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Conditions for a Rate-Maximizing Temperature in Heterogeneous Catalysis[1]

Conditions are derived for Langmuir–Hinshelwood and Eley–Rideal heterogeneous catalytic reactions to have a reaction rate maximum as a function of temperature. Experimental results contradict previously derived conditions which assumed that the surface diffusion was governed by a single transition rate. More than one transition rate will enter the analysis of surface diffusion if the surface is heterogeneous or, as observed in field ion microscope experiments, the reactant passes through several nonequivalent configurations while migrating. An analysis of the rate of reaction when more than one transition rate is involved leads to a condition which could facilitate the interpretation of rate maximum reaction mechanisms.

A number of heterogeneous catalytic reactions exhibit a reversible maximum rate of reaction as a function of temperature (*1–4*). For example, Moffat and Clark (*4*) found a rate–temperature maximum in their study of the disproportionation of olefins (propylene) on cobalt–molybdate–alumina (Co–Mo–Al_2O_3) catalyst. At temperatures below $T_{\max}$ they found the reaction rate, r, to obey a Langmuir–Hinshelwood equation for bimolecular reactions

$$r = k[Kp/(1 + Kp)]^2, \tag{1}$$

where k is the transition rate of diffusion and reaction of the reactants on the surface, K is the ratio of adsorption to desorption rates, and p is the pressure of the gaseous species. The factor in square brackets in the above equation is the equilibrium fractional surface coverage.

Usually, Arrhenius activated forms are assumed for both k and K (*4–6*), i.e.,

$$k = A \exp(-E/RT)$$

and

$$K = \exp(\Delta S/R) \exp(-\Delta H/RT), \tag{2}$$

where E is the activation energy for diffusion, ΔS is the differential entropy of adsorption, ΔH is the heat of adsorption, and A is a preexponential (frequency) factor. Substituting Eq. (2) into the equation for r and setting the derivative of the resulting expression with respect to temperature equal to zero yields the condition for a rate–temperature maximum. When the adsorption step of the reaction is exothermic ΔH is always negative, and the rate maximum condition is (*4–6*)

$$|\Delta H| > \frac{E(\beta + 1)}{2}, \tag{3}$$

where $\beta = p \exp(\Delta S/R)$ which is usually much smaller than unity. Note, that from Eq. (1), a plot of $1/r^{1/2}$ versus $1/p$ would yield values for k and K from which the activation energy E is obtained as

$$E = -\frac{\partial \ln k}{\partial(1/RT)}. \tag{4}$$

The heat of adsorption, ΔH, is obtained from the adsorption equilibrium constant K via

$$-\Delta H = \frac{\partial \ln K}{\partial(1/RT)}. \tag{5}$$

Moffat and Clark (*4*) found the values E = 8.2 kcal/mole and $|\Delta H|$ = 2.8 kcal/mole in a system which exhibited a rate–temperature maximum. However, these values violate the condition for a rate maximum as given in Eq. (3). To reconcile this problem Aldag and Clark (*5*) invoked het-

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erogeneity of the surface toward adsorption and desorption. A critique of their interpretation is presented in Appendix A.

We proceed to propose mechanisms where the Langmuir–Hinshelwood form of Eq. (1) is preserved, but the rate–temperature maximum condition (Eq. (3)) is modified, leading to conclusions consistent with the experimental data. Common to the mechanism which we propose is the property that the reactant transport (diffusion) on the surface is characterized by more than one rate constant. Two possible mechanisms are considered: (i) multistate diffusion, and (ii) diffusion on a heterogeneous substrate.

(i) *Multistate diffusion.* When the propagation of the diffusing species involves transitions between more than one state the mechanism is termed multistate diffusion. Such a mechanism occurs when the reactants perform transitions between several spatial configurations in the course of propagation. A number of systems exhibiting such a behavior have been observed using field ion microscopy (FIM) (*7*). For example, the motion of tungsten dimers on a W(211) surface (*8, 9*) involves transitions between alternating staggered and straight configurations which are characterized by different rate constants. It is plausible that the motion on a surface of a species as complex as an olefin would involve a number of transitions between distinct configurations of the molecule. Out of these transitions those with the highest activation energies would be the rate-limiting steps of the migration. Another multistate mechanism occurs when the adsorbed reactants may exist in two (or more) states which are distinguished as mobile and immobile states (Lennard-Jones mechanism (*10*)). When in the immobile state the particle merely vibrates in the potential well which binds it to the site and also performs transitions to a higher energy state through which it may propagate. (At normal temperatures propagation through the mobile state is the dominant mode of activated intersite transitions. At low temperatures one may include in addition spatial transitions through the lower-energy states which correspond to nonactivated, tunneling transport).

