REVIEW

Kinetics of adsorption: the S-shaped z-t plot

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Summary One characteristic property of the kinetics of adsorption is the fact that the plot of the reciprocal of the rate against the time is S-shaped. The initial part of this plot is convex and can be fitted by a power equation (i.e. with the amount adsorbed being proportional to a fractional power of the time), the final part is concave and can be fitted by a Langmuir-type equation (i.e. with the rate decreasing linearly with the amount adsorbed) and the intermediate region around the inflection point can be fitted by the Elovich equation (i.e. with the amount adsorbed increasing logarithmically with the time). In many cases the above regions are preceded by a region at which the rate is constant.

The equation $$\frac{d\theta}{dt} = \frac{A(1 - \theta)}{\theta}$$ where $\theta$ is the fractional coverage, $t$ is the time and $a$ is a constant, is consistent with these kinetics. It corresponds to kinetics in which the activation energy increases logarithmically with the coverage. It can be derived on the basis of a statistical-rate theory or on the basis of a precursor-state theory. The diffusion equation

$$\frac{q}{q_x} = 1 - \sum_{n=0}^{n=\infty} a_n \exp(-b_n t D/r^2)$$

where $q$ and $q_x$ are the quantities adsorbed at time $t$ and $t = \infty$, $a_n$ and $b_n$ are parameters determined by the integers $n$, $D$ is the diffusion coefficient and $r$ the length path, is also consistent with the above kinetics. Both equations have also been extended to heterogenous surfaces.

Isotherms with constant initial rate are associated with non-activated adsorption and measurements at low pressures. The constant initial rate corresponds to a state at which the kinetics are determined by the rate of arrival of the gas molecules to the surface.

1. EMPIRICAL RELATIONS

1.1. The z-t plot

A significant part of the literature on the kinetics of chemisorption deals with the search for empirical or theoretical isotherms characteristic of the adsorption process or of a
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given type of adsorption. The following equations were often applied:

1. The power equation or Bangham equation (Bangham & Burt 1924)
   \[ q = k b t^n \]  
   where \( k_b \) and \( n \) are constants and \( n < 1 \).

2. The logarithmic equation or Elovich equation (Low 1960; Aharoni & Tompkins 1970)
   \[ q = A + \frac{1}{b} \ln(t + t_0) \]
   where \( A, b \) and \( t_0 \) are constants. The differential forms of this equation are also of interest
   \[ \frac{dq}{dt} = a \exp(-bq) \]  
   where \( a \equiv (1/b) \exp(bA) \) and
   \[ \frac{dq}{dt} = \left[ b(t + t_0) \right]^{-1} \]

3. The Langmuir-type equation (Langmuir 1918; Pajares et al. 1978)
   \[ \frac{dq}{dt} = \alpha(q_x - q) \]
   where \( \alpha \) and \( q_x \) are constants, which gives on integration
   \[ \frac{q}{q_x} = 1 - k_i \exp(-\alpha t) \]
   where \( k_i \) is a constant.

More recent work shows however than eqns 1, 2, 6 are of limited validity. Thus they are valid for many adsorbent-adsorbate pairs but apply to limited parts of the kinetic isotherms. It was found that in order to fit the experimental isotherms over a wide range of coverages more complex rate equations must be used. These equations differ for various adsorbent-adsorbate pairs but have a common property in that they reduce to eqns 1, 2 and 6 at some limited ranges of coverage (Aharoni & Ungarish 1976, 1977a).

The general rate equation is conveniently characterised by a property of the reciprocal of the rate

\[ z \equiv (dq/dt)^{-1} \]

When \( z \) is plotted against \( t \) a sigmoid curve is obtained as shown in Fig. 1; convex at small \( t \), concave at large \( t \) and with an inflection point at \( t = t_p \).

\[ \frac{d^2z}{dt^2} < 0 \quad \text{at } t < t_p \]  
\[ \frac{d^2z}{dt^2} = 0 \quad \text{at } t = t_p \]  
and \[ \frac{d^2z}{dt^2} > 0 \quad \text{at } t > t_p \]

When \( t \) does not differ considerably from \( t_p \) the plot of \( z \) against \( t \) is approximated by the tangent at the inflection point and represented by the linear equation

\[ z = b(t + t_0) \]
where \( b \) is the slope and \( -t_0 \) the intercept with the \( t \) axis. Equation 11 is equivalent to the differential form of the Elovich equation (eqn 4) and gives eqn 2 when integrated. At small \( t \) the general isotherm can be fitted by equations for which the plot of \( z \) against \( t \) is convex (inequality 8). This condition is fulfilled by eqn 1 and there are many cases in which it is applicable at that range. At large \( t \) the required condition is inequality 10. Equation 6 fulfills this condition and it is often applicable at that range.

There are isotherms for which the \( z-t \) plot comprises a convex portion and a linear portion only (Fig. 2), i.e. they approach a power equation at small \( t \) and an Elovich equation at large \( t \). It should be assumed that such isotherms are necessarily incomplete, and at some time not attained during the run \( z \) should tend to infinity (\( dq/dt \rightarrow 0 \)) and this implies a reversal of the curvature of the \( z-t \) plot and formation of a concave portion. An equivalent argument is that neither eqn 1 nor eqn 2 predict a finite value of \( q \) at \( t \rightarrow \infty \), and so neither of these equations can remain valid when saturation is approached. Incomplete isotherms are likely when the energy of activation increases significantly with coverage. An increase of the activation energy causes a decrease of the rate of adsorption, and it may approach zero while the amount adsorbed is still considerably smaller than the equilibrium amount (Aharoni & Ungarish 1977b).

On the other hand there may be cases in which the initial part of the isotherm, corresponding to inequality 8 or to inequality 8 and eqn 9, is not noticeable (see Fig. 3) and the plot of \( q \) against \( t \) then appears to obey eqn 6 throughout the run. This type of isotherm is likely to occur in fast adsorptions in which true equilibrium is approached;
Figure 2. Adsorption of hydrogen on chromia at \( p = 0.5 \text{ atm} \). Data of Burwell & Taylor (1936a). Repotted (Aharoni & Ungarish 1976) as \( t \) against \( z \). (●) 457 K; (+) 427 K; (x) 405 K; (○) 383.5. (Reproduced with permission).

Figure 3. Adsorption of hydrogen on Scandia plotted as \( t \) against \( z \). (a) \( p = 4 \text{ kPa} \); (○) \( T = 648 \text{ K} \); (△) \( T = 681 \text{ K} \). (b) \( T = 648 \text{ K} \); (●) \( p = 8.72 \text{ kPa} \); (△) 3.97, (●) 1.08 kPa. Reproduced from Garcia-Fierro & Pajares (1980) with permission. Copyright Academic Press Inc. (New York).

The initial adsorption may be too rapid to be measurable and the measured kinetics therefore refer mainly to the final part.

Kinetic isotherms may therefore be classified into three types: Type A incomplete isotherms obeying eqn 1 at small \( t \) and eqn 2 at large \( t \) or only one of these equations. Type B isotherms obey successively eqns 1, 2, 6 and Type C isotherms are mainly represented by eqn 6. When the temperature is raised, an isotherm of Type A may change into Type B and finally into Type C.

