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Stochastic Theory of Bimolecular, Heterogeneous, Surface Catalytic Reactions

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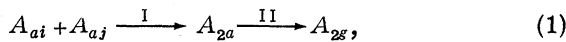
A stochastic theory of heterogeneous bimolecular reactions catalyzed by active sites is formulated using a defect-renormalized propagator method. Reaction between adsorbed migrating species occurs upon their coincidence on active sites and may demand proper internal-state configurations. Effects due to spatial heterogeneity, lattice structure, and internal states on the reaction evolution are analyzed.

We present a stochastic theory of bimolecular reactions catalyzed by a surface, which follow a *generalized Langmuir-Hinshelwood mechanism*,^{1,2} where adsorbed reactants *migrate* on the surface and reaction occurs only upon their coincidence on *active sites*.³ Additionally, the particles may possess *internal states* (energetic, spin configuration, or orientational) and the reaction cross section may depend on the internal states of the reacting species. Mechanisms involving reactant surface diffusion to active sites have been invoked recently in the analysis of several catalytic systems of interest: For example, based on statistical thermodynamics considerations it has been concluded that the disproportionation reaction of ethylene on a supported rhenium oxide catalyst⁴ (and similarly^{5a} for propylene on WO₃) proceeds via surface migration and subsequent

reaction on specific surface sites ("site-localized diffusion"^{5b}); molecular beam data of H₂/D₂ exchange on stepped Pt(111) surfaces have been interpreted in terms of adatom surface migration to surface steps where reaction occurs⁶; surface migration was found to be the rate-limiting step in a number of high-temperature reactions—the oxidation of polycrystalline Mo,⁷ the decomposition of formic acid⁸ above 455°K, the halogenation of Si and Ge surfaces,⁸ and the oxidation of the basal plane of graphite.⁹ In order to achieve a comprehensive understanding of catalytic systems of the type considered in this study, such as to allow an optimization of system parameters for maximum yield, it is necessary to construct a microscopic theory which goes beyond the traditional "mass action law" approaches. Our formulation and the derived expressions for the mean

and variance of the number of reactive particles incorporate characteristic parameters of the catalytic system (such as active-site and reactant concentrations, internal-state transition rates, site residence times, and lattice topology) and allow a systematic study of the time evolution of the reaction. In addition, considerations of defects other than the active sites (e.g., promoters or inhibitors of particle migration), which are of fundamental and practical interest, are included.

Consider an irreversible reaction scheme¹⁰ (a and g denoting adsorbed and gaseous species, respectively, and i and j specifying internal states of the reactants)



where the desorption step (II) is much faster compared to the binary collisional step (I) which involves a coincidence of reactants on active sites. The master equation governing step I is given by¹¹

$$\frac{dP(N, t)}{dt} = K(t) \left[\binom{N+2}{2} P(N+2, t) - \binom{N}{2} P(N, t) \right], \quad (2)$$

where $N(t)$ is a discrete random variable governed by the probability $P(N, t)$ of finding N particles (A_a) on the surface at time t , given $P(N, t=0) = \delta_{N, N_0}$; $K(t)$ is the reaction rate between any two adsorbed particles and all such binary events are included via the binomial factors. The solution to Eq. (2) is found via a generating-function technique from which moments of the probability $P(N, t)$ are obtained,¹¹ e.g., for the mean

$$\langle N(t) \rangle = - \sum_{n=2}^{N_0} A_n \exp\left[-\frac{1}{2} n(n-1)\theta(t)\right], \quad (3)$$

where the coefficients A_n are determined in closed form from the boundary conditions, and

$$\begin{aligned} C(t) &\equiv \sum'_{\bar{I}_1, \bar{I}_2} \sum_{i, j} \sum_{[m, n]} c_{mn}(\bar{I}^*, t | \bar{I}_1^i, \bar{I}_2^j) p_i(\bar{I}_1) p_j(\bar{I}_2) \\ &= \sum'_{\bar{I}_1, \bar{I}_2} \sum_{i, j} \sum_{\substack{[m, n] \\ [r, s]}} \int_0^t d\tau f_{mn}(\bar{I}^*, t - \tau | \bar{I}_1^i, \bar{I}_2^j) p_i(\bar{I}_1) p_j(\bar{I}_2) c_{rs}(\bar{I}^*, \tau | \bar{I}^*m, \bar{I}^*n), \end{aligned} \quad (5)$$