For systems in which the motion of the diffusing particles involves more than a single transition rate, the diffusion constant and hence the rate k (see Eq. (1)) is modified from the customary single-exponential, Arrhenius activated form (see Eq. (2)). For example, for the motion of a species which is characterized by two distinct states (configurational or energetic in origin) participating in the migration mechanism (with corresponding transition rates A and B), a random-walk model allowing for the presence of internal states yields (*8, 9, 11–13*) (see also Appendix B) for k the expression

$$k = \frac{AB}{A + B} \tag{6}$$

where the rates A and B may both be written in activated Arrhenius forms. We choose

$$A = \nu_A \exp(-E_A/RT)$$
$$B = \nu_B \exp(-E_B/RT) \tag{7}$$

where ν_A, ν_B are frequency factors and E_A, E_B are the activation energies for the two states, respectively. If a straight line results from an experimental plot of log k versus $(RT)^{-1}$, this does not necessarily imply that $k = \nu \exp(-E/RT)$ and that k cannot be of the form given in Eqs. (6) and (7). In practice, a plot of log k given by Eqs. (6) and (7) versus $(RT)^{-1}$ for typical experimental temperature ranges will yield a straight line of slope $-E_A$ if

(i) $E_A \approx E_B$;

$$\text{or (ii) } E_A \gg E_B + RT \ln \frac{\nu_A}{\nu_B}. \tag{8}$$

Such cases have been encountered in the analysis of multistate cluster motion on surfaces observed via FIM (*9*), where more than one rate-limiting step is involved in the transport, but still the semilogarithmic plot of mean squared diffusion distance versus inverse temperature yields an apparent straight line. It is only recently (*11, 12*) that an analysis has been given to find all the individual activation energies and frequency factors which comprise the diffusion constant, from field ion microscope data.

Using the transition rate as given in Eqs. (6) and (7) the following condition is found for a rate maximum of r to occur,

$$\frac{1 + p\exp[\Delta S/R - |\Delta H|/RT_m]}{2|\Delta H|} = \frac{A + B}{E_B A + E_A B}, \quad (9)$$

where T_m is the maximizing temperature. Let us denote the RHS by Γ. A linear analysis shows that if p is decreased by an amount δp then T_m will be decreased by an amount δT_m, where

$$\delta T_m = \delta p \exp[\Delta S/R + |\Delta H|/RT_m] RT_m^2/|\Delta H| \times \{2|\Delta H|\Gamma - 1 + 2AB [\Gamma(E_A - E_B)/(A + B)]^2\}^{-1}. \quad (10)$$

This is in accord with the experimental result that a decrease in pressure lowers the maximizing temperature (*4*). Neglecting $p \exp(\Delta S/R)$ compared to unity (*4*) we find for the existence of a rate maximum the inequality

$$\nu_A(2|\Delta H| - E_B) > \nu_B(E_A - 2|\Delta H|), \quad (11)$$

where we have assumed, without loss of generality, that $E_A > E_B$. In contrast to Eq. (3) this inequality could be satisfied by the measurements of Moffat and Clark (*4*) who found E_A = 8.2 kcal/mole, $|\Delta H|$ = 2.8 kcal/mole, if $0 < E_B < 5.6\text{–}2.6\ (\nu_B/\nu_A)$ kcal/mole. In order for the diffusion to apparently be well described by a single transition rate, the second inequality in Eq. (8) must also be obeyed.

(*ii*) *Diffusion on a heterogeneous substrate.* Another possible mechanism for introducing more than one transition rate in the description of reactant diffusion is if the surface is heterogeneous. Consider a surface consisting of N_A and N_B sites, characterized by release rates A and B, respectively, of the diffusing species (with A and B given as in Eq. (7)). For a random placement of the two types of sites, in an approximation which neglects correlations between sites, the diffusion rate for the system is given by (*14*)

$$k = k_0 \left\{1 - c\left[\frac{\nu_B}{\nu_A} e^{(E_A - E_B)/RT} - 1\right]\right\}, \quad (12)$$

where $k_0 = \nu_B \exp\left(-\frac{E_B}{RT}\right)$ and $c = \frac{N_A}{N_A + N_B}$. Using the above expression the condition for a rate–temperature maximum is

$$(1 - c)\nu_A(2|\Delta H| - E_B) > c\nu_B(E_A - 2|\Delta H|) \quad (13)$$

for $E_A > E_B$. For the system studied by Moffat and Clark (*4*) the above inequality will be consistent with the data if $0 < E_B < \left[5.6 - 2.6\frac{c\nu_B}{(1 - c)\nu_A}\right]$ kcal/mole.