It is shown below that representation of the kinetics by a sigmoid \( z-t \) plot does not cover all the possibilities and an isotherm with \( z \) constant at small \( t \) is discussed in section 4.
1.2. Applications and misapplications of the Elovich equation

It has been stated above that the Elovich equation is applicable to a limited part of the isotherm; the part in which eqn 9 is valid. This equation is applicable to the totality of the isotherm only in the fortuitous case in which the initial part of the isotherm is not observable and the final part not attainable. However, following the reasoning first suggested by Taylor & Thon (1952), the Elovich equation has been considered as an equation of general validity, and it has been erroneously applied to isotherms of types A, B and C from the beginning to the end of the runs (Low 1960; Aharoni & Tompkins 1970).

The arguments that were used in order to represent isotherms of type A as Elovichian, are conveniently discussed in relation to a specific example, e.g. the data of Burwell & Taylor (1936a) for the adsorption of H$_2$ on chromia (see Figs 2 and 4). Taylor and Thon (1952) found that eqn 2 is applicable to the data of Burwell and Taylor but only on condition that the three parameters A, b and $t_0$ are independently adjusted (Fig. 4, curve b). This excludes the possibility that all the adsorbate is taken up according to eqn 3, because in that case integration has to be performed with the condition $q = 0$ at $t = 0$ and $t_0$ in eqn 2 becomes entirely determined by A and b. However, by assuming a rapid adsorption preceding the Elovichian one, the condition $q = q_0 = 0$ at $t = 0$ is introduced and $t_0$ becomes an arbitrarily adjustable parameter, dependent on the assumed value of $q_0$.

The inconsistency of this argument becomes evident (Aharoni & Ungarish 1976), if one considers the other differential form of the Elovich equation, i.e. eqn 4 or 11. It is seen that $t_0$ is not an adjustable parameter, but is obtainable when the experimental results are plotted as $z$ against $t$ (Figs 2 & 4) and the range of validity of the Elovichian kinetics is not a subject for speculation, it is given by the curvature of the experimentally obtained $z$-$t$ plot, (see Fig. 2).

The observation, made by Taylor and Thon (1952) that one can always find a value of $t_0$ that completely linearises the plot of $q$ against log($t + t_0$) (curve b in Fig. 4), was critically analysed (Ungarish & Aharoni 1981). Curve a in Fig. 5A represents an assumed experimental isotherm obeying eqn 1, and it is convex as required by inequality 8.

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**Figure 4.** Adsorption of hydrogen on chromia at $T = 427$ K, $p = 0.5$ atm (1 atm. = 50.66 kPa). Data of Burwell & Taylor (1936a). Replotted (Aharoni & Ungarish 1976) as $q$ against log($t + t_0$).
(a) $t_0 = 120$ min (calculated from Fig. 2); (b) $t_0 = 65$ min, ($t_0$ that linearises the plot); (c) $t_0 = 0$.
(Reproduced with permission).
Applying an Elovich equation to this isotherm means approximating the convex curve by a straight line (eqn 9). A good approximation can be obtained if one chooses a tangent at an adequate position, e.g. line b. Choosing arbitrarily a value of $t_0$ as suggested by Taylor & Thon ($t_0 = 7$ in this case) means choosing the intercept of the tangent and therefore the point of tangency. The plot of $q$ against $\log(t + t_0)$ for curve a with $t_0 = 7$ is fairly linear (Fig. 5B).

Obviously, the fitting of an isotherm of type 1 by an Elovichian plot is still more easy to perform if one is content with a ‘broken’ Elovichian plot ($t_0 = 1$ in Fig. 5). Many broken Elovichian plots in the literature (Low 1960a; Aharoni & Tompkins 1970) represent isotherms of type A, that could not be fitted with sufficient accuracy by a single Elovichian plot. In these cases, as in Fig. 5B, with $t_0 = 1$, the later segment has a greater slope than the first.

In isotherms of type B (Fig. 6) and type C, (Fig. 7), there is a non-Elovichian component following the Elovichian portion at which the plot of $q$ against $\log(t + t_0)$ has a lower gradient. The Elovich equation can only be applied by cutting the plot arbitrarily into segments approaching straight lines, and the final segment necessarily has a smaller slope than the preceding one.

Some of the inconsistencies concerning the applicability of the Elovich equation that have been observed (Low 1960a; Aharoni & Tompkins 1970) are presumably due to the arbitrary choice of $t_0$ and to arbitrary cutting of the logarithmic plots into linear segments; e.g. the adsorption $q_0$ at $t = 0$ implied by the assumed value of $t_0$ is often
Figure 6. Adsorption of hydrogen on rhodium (530 K, 51.7 cm DBP) and palladium (329 K, 50.88 cm DBP), plotted as q against log t (Low 1960b) (1 cm DBP = 103 Pa).

Figure 7. Adsorption of NO on supported chromia at 318 K and 2.8 Torr plotted as q against log t (Reproduced from Otto & Shelef 1969 with permission. Copyright Academic Press Inc. New York.) (1 Torr = 133 Pa).

inconsistent with the observed rates of adsorption at small t. The effects of pressure and temperature on the number of Elovichian segments and on the parameters A and b do not appear to follow a consistent pattern.

By plotting experimental data as q against log t, without trying to artificially impose linearity, it is often possible to determine if the isotherm is of type A, B or C. For isotherms of type B, the plot is S-shaped, concave at small t and convex at large t (e.g. Fig. 6 disregarding the straight lines); for isotherms of type A the final convex part is missing (Fig. 4C) and for isotherms of type C the initial concave part is missing.
Figure 8. Reduction of supported MoO₃. Plots of extent of reduction $\theta$ against $\log t$ (Hashimoto, Watanabe & Tarama 1976; reproduced with permission), hydrogen pressure 170 Torr. (○) 623 K; (●) 673 K; (□) 723 K (1 Torr = 133 Pa). (A) oxide III. (B) oxide I (dotted line) oxide II (solid line).

(Fig. 7). Application of this method of interpretation to data on the reduction of molybdenum oxides (Hashimoto, Watanabe & Tarama 1976) (Fig. 8) reveals a correlation between their solubility and reducibility. The reduction of the more soluble oxide (sample III) obeys an isotherm of type B at low temperature and an isotherm of type C at higher temperature (Fig. 8A). The isotherms for the reduction of the less soluble oxides I and II, do not have a final convex part and presumably reduction does not approach equilibrium (see Fig. 8B).

The characteristics of the plot of $q$ against $\log t$ are emphasised when the data are plotted (Ungarish & Aharoni 1983) as $dq/d(\ln t)$ against $t$. The plot has a maximum corresponding to the Elovichian part, which may extend over a wide range, be a flat plateau, or it may be a transient sharp peak.

1.3. The Power Equation

The power equation (eqn 1) is applicable to the initial part of the adsorption isotherm characterised by inequality 8. However, there are adsorptions in which the rate of uptake is not easily measurable at large coverages, and most of the experimental data obtainable are in the range of validity of the power equation. In these cases the plot of $\log q$ against $\log t$ appears to be mostly linear (Bangham & Burt 1924; Kwan 1956) and deviations are observed only at large $t$ and high temperatures, the deviations are always in the same direction, and the slope of the plot of $\log q$ against $\log t$ tends to decrease.

The equation (Ghosh, Sastri & Kini 1952)

$$dq/dt = k_p P/q'$$

(12)

where $v$ is a constant, is obviously a form of eqn 1. Another equation consistent with eqn 1 is

$$dq/dt = n k_b (q_0 - q)t^{n-1}$$

(13)
This equation was applied (Aharoni, Sideman & Hoffer 1979) to the adsorption of a solute from a limited amount of solution and \( q_0 \) is the initial amount of solute. Equation 13 implies that the rate of adsorption is governed by eqn 1 but it takes into account the depletion of the solution surrounding the adsorbent and its effect on the rate of adsorption. Equation 13 is tested by rewriting as

\[
\log\left(\frac{q_0}{q_0 - q}\right) = k_n t^n
\]  
(14)

and plotting \( \log(\log(q_0/(q_0 - q))) \) against \( \log t \). On the other hand the equation

\[
dq/dt = nk_q(q_* - q)t^{n-1}
\]  
(15)

(Bangham & Sever 1925; Maxted & Moon 1936; Paryjezak & Gebauer 1979) where \( q_* \) is the amount taken up by the adsorbent at equilibrium is not consistent with eqn 1.

