proposed previously by Taylor and Thon (13, 77, 78) following Volkenshtein's theory of activated excitation of surface sites by the act of adsorption; e.g., the consequences of a spontaneous unimolecular decay and a bimolecular destruction of excited sites were deduced, and a possible alternative interpretation of interaction between sites in the course of adsorption was also indicated.

A different type of model was proposed by Landsberg (79); he denoted the site area by a , and assumed that over an area b ($>a$) sites are invalidated by the adsorption of a single molecule. The rate of invalidation is given by the product of the rate of adsorption and the total area invalidated at any time, i.e.,

$$-dn/dt = (dq/dt)bn; \quad (10)$$

but since

$$dq/dt = K(p)n,$$

an equation similar to Eq. (8), leading to the Elovich equation, is obtained.

Barriol and Rivail (80) also derived an equation of the Elovich form using a model in which it was assumed that all sites in a particular region must be simultaneously unoccupied before adsorption could occur, and obtained appropriate expressions for the probable existence of such regions. Meller (81) also obtained an exponential variation of the number of adsorption sites by another different approach.

VII. Models Based on a Variable Activation Energy

In all the above models, a constant activation energy for adsorption, i.e., a homogeneous surface, was assumed. A mathematically equivalent model is one in which the site number on the adsorbent is constant but the activation energy for adsorption increases linearly with increased coverage. Site heterogeneity may be assumed, i.e., the activation energy for adsorption varies for the different sites on the adsorbent; or induced heterogeneity may be postulated, i.e., (i) there are lateral interactions between adsorbate molecules on the surface, or (ii) the adsorbate molecules, by perturbation of the adsorbent surface, change the properties of the remaining free sites such that the activation energy increases with coverage, or both. In the general case, heterogeneity may comprise both site and induced effects. We first consider the site heterogeneity model in absence of any induced effects.

VIII. Nonuniform Surface

The equation describing the kinetics of adsorption on a nonuniform surface with a linear increase of activation energy of adsorption with coverage was first deduced by Brunauer *et al.* (82). The surface is divided into a series of equal areas ds ; each area constitutes a uniform element of surface having an activation energy for adsorption given by $E_s = E_0 + \alpha's$, where s is the reference number of the uniform patch and α' is a constant. The rate of adsorption is then given by

$$dq/dt = k \int_0^1 (1 - \theta_s) \exp[-(E_0 + \alpha's)/RT] ds, \quad (11)$$

where k is an effective collision number; $(1 - \theta_s)$ is the fraction of sites still bare at time t ; and integration replaces the summation since ds is assumed to be very small. Integration is effected with the assumption that at time t all areas having activation energies less than E_t are completely covered and all those associated with energies greater than E_t are bare. Integration is carried out only over the bare surface, $(1 - \theta_s) \rightarrow 1$, the limits being $s = \Theta$ to $s = 1$, where Θ is the fraction of the *total* surface covered at time t . The result is

$$dq/dt = k(RT/\alpha') \exp(-E_0/RT) \{ \exp(-\alpha'\Theta/RT) - \exp(-\alpha'/RT) \} \quad (12)$$