A similar analysis of an Eley–Rideal mechanism, with rate r given by

$$r = \frac{kKp^2}{1 + Kp}, \quad (14)$$

when the diffusion rate k is governed by two transition rates (Eq. (6)), yields the following expression for the maximizing temperature, T_m,

$$T_m = \frac{E_A - E_B}{R} \times \left\{\ln \frac{\nu_A}{\nu_B}\left(\frac{|\Delta H| - E_B}{E_A - |\Delta H|}\right)\right\}^{-1}. \quad (15)$$

In the above $p \exp(\Delta S/R) \ll 1$, and $\Delta H < 0$ have been used. Assuming $E_A > E_B$ yields the following inequality

$$\nu_A(|\Delta H| - E_B) > \nu_B(E_A - |\Delta H|) \quad (16)$$

for the existence of a rate-maximizing temperature. When k is governed by only one rate-limiting step, i.e., $k = \nu \exp(-E/RT)$ then the analogous inequality is (*4*)

$$E(\beta + 1) < |\Delta H|. \tag{17}$$

As is the case with a Langmuir–Hinshelwood reaction mechanism when Eq. (17) is not satisfied by the experimental data but a rate maximum occurs nevertheless, this may suggest that the surface diffusion of the reactants involves more than one transition rate, perhaps due to multistates (spatial or energetic) of the reactants, or surface heterogeneities. If more than two transition rates are involved inequalities more complicated than Eq. (11) can be derived.

Our objective in this note has been to incorporate possible diffusion mechanisms in the analysis of reactions obeying Langmuir–Hinshelwood or Eley–Rideal mechanisms which exhibit rate–temperature maxima. We have derived inequalities which constitute conditions for the existence of such rate maxima for heterogeneous systems and for multistate diffusion mechanisms. Subject to certain constraints the above derived inequalities could be satisfied by the experimental data. It is suggested that additional controlled experiments such as measurements of the rate-maximizing temperature as a function of pressure or field ion microscope multistate diffusion data would allow the estimation of the additional parameters [ν_B and E_B, see Eqs. (11) and (16)] introduced by our model.

APPENDIX A

In a recent study, Aldag and Clark (*5*) reconsidered the analysis of the experiments (*4*) of olefin disproportionation which exhibited a rate–temperature maximum for a Langmuir–Hinshelwood reaction. Their investigation was motivated by the fact that the values for ΔH and E determined from the pressure and temperature dependence of the data were inconsistent with the inequality given in Eq. (3). They consider that the Langmuir–Hinshelwood rate for a nonuniform surface can be represented by

$$r = kp^2 \sum_{i=1}^{N} \frac{K_i^2}{(1 + K_i p)^2} \tag{A1}$$

or an appropriate continuum limit. In the above the summation incorporates heterogeneity of the surface toward adsorption–desorption while the diffusion represented by k is regarded as taking place on a uniform surface. However, since the data (*4*) fit Eq. (1), i.e., the $N = 1$ case, they attempted to rewrite Eq. (A1) in a form with $N = 1$. They denote the sum in Eq. (A1) by $F(p)$, and write what is equivalent to the following identities:

$$\begin{aligned} r = kp^2F &\equiv kp^2F^3/F^2 \\ &\equiv \frac{kp^2F^3}{(F - H)^2}\,\frac{(F - H)^2}{F^2} \\ &\equiv \left[\frac{kp^2F^3}{(F - H)^2}\right] \\ &\quad \times \left[\frac{F/H - 1}{1 + (F/H - 1)}\right]^2. \end{aligned} \tag{A2}$$

The first bracket in Eq. (A2) is identified with k in Eq. (1) and pK in Eq. (1) is identified with $[F(p)/H(p)]-1$. $H(p)$ is chosen to be equal to $\sum_{i=1}^{N} K_i^2/(1 + K_i p)^3$. After these identifications, the resemblance of Eq. (A2) to Eq. (1) is only symbolic. The essential point is that Eq. (A1) is not equivalent to Eq. (1) and $H(p)$ which enters Eq. (A2) is completely arbitrary, thus making the choice of K arbitrary, as well as the apparent heat of adsorption, ΔH, which is calculated from K.