A particular case of the power equation, the parabolic equation, (see eqn 46 below) has received considerable attention and is widely used as a criterion for diffusion-limited kinetics. It has been applied to adsorption in which the rate-controlling effect of diffusion seems obvious such as adsorption by porous materials, but it has also been applied to adsorption processes in which there is no evidence for rate control by diffusion (Simard et al. 1955) and which were also interpreted on the basis of equations related to other models (Bhattacharyya & Mahanti 1971). The value of the exponent does not indicate unequivocally if a power equation is associated with diffusion or with a chemical reaction: (a) the values of \( n \) for chemisorption on non-porous solids are often close to 0.5; (b) theoretical equations for diffusion (e.g. eqn 45 below) can give good fits at small \( t \) with \( n \) larger than 0.5.

### 1.4. Langmuir-type equations

Equation 6 is applicable to the final part of the isotherm characterised by inequality 10 provided that this range is attained during the run. In some cases (adsorption of type C) it is applicable to most of the isotherm (Pajares, Fierro & Weller 1978; Apostegui & et al. 1982).

The significance of eqn 5 depends on the significance of the parameter \( q_* \). Langmuirian kinetics and first-order kinetics are given by eqn 5 with \( q_* \equiv q_m \), the amount corresponding to monolayer coverage, a parameter independent of pressure and temperature. However, Pajares, Garcia Fierro & Weller (1978) found that their data for the adsorption of CO\(_2\) on scandia obey a different equation, i.e. eqn 5 with \( q_* \equiv q_e \), which is the amount adsorbed at equilibrium, a parameter that varies with temperature and pressure (Fig. 9). It is worthwhile noting that eqn 5 can account for the concave part of the \( z-t \) plot only if it is consistent at large \( t \). The equation of Pajares et al. (1978) fulfills this condition and gives \( q = q_e \) at \( t \to \infty \). The Langmuir equation written as eqn 5 or 6 is inconsistent at large \( t \) and requires the addition of a desorption term.

The parameter \( k_i \) in eqn 6 depends on the condition at which eqn 5 is integrated. It is equal to 1 if eqn 5 applies from the beginning of the run. The results obtained by Pajares et al. (1978) viz \( k_i > 1 \), indicate that adsorption according to eqn 5 is preceded by more rapid processes, presumably adsorption according to eqns 1 and 3.
Figure 9. Adsorption of $\text{CO}_2$ on Scandia plots of $q_e/(q_e - q)$ against $t$. (Pajares et al., 1978; reproduced with permission. Copyright Academic Press Inc. (New York)). $T = 523 \text{ K. (O) 8.0 Torr, (△) 4.9 Torr, (○) 3.8 Torr; (▽) 2.5 Torr (1 Torr = 133 \text{ Pa})}.$

Equation 5 was also applied to the adsorption of $\text{H}_2\text{S}$ on alumina (Apesteguia, Plaza de los Reyes, Garetto & Parera 1982), with $q_x \equiv q_e$. The value of $k$ in this case appears to be very close to 1 and the plot of $z$ against $t$ is concave as expected.

A second-order equation

$$dq/dt = a(q_x - q)^2$$

(16)

has been applied to a few adsorption isotherms (Ritchie 1977). However, it has been shown in another work (Ungarish & Aharoni 1981) that the plots of $z$ against $t$ for these isotherms are not concave and applicability of eqn 16 is therefore merely apparent.

2. THEORETICAL MODELS WHERE THE RATE OF ADSORPTION IS DETERMINED BY THE RATE OF A CHEMICAL REACTION

2.1. Variation of the activation energy with coverage

Adsorption can be viewed as a chemical reaction between a surface and a gas, where the rate $dq/dt$ is determined by $p$ the pressure of the gas, $N(\theta)$ the number of available sites at coverage $\theta$, and $E(\theta)$ the energy of activation at coverage $\theta$. For undissociated adsorption at constant pressure the rate equation is given (Clark 1970; Hayward &
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Trapnell 1964a) by

$$\frac{dq}{dt} = k(p)N(\theta)\exp[-E(\theta)/RT] \quad (17)$$

where $k$ is a constant determined by $p$.

Generally, no independent knowledge of the functions $N(\theta)$ and $E(\theta)$ is available, and it is justifiable to choose functions for which eqn 17 fits what is believed to be an empirical equation characteristic of the adsorption process. Langmuir-type equations (eqn 5) are derived from eqn 17 by assuming $E$ constant and $N(\theta)$ given by

$$N = N_0(1 - \theta) \quad (18)$$

where $N_0$ is a constant. The Elovich equation (eqn 3) was derived (Low 1960a; Aharoni & Tompkins 1970) by assuming

$$E(\theta) = E_0 + B\theta \quad (19)$$

and $N \approx N_0$, or alternatively by assuming

$$N(\theta) = N_0\exp(-b'\theta) \quad (20)$$

and $E$ constant. $E_0$, $B$ and $b'$ are constants. The power equation is derived by assuming

$$E(\theta)/RT = E_0/RT + \ln(g.\theta + \gamma) \quad (21)$$

with $N \approx N_0$, $E_0$, $g$ and $\gamma$ are constants, and $\gamma \ll g.\theta$ for any measurable adsorption.

The functions $N(\theta)$ and $E(\theta)$ required in order to obtain an equation consistent with an S-shaped $z$-$t$ plot were deduced (Aharoni & Ungarish 1977a) from the expression for $d^2z/dt^2$ corresponding to eqn 17. With $\theta$ defined by $q/N$,

$$N_0 \frac{d^2z}{dt^2} = \frac{d\theta}{dt} \left[ \frac{1}{RT} \frac{d^2E}{d\theta^2} + \frac{1}{N^2} \left( \frac{dN}{d\theta} \right)^2 - \frac{1}{N} \frac{d^2N}{d\theta^2} \right] \quad (22)$$

At small $t$ the two last terms in eqn 22 are necessarily negligible and in addition applicability of ineq 8 is required. Simultaneous application of these two conditions implies for small $t$ that

$$d^2E/d\theta^2 < 0 \quad (23)$$

It is not necessary to assume that ineq 23 is reversed at large $t$. With $N(\theta)$ given by eqn 18 and $E(\theta)$ obeying ineq 23 at all coverages, the value of $d^2z/dt^2$ predicted by eqn 22 is negative at small $t$, zero at intermediate $t$ and positive at large $t$ in agreement with ineq 8, eqn 9 and ineq 10.