APPENDIX B

In this appendix we outline the derivation of the expression for the diffusion constant for a system which exhibits a multistate diffusion mechanism. The derivation proceeds via the continuous-time-random-walk with internal states model which we have developed recently. Since detailed discussions of the technique can be found elsewhere (*11–14*) we limit ourselves to a presentation of the main underlying ideas.

Consider a crystalline system where the propagation of the diffusing entity (single particle, multiparticle cluster) is characterized by transitions between internal states (energetic, e.g., mobile and immobile states, configurational). The spatial motion of the centroid of the diffusant can be mapped onto a lattice with a number of states in each unit cell. Such a mapping is shown in Fig. 1 where the case of a diffusant with two configurational internal states is considered. Transitions in the system are governed by a waiting-time probability density function $\Psi_{ij}(\mathbf{l},\mathbf{l}';\tau)$, for transitions $(\mathbf{l}',j) \rightarrow (\mathbf{l},i)$, where the couple $(\mathbf{l},i)$ represents position $\mathbf{l}$ in internal state i. For the above function we choose the form

$$\Psi_{ij}(\mathbf{l},\mathbf{l}';\tau) \equiv p_{ij}(\mathbf{l}' - \mathbf{l})\psi_j(\tau). \qquad \text{(B1)}$$

The factor $p_{ij}(\mathbf{l}' - \mathbf{l})$, structural in origin, is the probability that the transition is from $(\mathbf{l}',j)$ to $(\mathbf{l},i)$ and $\psi_j(\tau)d\tau$ is the probability that a transition out of state j occurs in the time interval $(\tau,\tau + d\tau)$. The function $\psi_j(\tau)$ reflects the underlying potential surface, and in the following we would take it to be of the form

$$\psi_j(\tau) = \lambda_j e^{-\lambda_j \tau}, \qquad \text{(B2a)}$$

$$\lambda_j = \nu_j e^{-E_j/RT}, \qquad \text{(B2b)}$$

where λ_j is the total rate of leaving state j and ν_j,E_j are the frequency factor and activation energy in the Arrhenius activated form for that rate.

The diffusion coefficient, D, is related to the variance, $\sigma^2(t)$ $[\sigma^2(t) = \langle l^2(t)\rangle$, for an unbiased motion], in the position of the centroid, in the long-time (diffusion) limit via

$$D = \lim_{t\to\infty} \frac{\sigma^2(t)}{2\,\epsilon t}, \qquad \text{(B3)}$$

where ϵ is the dimensionality of the random-walk lattice. Thus to calculate $\sigma^2(t)$ we need to derive an expression for the second moment of the probability distribution, $P_{ij}(\mathbf{l},\tau)$. The probability P of being at $(\mathbf{l},i)$ at time t (starting from the origin in internal state j at $t = 0$) is related to the probability propagator R of reaching $(\mathbf{l},i)$ *exactly* at time t by

$$P_{ij}(\mathbf{l},t) = \int_0^t R_{ij}(\mathbf{l},t - \tau) \times \left[1 - \int_0^\tau \psi_j(\tau')d\tau'\right] d\tau, \qquad \text{(B4)}$$

where the factor in square brackets takes into account events in which the centroid arrived at $(\mathbf{l},i)$ at an earlier time $t - \tau$ and no further transition has occurred by time t. The variance, $\sigma^2(t)$, is related to P as follows (*12*):

$$\langle l^2(t)\rangle = -\lim_{\mathbf{k}\to 0} \left[\frac{\partial^2}{\partial k^2} \sum_{ij} \sum_{\mathbf{l}} e^{i\mathbf{k}\cdot\mathbf{l}}\, P_{ij}(\mathbf{l},t) g_j\right], \qquad \text{(B5)}$$

where g_j is the initial occupation probability of state j.