The logarithmic dependence of $E$ on coverage, expressed by eqn 21 is consistent with the condition expressed by ineq 23. Introducing this equation into eqn 17 together with eqn 18 one obtains the simplest relation consistent with an S-shaped $z$-$t$ plot

$$\frac{d\theta}{dt} = A(1 - \theta)/\theta \quad (24)$$

or

$$-\ln(1 - \theta) - \theta = At \quad (25)$$
where $A$ is a constant given by

$$A = \frac{k}{g} \exp\left(-\frac{E_0}{RT}\right) \quad (26)$$

Equation 24 reduces at small $t$ to a power equation (see eqn 1)

$$\theta = (2A)^{1/2}t^{1/2} \quad (27)$$

and at large $t$ to a Langmuir-type equation (see eqn 6)

$$\theta = 1 - \exp(-At) \quad (28)$$

At about $\theta = 0.5$ it reduces to an Elovich equation (Aharoni & Birnholtz 1980) (eqn 2)

$$\theta = 0.435 + 0.25 \ln[5.18At + 0.295] \quad (29)$$

### 2.2. Derivation of eqn 24 based on statistical rate theory

The above derivation of eqn 24 is essentially empirical. Ineq 23, which led to the choice of eqn 21, reflects the experimental fact that the adsorption isotherms obey an S-shaped $z$-$t$ plot. However, eqn 24 can also be derived on the basis of theoretical considerations. Ward et al. (Ward, Findlay & Rizk 1982; Ward & Findlay 1982a, b) have developed a statistical rate theory of interfacial transport, and obtained an equation equivalent to eqn 24 by applying this theory to adsorption. Using a first-order perturbation analysis of the Schrödinger equation, and assuming constant average rate of transport between microscopic states of neighbouring molecular distributions they derived an equation relating the rate of gas to surface transport $J_{gs}$, to the chemical potential of the gas molecules at these phases $\mu^g$ and $\mu^*$

$$J_{gs} = K_g \left[ \exp\left(\frac{\mu^g - \mu^*}{kT}\right) - \exp\left(-\frac{(\mu^g - \mu^*)}{kT}\right) \right] \quad (30)$$

where $K_g$ is an equilibrium exchange rate, $k$ the Boltzmann constant and $T$ the temperature (Ward, Findlay & Rizk 1982).

A rate equation for adsorption was obtained (Ward & Findlay 1982a) by assuming that $\mu^*$ is given by

$$\mu^* = kT \ln\left[\frac{N^*(M - N^*)}{j}\right] \quad (31)$$

where $N^*$ is the number of adsorbed molecules per unit area, $M$ the number of sites per unit area and $j$ a constant related to energetic properties of the adsorbed molecules. Assuming also that $\mu^g$ is proportional to $\ln p$, one obtains eqn 32 which is similar to eqn 24 but contains the desorption term omitted in eqns 24 and 17

$$\frac{d\theta}{dt} = a_k \frac{1 - \theta}{\theta} - b_k \frac{\theta}{(1 - \theta)} \quad (32)$$

where $\theta = N^*/M$ is a fractional coverage and $a_k$ and $b_k$ are constants. Application of eqn 32 to the adsorption of CO on ZnO (Burwell & Taylor 1936a) is depicted in Fig. 10.

The model was also applied to dissociative adsorption (Ward & Findlay 1982b) and gives an equation similar to eqn 32 with the ratios $(1 - \theta)/\theta$ and $\theta/(1 - \theta)$ squared.
Figure 10. Adsorption of CO on zinc oxide \( T = 491 \) K, \( p = 101.3 \) kPa. Data of Burwell and Taylor (1936a) (A) Solid dots: experimental data. Solid line: curve calculated according to eqn 32 and fitted to the experimental data. (B) Solid dots: experimental data replotted as \( dq/dt \) against \( q \). Solid line: rate inferred from measured amounts. Dotted line: optimum Elovichian representation (Ward & Findlay 1982a).

2.3. Derivation of eqn 24 based on precursor-state theory

Equation 24 is also a special case of eqn 56 derived on the basis of a precursor state theory (see part 4). Equation 56 can be rewritten as

\[
S = S_\theta m(1 - \theta)/(\theta + m) \tag{33}
\]

where \( m = (K - 1)^{-1} \). For \( m \ll \theta \) it reduces to eqn 24 with \( A = S_\theta m \) the assumption \( m \ll \theta \) is equivalent to the assumption \( \gamma/g \ll \theta \) used in the derivation of eqn 24 from eqn 21.

2.4. Heterogeneous surfaces

The kinetics expressed by eqn 24 were also extended to heterogeneous surfaces (Aharoni & Ungarish 1977a, 1977b; Ungarish & Aharoni 1983). The heterogeneous surface is regarded as an array of homogeneous patches characterized by the energy of adsorption \( H \). It is assumed that \( E_p \), the activation energy at a patch, is related linearly to \( H \), and varies with the local coverage \( \theta \) according to an equation similar to eqn 21

\[
E_p/RT = \alpha H/RT + \ln(g\theta + \gamma) \tag{34}
\]

where \( \alpha, g \) and \( \gamma \) are constants and \( \gamma \ll g\theta \). Rate and equilibrium equations are derived for the patches (Ungarish & Aharoni 1983) by using an equation similar to eqn 17 with a desorption term and combining it with eqn 34. The equations obtained are

\[
d\theta/dt = (k/g) \exp(-\alpha H/RT)(1/\theta - 1/\theta_e) \tag{35}
\]

\[-\ln(1 - \theta/\theta_e) - \theta/\theta_e = (k/g\theta_e^2)t \exp(-\alpha H/RT) \tag{36}\]

and

\[
\theta_e = [k_e^{-1} \exp(-H/RT) + 1]^{-1} \tag{37}\]
where $\theta_e$ is the equilibrium coverage of the patch, $k$ a kinetic constant, and $k_e$ an equilibrium constant.

The distribution of the adsorbate over patches of increasing energy $H$ is given in Fig. 11. The plot of $\theta_e$ against $H$ is an ascending curve, with an inflection point at $\theta_e = 0.5$ and approaching a horizontal line at $\theta_e = 1$ and its form is unchanged by change of pressure. Plots of $\theta$ against $H$ are descending curves with an inflection point at $\theta = 0.684$ and slope determined by $\alpha$; change of $t$ causes displacement along the $H$ axis but causes no change of shape. Coverage is maximum at $H_e$; $\theta_e$, the intersection between two plots $\theta_e(H)$ and $\theta(H)$, is small and determined by equilibrium at low $H$, and small and determined by the kinetics at high $H$.

The amount adsorbed at $t$ corresponds to the area under $\theta_e(H)$ from $H_0$ to $H_1$ and under $\theta(H)$ from $H_1$ to $H_m$ and it is given by

$$\frac{1}{n_{i1}}(dq/d \ln t) = \frac{1}{\alpha}(\theta_{e1} - \theta_m)$$

(38)

where $n_{i1}$ is the number of sites at the patch where $H$ is assumed to be constant and the subscripts 0 and m refer to the patches with lowest and highest energy. Rate equations are obtained by introducing approximate expressions for $\theta_e(t)$ and $\theta_m(t)$ which are valid over limited ranges of $t$. One obtains the following sequence of equations

$$(\alpha/n_{i1})(dq/d \ln t) = A(kt/g)^{1/2}$$

(39)

$$(\alpha/n_{i1})(dq/d \ln t) = B \ln(kt/g) + C$$

(40)
(\alpha/n_{ii})(dq/d \ln t) = 1 \quad (41)
(\alpha/n_{ii})(dq/d \ln t) = 1 - D(kt/g)^{1/2} \quad (42)
(\alpha/n_{ii})(dq/d \ln t) = \exp(-k_mkt/g) \quad (43)

where A B C D and k_m are constants.

Equations 39, 41 and 43 are respectively equivalent or close to eqns 1, 2 and 6 and the sequence shows that the overall rate function is consistent with an S-shaped z-t plot. It can be represented by a plot of dq/d \ln t against t with a maximum corresponding to the Elovichian region (eqn 41). Figure 11 indicates that the Elovichian region has a wide range of validity when \alpha is large and the range H_m - H_0 is wide, i.e. when the surface is highly heterogeneous.