For a semi-Markovian (continuous time)

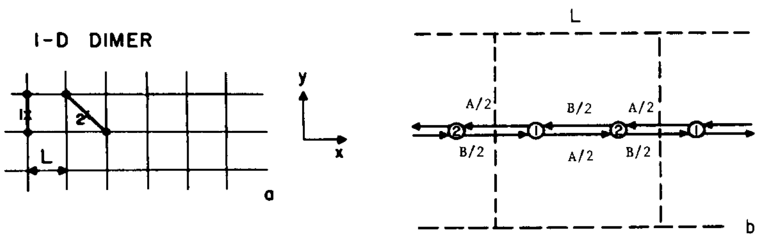

FIG. 1. One-dimensional two-state migration of a dimer. (a) The two nonequivalent states of the dimer which participate in the migration mechanism on the lattice are denoted by 1 (straight) and 2 (staggered). The lattice spacing is denoted by L and the dimer centroid is marked by x. (b) A mapping of the two-state mechanism shown in (a) onto a random-walk lattice with two states in the unit cell. The total transition rates out of states 1 and 2 are denoted by A and B, respectively. The arrows show the direction of the transitions between the states.

random walk the probability propagator R is related to $\underline{\Psi}_{ij}(\mathbf{l},\mathbf{l}';\tau)$, the fundamental function characterizing the motion, via (*12, 14*)

$$R_{ij}(\mathbf{l},t) - \sum_{s}\sum_{\mathbf{l}'} p_{is}(\mathbf{l}-\mathbf{l}') \int_0^t \psi_s(\tau) R_{sj}(\mathbf{l}',t-\tau)d\tau = \delta_{\mathbf{l},0}\delta_{ij}\delta(t). \quad \text{(B6)}$$

Since the above is in convolution form in both the spatial and temporal variables, Fourier ($\mathbf{l} \rightarrow \mathbf{k}$) and Laplace ($t \rightarrow u$) transformations, respectively, allow us to solve Eq. (B6) for R. Expressing all quantities as matrices of dimensions $N \times N$, where N is the number of internal states we obtain (*12, 14*)

$$\underline{\mathbf{R}}(\mathbf{k},u) = [\underline{1} - \underline{\mathbf{p}}(\mathbf{k})\,\underline{\Psi}(u)]^{-1}. \quad \text{(B7)}$$

Substitution of Eq. (B7) in Eq. (B4) for P and subsequent use of Eq. (B5) allow the calculation of the diffusion constant by taking the long-time limit of the resulting expression. We emphasize that the quantities specifying the transition rates between the internal states (frequency factors ν_j and activation energies E_j) determine Ψ and thus the diffusion constant D (denoted by k in the main text, see Eqs. (1), (2), and (6)).

For the special case of propagation via a two-internal-state mechanism in one dimension specific to the motion of a dimer (see Fig. 1) (other cases of higher dimensionality and increased complexity have been discussed by us elsewhere (*11–14*)) the matrix $\underline{\boldsymbol{\Psi}}$ is given by (for nearest-neighbor transitions)

$$\underline{\boldsymbol{\Psi}}(\mathbf{l},t) = \begin{pmatrix} 0 & \tfrac{1}{2}Be^{-Bt}(\delta_{l,0} + \delta_{l,L}) \\ \tfrac{1}{2}Ae^{-At}(\delta_{l,0} + \delta_{l,-L}) & 0 \end{pmatrix}, \quad \text{(B8)}$$

where L is the lattice spacing. Substituting Eq. (B8) in (B7) and following the subsequent steps yield

$$\sigma^2(t) \equiv \langle l^2(t) \rangle = \frac{AB}{A+B}(L^2 t/2). \quad \text{(B9)}$$

A similar analysis has been performed for other two-state diffusion mechanisms, such as mobile and immobile states (*12–14*). In all these cases the expressions for $\sigma^2(t)$ are in terms of the transition rates between states of the diffusant, and the transition rate of diffusion, k, in the kinetic equation (Eq. 1) cannot be expressed as a simple single-exponential Arrhenius form.

Turning to the case of diffusion on a heterogeneous surface, i.e., a surface which contains two types of sites, with different rates of release out of these sites, two alternative methods of calculation have been developed (*14*). The first is a defect-renormalization technique, in which the probability propagators are renormalized to include the effect of the nonhomogeneity of the surface. For lack of space we will not describe it further, and refer the reader to a recent publication (*14*). A second method is a generalization of the internal-state technique described above and consists of constructing superlattices with equivalent unit cells each containing an identical distribution of sites A and B. Thus, for example, the mapping in Fig. 1 can be considered as representing diffusion on a lattice with alternating sites A and B. For sites B a distance n lattice spacings apart, a unit cell with $n - 1$ sites of type A, and one of type B is used. The resulting expression for the diffusion constant is that given in Eq. (12). It is of interest to note that this expression is equivalent to that which is derived for a random distribution of the defects (sites B) in the average-t-matrix approximation, in which correlations between sites are neglected.

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