A heterogeneous model (Aharoni & Ungarish 1977a,b) with the simplifying assumptions that \theta \ll 1 and \theta_e \ll 1 leads to the rate equation.

Figure 12. Adsorption of ammonia on gold-plated walls of an opto-acoustic cell. Plot of gas phase concentration against time. The points are experimental. The curve is calculated according to equations derived from eqn 44. (Richton & Farrow 1981; reproduced with permission. Copyright American Chemical Society).
\[ \frac{q}{n_HRT} = \frac{\alpha}{\alpha + 2} k^2(\frac{t}{2})^{1/(\alpha + 2)} \exp\left(\frac{H_0}{RT} - \frac{2(2k/g)^{1/2}t^{1/2}/\alpha}{2^{1/2}}\right) \]

Equations derived from eqn 44 and adapted to adsorption at decreasing pressure were applied to the adsorption of ammonia by the walls of a gold-plated opto-acoustic cell (Richton & Farrow 1981) (Fig. 12).

3. THEORETICAL MODELS BASED ON DIFFUSION

3.1. Diffusion in a homogeneous medium

S-shaped z-t plots can be derived from models based on diffusion. Diffusion is often assumed to be the main factor determining the kinetics of adsorption when the adsorbent is porous; however, models based on diffusion have also been applied to non-porous solids. The rate of adsorption on a non-porous solid is determined by diffusion if the adsorbate is taken up on some low-activation energy patches and subsequently migrates at the surface into regions of higher activation energy. A kinetic model based on these assumptions is discussed by Birnholtz et al. (in press) and Aharoni & Birnholtz (1980). Various workers (Polizzotti 1974; Liu & Ehrlich 1976; Bonzel 1977) have previously suggested that a low index-planar region is likely to take up adsorbate by surface diffusion from a neighbouring high index plane region rather than by direct adsorption from the gas phase. The kinetics are also likely to be determined by diffusion when the final location of the sorbate is a sub-surface layer, the selvedge (Wood 1964; Hagstrum, Rowe & Tracy 1976) or if adsorption is accompanied by absorption into the bulk of the solid (Hayward & Trapnell 1964b; Nagasaka & Yamashina 1972; Nagasaka et al. 1973; Ablow & Wise 1982).

In order to derive rate equations it is convenient to consider initial sorption by microporous solids. If the pores are sufficiently narrow all the adsorbate occluded in the pores is in condensed state and the amount sorbed at time t is the amount that has penetrated into the pores from \( t = 0 \) and \( t = t \). It can be evaluated by integrating Fick's equation with suitable initial and boundary conditions and averaging over the length of the diffusion path (Dacy & Thomas 1954; Barrer 1978). If the solid contains a homogeneous network of pores with equal and constant diffusion coefficient, \( D \), and if the particles have the same size and the same regular shape, one obtains for a gas phase at constant pressure and composition (Jost 1960) the following expression

\[ \frac{q}{q_x} = 1 - \sum_{n=0}^{\infty} a_n \exp(-b_n tD/r^2) \]

where \( r \) is the length of the diffusion path (i.e. half the thickness in case of slabs or the radius in elongated cylinders and in spheres, etc.) \( a_n \) and \( b_n \) are parameters with an infinite number of discrete values determined by \( n \), the integers between 0 and \( \infty \). Equation 45 reduces at small \( t \) to

\[ \frac{q}{q_x} = k_1(tD/r^2)^{1/2} \]

and at large \( t \) to

\[ \frac{q}{q_x} = 1 - k_1 \exp(-\alpha tD/r^2) \]
**Table 1.** Parameters of diffusion equation and its approximations, eqns 45 to 48 (including parameters related to eqn 24)

| Case          | Case 1 | Case 2 | Case 3 | Case 4 | Case 5 |
|---------------|--------|--------|--------|--------|--------|
| Non-approximated diffusion equation (eqn 45) |        |        |        |        |        |
| $a_n$         | $8/\pi^2(2n+1)^2$ | $4/\xi_0^2$ | $6/\pi^2n^2$ | $4A_n/\lambda_0^2(\rho^2 - 1)$ | —     |
| $b_n$         | $\pi^2(2n+1)^2/4$ | $\xi_0^2$ | $\pi^2n^2$ | $\lambda_0^2(\rho - 1)^2$ | —     |
| Small $t$ (eqn 46) |        |        |        |        |        |
| $k_s$         | $2/\pi^{1/2}$ | $4/\pi^{1/2}$ | $6/\pi^{1/2}$ | $4/\pi^{1/2}(\rho + 1)$ | $\sqrt{2}$ |
| Large $t$ (eqn 47) |        |        |        |        |        |
| $k_l$         | $8/\pi^2$ | $4/\xi_1^2$ | $6/\pi^2$ | $4A_1/\lambda_1^2(\rho^2 - 1)$ | $1$   |
| $a_l$         | $\pi^2/4$ | $\xi_1^2$ | $\pi^2$ | $\lambda_1^2(\rho - 1)^2$ | $1$   |
| Elovichian range (eqn 48) |        |        |        |        |        |
| $A/q_x$       | 0.238  | 0.441  | 0.449  | 0.0164 | 0.435  |
| $b_{q_x}$     | 2.281  | 3.136  | 3.535  | 1.930  | 4      |
| $t_i$         | 0.793  | 0.402  | 0.333  | 1.179  | 0.295  |
| Inflection point of z-t plot |        |        |        |        |        |
| $t_p$         | 0.192  | 0.078  | 0.035  | 0.219  | 0.193/A |
| $q_p/q_x$     | 0.494  | 0.549  | 0.530  | 0.420  | 0.5     |
| $z_{p/q_x}$   | 0.785  | 0.343  | 0.167  | 0.921  | 1/A     |

Case 1, Diffusion in parallel paths, e.g. occlusion by slabs, surface diffusion in rectangular areas etc.
Case 2, Diffusion converging towards the center of a circle, e.g. occlusion by elongated cylinders, converging surface diffusion in circles, etc.
Case 3, Diffusion converging towards the center of a sphere, e.g. occlusion by spherical particles, etc.
Case 4, Diffusion diverging from an inner circular region into an annulus. Numerical data refer to $\rho = 2$ (\(\rho\) is the ratio between outer and inner radii and $r$ the difference between these radii). The model applies for instance to surface diffusion from easily replenished circular regions into surrounding diffusion medium (Birnholtz et al. in press).
Case 5, Equation 24 derived on the basis of chemical reaction-limited kinetics treated (Aharoni & Birnholtz 1980) like an equation derived from eqn 45 with $A^1$ representing $r_i^2/D$.

The parameters $a_n$, $b_n$, $k_s$, $k_l$ and $\alpha_i$ depend on the geometry of the particles and are given in Table 1 for a few cases.

The small $t$ approximation (eqn 46) is a parabolic equation consistent with eqn 1 and the large $t$ approximation (eqn 47) is a Langmuir-type equation consistent with eqn 6.

The plot of $z$ against $t$ corresponding to eqn 45 is necessarily convex at small $t$ and concave at large $t$ and is consistent with ineq. 8 and 10 (Aharoni & Suzin 1982a) (Fig. 13). In the region of the inflection point eqn 9 is valid and an Elovich equation (eqn 2) is applicable (Fig. 14). This equation is conveniently rewritten in dimensionless form and in terms of the coordinates of the inflection point $z_p$, $t_p$ and $q_p$

$$q/q_x = A/q_x + (1/bq_x)\ln(t/t_p + t_i)$$  \hspace{1cm} (48)

where

$$A/q_x = q_p/q_x + (1/bz)\ln(bt_p/z_p)$$  \hspace{1cm} (49)

$$t_i = z_p/bt_p - 1$$  \hspace{1cm} (50)
Figure 13. Plots of \((q/\tau)\ Z\) against \(t/\tau\) (1) Slabs, \(\tau \equiv (4/\pi^2)(r^2/D)\) (2) Cylinders, \(\tau \equiv (1/2\cdot405)(r^2/D)\) (3) Spheres, \(\tau \equiv (1/\pi^2)(r^2/D)\). (Aharoni & Suzin 1982; reproduced with permission).

Figure 14. Plots of \(q/q_x\), against \(\ln(t/t_p + t_f)\) (1) Slabs, (2) Cylinders, (3) Spheres (Aharoni & Suzin 1982a; reproduced with permission).
For a given particle geometry $t_p$ and $z_p q_x$ depend on the ratio $r^2/D$, whereas $q_p/q_x$, $A/q_x$, $bq_x$, and $t$, are independent of $r$ and $D$ (see Table 1). For diffusion at the surface of a non-porous solid (Aharoni & Birnholtz 1980; Birnholtz et al. in press), eqns 45 to 50 are applicable if the high energy regions have the same diffusion coefficient, the same regular shape and the same size, and if the low energy regions are at equilibrium with a gas phase at constant pressure throughout the whole run; the parameters for slabs apply to rectangles, and the parameter for cylinders apply to circles etc.

Plots according to the parabolic equation (eqn 46) have been used widely as a test for the applicability of diffusion models (Dacey & Thomas 1954; Barrer 1978) often in preference to tests based on the non-approximated equation (eqn 45). On the other hand the fact that the Elovich equation is an approximation for a diffusion equation at intermediate coverage has been largely unnoticed. Applicability of this equation has been considered to be a proof for the validity of a chemical mechanism and non-validity of a diffusional one. Nevertheless, a few sporadic observations have been made pointing to the existence of a correlation between the Elovich equation and diffusional kinetics. Freund (1957) referring to the approximate expression (Sutherland & Winfield 1953)

\[ \frac{p}{p_0} = \exp(at)\left[ 1 - \text{erf}\left( \frac{at}{\sqrt{2}} \right) \right] \]

derived for Knudsen diffusion with rapid adsorption in a constant volume system, showed that $p/p_0$ is proportional to $\ln(t + t_0)$ for kinetic data satisfying this equation; $p_0$ is the initial pressure, $a$ is a parameter related to the diffusion process and $t_0$ an adjustable parameter. Peers (1965) applied a similar treatment to various adsorptions and the limits of applicability of the Elovich equation appeared to be $0.5 < p/p_0 < 0.8$. Barrer and Oei (1974) found that the rate of polymerisation of vinyl ethers over HY zeolites obeys an Elovich equation whereas the rate over mordenite obeys a power equation. Harris and Evans (1975), studying the oxidation of coal, found that artificially generated diffusion data computed according to eqn 45 with spherical particles could be related by an Elovich equation with value $t_p$ obtained by trial and error. The above-mentioned derivation based on the linearisation of the $z$-$t$ curve around the inflection point (Aharoni & Suzin 1982a) (Figs 13 and 14) shows that the Elovichian approximation applies to any diffusion equation that reduces to eqn 46 at small $t$ and eqn 47 at large $t$, and the parameters of this approximation are related to physical constants that determine the diffusion process.

The Elovichian approximation was used in conjunction with the parabolic equation in order to characterize various adsorptions (Aharoni & Suzin 1982b) viz: n-hexane vapour by Ca Zeolite 4A powder (Barrer & Clarke 1974), liquid mesitylene by Na Y zeolite approximate spheres (Satterfield & Cheng 1971), isopropyl N (3-chlorophenyl) carbamate in aqueous solution by active carbon powder (Schwartz 1967), and potassium ions by polystyrene sulphonic acid and cation exchange resin spheres (Tetenbaum & Gregor 1954). The parameters $r^2/D$ corresponding to spheres and to slabs were calculated according to the Elovichian approximation eqn 48. The results obtained were used in order to calculate plots of $q/q_x$ against $k_v(tD/r^2)^{1/2}$ that were compared with experimental plots of $q/q_x$ against $t^{1/2}$ at small $t$. In all the cases (see Fig. 15) the ‘slabs’ models gave consistent results but the spheres model was inapplicable.
3.2. Diffusion in a heterogeneous medium

If diffusion takes place in parallel in pores with different $D$, (or patches with different $D$ in the two dimensional case), eqn 45 has to be applied to a small fraction of the pores (or patches) and a summation over all the values of $D$ has to be performed. Aharoni & Suzin (1982c) characterized the array of pores by $T = (4/\pi^2)(r^2/D)$ and by $v(\tau)\ dr$, where the available pore volume corresponded to a given value of $\tau$. Equation 45 was approximated by eqn 47 for pores with $\tau < \tau_i = (t/0.192)(4/\pi^2)$ and by eqn 46 for pores with $\tau > \tau_i$. For the distribution $v_f(\tau)$ proportional to $1/\tau$ which corresponds to the distribution $v_E(E)$ constant ($E$ is the activation energy for diffusion) one obtains

$$\ln(\tau_m/\tau_i) \frac{d(q/q_\infty)}{d \ln t} = 1 - 4 \pi^{3/2}(t/\tau_{\infty})^{1/2} - (8/\pi^2) \exp(-t/\tau_i)$$

(52)

where $\tau_i$ and $\tau_m$ are respectively the lowest and highest values of $\tau$ in the system.

The plot of $q/q_\infty$ against $\ln t$ predicted by this equation is concave at small $t$ convex at large $t$ and linear at intermediate $t$. The linear part is given by

$$\ln(\tau_m/\tau_i) \frac{d(q/q_\infty)}{d \ln t} = 1$$

(53)

and it applies at a wide range of time when the heterogeneity is high (wide range of validity for the relation $\tau_i \ll t \ll \tau_m$). High heterogeneity also manifests itself by a decrease of the slope of the linear part. These results are analogous to those obtained when eqn 24 is extended to heterogeneous surfaces, (see the sequence of equations 39 to 43).

3.3. Application of theoretical equations to experimental data

Equation 45 represents a family of equations all of which reduce to the approximations given by eqns 46, 47 and 48 at appropriate coverages. An equation in this family, e.g. cases 1 to 4 in Table 1, is characterized by a single set of related parameters ($a_n$, $b_n$, $k_i$, $k_f$ etc); but an experimentally determined isotherm is characterized by the above-mentioned set of parameters and by a specific parameter $r^2/D$. Equation 24 although derived from kinetics determined by a chemical reaction, largely behaves as a member of...
this family of equations (Aharoni & Birnholtz 1980) (case 5 in Table 1). It obeys eqns 46, 47, 48 (see eqns 27, 28, 29), and assuming that $A^{-1}$ represents the parameter $r^2/D$ one can assign a characteristic set of parameters $k_0$, $k_f$, $\alpha$, $A/q_\infty$ etc.

One can fit a theoretical equation to experimental results and deduce the set of parameters characteristic of the geometry and the parameter $r^2/D$ if data extend through a sufficiently wide range of coverage viz ranges of applicability of eqns 46 to 47 (see Fig. 15). In some cases obtainable data are in the range of applicability of one of the approximations only and one cannot deduce both the geometry and $r^2/D$.

For models based on a reaction at a heterogeneous surface or diffusion in a heterogeneous medium (eqns 39 to 43, eqn 44, eqn 52), additional parameters are required; mostly parameters related to equilibrium properties of the system and application of a theoretical model requires a set of measurements at various temperatures and pressures. Data at a single temperature suggests the degree of heterogeneity: in highly heterogeneous materials the plot of $q$ against $\ln t$ is linear at a wide range of $t$ and its slope is small.

4. ISOTHERMS LINEAR AT SMALL COVERAGE

4.1. Empirical relations

It has been observed (Hayward & Trapnell 1964a) that in isotherms for activated chemisorption the rate continuously falls with increasing coverage, whereas in isotherms for non-activated chemisorption the initial rate is independent of coverage. The plot of $dq/dt$ against $q$ corresponding to an S-shaped $z$-$t$ isotherm is generally a plot governed by eqns 12, 3 and 5 successively, at increasing coverage, i.e. it is a descending curve concave towards the $dq/dt$ axis with $|d(dq/dt)/dq|$ continuously decreasing (e.g. Fig. 10B). This means that the S-shaped $z$-$t$ plots apply to kinetics that have been generally associated with activated chemisorption. Examples of isotherms associated with non-activated chemisorption with $dq/dt$ changing slightly at small $q$, are depicted in Fig. 16 (Tompkins 1978). They also comprise a concave part similar to the graph in Fig. 10, but this part is delayed and preceded by a part that is almost horizontal. The plots of the sticking coefficient against coverage for adsorption of various gases on single crystal-planes (Schmidt 1974) in Fig. 17 seem to have a form similar to that of the graphs in Fig. 16 or at least to a part of these graphs.

The studies of Nagasaka & Yamashina (1971, 1972) and Nagasaka et al. (1973) on the adsorption of gases a low pressure show that isotherms with rapidly dropping initial rate and isotherms with constant initial rate can be obtained with the same adsorbent-adsorbate pair by merely varying the pressure. Figure 18 depicts the adsorption of nitrogen on titanium at 973 K. It shows that at low pressure (e.g. $10^{-5}$ Torr, 1.3 mPa) the slope of the log log plots is 1 and the adsorption obeys the linear relation

$$q = k_n t$$

where $k_n$ is a constant. At higher pressure (e.g. $10^{-4}$ Torr, 13 mPa) eqn 54 is valid during a small range of $t$ at the beginning of the run and a range consistent with eqn 1 follows (i.e. the slope of the log-log plot = 0.5). When pressure is increased further (e.g.
Figure 16. Sticking probabilities as function of amount adsorbed for tungsten and different adsorbates: (A) Caesium, (B) Nitrogen at surface temperature $T_s = 113$ K, (C) CO at $T_s = 340$ K, (D) $N_2$ at $T_s = 298$ K (Tomkins, F. C. 1978 Chemisorption of Gases on Metals p. 34. Reproduced with permission. Copyright Academic Press Inc. (London) Ltd.).

Figure 17. Sticking coefficients $S$ against fraction of saturation coverage $\theta$ on several single-crystal planes at 300 K. (The shapes of the curves have more significance than absolute values of $S$) (Reproduced from Schmidt 1974, p. 115, by courtesy of Marcell Dekker, Inc.).
10^{-1} \text{Torr, 0.13 Pa) eqn 1 is applicable from the beginning of the run. The critical range of pressure at which the rate law changes, increases with temperature. Similar changes from a linear relation to a parabolic relation are also obtained in the sorption of oxygen on titanium (Nagasaka & Yamashina 1971) and on zirconium (Nagasaka, Uyeda & Yamashima 1973).

The suggestion that isotherms with constant initial rate (eqn 54) are associated with chemisorption at low pressures is not in opposition with the experimental evidence that led to the association of these isotherms with non-activated chemisorption. Typical non-activated chemisorptions are adsorptions on clean and small specific surface area solids, such as evaporated films, filaments, single crystal planes, etc and these adsorptions are generally conducted at low pressures. Activated chemisorption often applies to granulated and powdered materials, supported catalysts and other large specific surface area materials and generally refers to experiments conducted at high pressures.

An unusual effect of pressure on the adsorption of hydrogen on ZnO (Cimino et al. 1963) is possibly related to the above-mentioned effects observed by Nagasaka, Yamashina et al. Slow introduction of hydrogen on the adsorbent appeared to cause a considerable increase of the rate of adsorption as compared with rapid addition.

The isotherms obtained by Nagasaka, Yamashina et al. at high pressures can be regarded as isotherms of type A (see section 1.1 above), consistent with ineq. 8. When pressure is lowered, a range at which

\[
\frac{dz}{dt} = 0
\]  

appears, preceding the range at which ineq. 8 is obeyed. Equation 55 is also applicable to the initial part of the graphs in Fig. 16 and to many other isotherms associated with non-activated chemisorption (or with low-pressure adsorption). The possibility that the concave part of these plots (that looks like the graph of Fig. 10B) is given by ineq. 8,
eqn 9 and ineq. 10 has not been investigated. The plots of the amount adsorbed against log t for the adsorption of oxygen on tungsten (Lopez-Sanchio & Segovia 1972) (Fig. 19) indicate that this is likely to be the case (cf Fig. 6).

Linear isotherms obeying eqn 54 are also observed in physical adsorptions on microporous materials, water on Saran charcoal (Dacey, Clunie & Thomas 1958), nitrogen and carbon dioxide on carbons with controlled pore openings (Koresh & Soffer 1981). However in these systems, change to parabolic kinetics occur when pressure is lowered.

4.2. The precursor-state theory

The precursor-state theory (Becker 1955; Ehrlich 1956; Kisliuk 1957, 1958; King & Wells 1972) has been widely applied to adsorption isotherms with initial rate independent of coverage (Weinberg, Comrie & Lambert 1976; Tompkins 1978). It is based on the assumption of an irreversible chemisorption preceded by a reversible precursor-state. In the treatment of Kisliuk (1957), a molecule in the precursor state at an empty site has a probability $P_a$ of becoming chemisorbed, a probability $P_b$ of desorbing and a probability $(1 - P_a - P_b)$ of moving to a new site. On a filled site the probability of becoming chemisorbed is zero, and the probability of desorbing $P'_b$ differs from $P_b$, the probability of moving to a new site is $1 - P'_b$. The sticking probability $S$ is taken as the sum of the probabilities of chemisorption on the first second third etc site visited by the molecule. It depends on the coverage $\theta$, and using simplifying assumptions it is found to be given by

$$S = S_0\left[1 + \theta K/(1 - \theta)\right]^{-1}$$

where $S_0$ is the sticking probability at zero coverage given by

$$S_0 = P_a/(P_a + P_b)$$
and $K$ a parameter given by

$$K = \frac{P'_a}{(P_a + P_b)}$$  \hspace{1cm} (58)

(Fig. 20). For dissociate adsorption (Kisliuk 1958), $S$ is given by

$$S/S_0 = \frac{(1 - \theta)^2}{1 - \theta(1 - K) + \theta^2 S_0}$$ \hspace{1cm} (59)

where

$$K = \frac{(P'_b - P'_a)}{(P'_a + P'_b)}$$ \hspace{1cm} (60)

For small values of $K$ (see Fig. 20) the plot of $S$ against $\theta$ varies slightly at small $\theta$ and drops abruptly at a larger $\theta$, and it can be fitted to isotherms with initial rate independent of coverage (Kisliuk 1957). It was noted however that in the region of large coverage, experimental isotherms often have a tail and approach the $S = 0$ axis asymptotically rather than at a finite slope as required by any of the precursor-state models (see Fig. 16 and Fig. 20).

For large $K$ eqn 56 reduces to eqn 24 (see eqn 33) the plot of $S$ against $\theta$ drops from the beginning of the run and the plot of $z$ against $t$ is $S$-shaped. It may be noted that a large value of $K$ means that a molecule in a precursor state at an empty site has a small probability of either being chemisorbed or desorbing (eqn 58) a situation consistent with activated chemisorption.

![Figure 20. Plots of $S/S_0$ against $\theta$ for various $K$ calculated according to eqn 56 (Kisliuk 1957, J. Phys. Chem. Solids 3. Reproduced with permission. Copyright Pergamon Press, Ltd.).](image)

### 4.3. Multistage chemical reaction

Turner (1975) applied to the data on the adsorption of oxygen on polycrystalline tungsten (Lopez-Sancho & Segovia 1972) (Fig. 19) a model that is also based on a reversible stage preceding irreversible ones. Assuming that reversible decomposition of $W_2$ proceeds a two-stage oxidation reaction one can write

$$W_2 \xrightleftharpoons[k_1]{k_2} 2W$$ \hspace{1cm} (61a)

$$W + O_2 \xrightarrow{k_3} WO + O$$ \hspace{1cm} (61b)

$$WO + O_2 \xrightarrow{k_4} WO_2 + O$$ \hspace{1cm} (61c)

$$O + O \xrightarrow{} O_2$$ \hspace{1cm} (61d)

The reactions were assumed to be of first-order with the constants $k_1$ to $k_4$. 

4.4. Theoretical models based on penetration of the sorbate into the bulk of the solid

Models based on penetration into the bulk of the solid, were applied to isotherms in which linear and parabolic ranges were identified. It is assumed that the linear range reflects unimpeded adsorption and dissolution and the parabolic one a diffusion process. Nagasaka, Yamashina et al. (1972, 1973) explained their above-mentioned results (Fig. 18) on the basis of the tarnishing model of Wagner (1958). The rate of dissolution is determined by the rate of arrival of the gas molecules to the surface and obeys a linear law until the limiting concentration for scale formation is attained. The kinetics for further adsorption are determined by diffusion through the scale and obey a parabolic law. Most of the gas is consumed by formation of more scale at the interphase with the bulk of the solid.

Beck and Miyazaki (1975) and Ablow and Wise (1982) explained the experimental results of Nagasaka, Yamashina et al., without assuming compact scale formation. Their models are based on Langmuirian behaviour at the surface and transport according to Fick's law in the bulk and they include assumptions concerning a relationship between the parameter values at the surface and in the bulk just below the surface. In the treatment of Ablow and Wise, the rate equation for associative adsorption is taken as

\[ \frac{dn_s}{dt} = k_a n_g (s_0 - n_s) - k_d n_s - (J_{ds} - J_{seg}) \]  (62)

where \( n_s \) is the surface density of the adsorbate \( s_0 \) its saturation value, \( J_{ds} \) and \( J_{seg} \) are respectively the dissolution and segregation fluxes across the selvedge from the surface to the bulk, and \( k_a \) and \( k_d \) kinetic constants. Bulk transport is given by

\[ \frac{\partial n_b}{\partial t} = D \frac{\partial^2 n_b}{\partial x^2} \]  (63)

where \( D \) is a diffusion coefficient and \( x \) the distance from the surface. Various models for the surface to bulk flux were considered, viz. eqns 64(a) to 64(c) for the dissolution flux and corresponding ones for the segregation flux.

\[ J_{ds} = (k_{ds}/s_0)n_s \]  (64a)

\[ J_{ds} = (k_{ds}/s_0)(n_s - b_{bp}) \]  (64b)

\[ J_{ds} = (k_{ds}/s_{bp}b_{bp})n_b (s_{bp} - n_{bp}) \]  (64c)

where \( n_{bp} \) is the bulk planar concentration and \( s_{bp} \) its saturation value. The kinetics for the overall sorption process are obtained by combining eqns 62, 63 and one of eqns 64; analytical solutions for early and late times were formulated. The model represented by eqn 64c is consistent with the experimental results and leads to a linear equation valid at a sufficiently wide range of coverage at early time.

In physical adsorption on microporous solids linear isotherms are assumed to occur when normal penetration into the pores is impeded. Koresh & Sofer (1981) suggest that a surface barrier arises from a thin layer close to the outer surface of the adsorbent.
4.5. Relation between models leading to an S-shaped z-t plot and models leading to an isotherm linear at small coverage

Models based on penetration of the sorbate into the bulk of the solid or into a sub-surface zone lead to eqn 45 and to an S-shaped z-t plot if the range of unimpeded uptake is negligible and if the zone accessible to the sorbate is of limited thickness (limited value of \( r \) in eqn 45). However, if there is a significant range of unimpeded uptake, the model leads to an equation with linear initial rate. If the accessible region is unlimited \( r \rightarrow \infty \), equilibrium is not approached during a finite period of time, the parabolic equation eqn 46 persists indefinitely and the ranges corresponding to the Elovich equation (eqn 48) and to the Langmuir-like equation (eqn 47) are never attained.

The model based on surface migration from patches of low activation energy into patches of high activation energy mentioned in the first paragraph of Section 3.1 also leads to eqn 45 and to an S-shaped z-t plot. The assumption that the low energy patches are instantly filled was included in the model. This assumption is not valid under all conditions and a situation of unimpeded uptake can be assumed for this case also.

The models based on a chemical reaction discussed in section 2 can also lead to an equation with a linear initial rate. The rate of adsorption \( d\theta/dt \) predicted by eqn 32 is very high at small \( \theta \) and reaches infinity at \( \theta \rightarrow 0 \). There is obviously a range at which the rate of adsorption is smaller than the one predicted by the equation and at which it is limited by the rate of collision of the gas molecules with the surface (Ward & Findlay 1972). This corresponds to the range at which the assumption \( \gamma \ll g\theta \) introduced (Aharoni & Ungarish 1977a) in the derivation of eqn 24 is not valid. By introducing suitable assumptions linear kinetics can be assigned to the initial range in these models.

5. CONCLUSION

A rate equation for adsorption is expected to be affected by characteristics of the surface and of the surface-adsorbate bond and to reflect some of these characteristics. This means that one should expect different rate equations for different adsorbent-adsorbate pairs. They should have some common properties, however, that are to be associated with the process of adsorption itself, independently of the nature of the reactants.

This review attempts to show that the rate equations for various adsorbent-adsorbate pairs have a common property; the reciprocal of the rate against the time is convex at small t and concave at large t and a region of constant rate sometimes precedes the convex region. This property of the reciprocal of the rate means that there are limiting functions to which the rate equations reduce at certain limiting values of the coverage: a power function at small coverage, an Elovichian function at a particular point at intermediate coverage, and a Langmuir-type function at high coverage. A linear function may also precede these. This property of the reciprocal of the rate also defines a family of rate equations but it does not define a particular rate equation.
It was shown that equations consistent with the S-shaped z-t plot can be derived by assuming that the kinetics are determined by the rate of a chemical reaction or by assuming that they are determined by diffusion processes. In both cases one can assume either a homogenous surface or a heterogenous one and one can introduce various forms and degrees of heterogeneity. It is probable that only a detailed study of the applicability of the resulting equations will lead to discrimination between these possibilities.

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