where $p_i(\bar{I})$ is the initial probability of occupying site \bar{I} in state i , \bar{I}^* is the location of the active site in the unit cell, in the primed summation the term $\bar{I}_1, \bar{I}_2 = \bar{I}^*$ is omitted [thus subtracting the event that two particles reacted at $t=0$, violating the initial condition $P(N, t=0) = \delta_{N, N_0}$], and $[v, w]$ indicates the set of reactive internal states. $c_{\mu\nu}(\bar{I}^*, t | \bar{I}_1^{\lambda_1}, \bar{I}_2^{\lambda_2})$ is the PD for bimolecular coincidence at time t on \bar{I}^* in the reactive internal states μ, ν given the initial positions and internal states $\bar{I}_1^{\lambda_1}, \bar{I}_2^{\lambda_2}$. The PD for the first such coincidence is denoted by $f_{\mu\nu}(\bar{I}^*, t | \bar{I}_1^{\lambda_1}, \bar{I}_2^{\lambda_2})$ which when averaged over initial states and reactive final states yields $F(t)$. Laplace transforming ($t \rightarrow u$) Eq. (5) we find

$$F(t) = \mathcal{L}^{-1} \left[C(u) / \sum_{[r, s]} \sum_{[m, n]} c_{rs}(\bar{I}^*, u | \bar{I}^*m, \bar{I}^*n) \right]. \quad (6)$$

the effective time $\theta(t) = \int_0^t K(t') dt'$.

The function $K(t)$ completely characterizes the reaction system and its evaluation is the major task involved. Novel results which emerge from our study are (a) the time dependence of $K(t)$ (achieving a constant value for large times), particularly for catalytic heterogeneous surfaces (containing active sites and defects), and for instances where the reacting species may have internal states, (b) the structural dependence of the rate $K(t)$.

Consider a crystalline surface with a periodic arrangement¹² of active sites and possibly other defects, on which adsorbed particles move independently unless they collide on an active site and both are in favorable internal states for reaction to occur (reactivity of an active site extending over an effective region can be easily incorporated in the formalism). The rate $K(t)$ is the *conditional probability density* (CPD) for reactant coincidence at an active site in the time interval $(t, t+dt)$ given that no such coincidence (reaction) occurred in the interval $(0, t)$. If we denote by $F(t)$ the PD for the first reactant coincidence (at an active site) at time t , $K(t)$ is given by

$$K(t) = F(t) / \int_0^\infty F(\tau) d\tau. \quad (4)$$

The 2D (two-dimensional) lattice is divided into unit cells of dimensionless area $\alpha\beta = \Omega^{-1}$ where α and β are the dimensions of the active-site-superlattice unit cell (with reference to the ideal lattice), each of which contains one active site at \bar{I}^* and periodic boundary conditions are employed. The first-coincidence PD, $F(t)$, can be calculated in terms of $C(t)$, the PD for coincidence (not necessarily the first) at time t [which is obtained via a random-walk formalism, see Eq. (7)], by considering that a first coincidence may have occurred at an earlier time $t - \tau$:

A reaction will occur on an active site at time t if (a) one reactant already resides on the site at time t , having arrived there earlier, and (b) the other reactant just arrives [or vice versa, thus the factor of 2 in Eq. (7)], and both are in the proper internal states. The probability corresponding to (a) of being at the active site, \bar{I}^* , in internal state i , given that at $t=0$ (\bar{I}, j) was occupied [with probability $p_j(\bar{I})$], is denoted by $P_{ij}(\bar{I}^*, t|\bar{I}, 0)$ and similarly $R_{mn}(\bar{I}^*, t|\bar{I}, 0)$ corresponding to (b). Averaging over initial positions and summing only over the set of internal states which lead to reaction (denoted by $[i]$), we obtain

$$C(t) = 2 \sum_{[i]} \sum_{\bar{I}, j} P_{ij}(0, t|\bar{I}, 0) p_j(\bar{I}) \sum_{[m]} \sum_{\bar{I}', n} R_{mn}(0, t|\bar{I}', 0) p_n(\bar{I}') - 2q\Omega^2\delta(t), \quad (7)$$

where q is the probability that both reactants are in reactive internal states. The last term in Eq. (7) subtracts the event that two particles reacted at $t=0$, violating the initial condition $P(N, t=0) = \delta_{N, N_0}$. The evaluation of P and R in Eq. (7) proceeds using a method of continuous-time random walk¹³ with internal states.¹⁴ In this method, motion of a particle is mapped onto a "random-walk lattice" composed of cells each of which contains internal states. The particle performs both inter-cell and intracell (between internal states) transitions, which are characterized by a function $\Psi(t) = \psi_{(\bar{I}', j)}(t) p_{ij}(\bar{I}, \bar{I}')$ where $\psi_{(\bar{I}', j)}(\tau) d\tau$ is the probability that a jump occurs in the interval $(\tau, \tau + d\tau)$ from (\bar{I}', j) given that (\bar{I}', j) has been occupied since $\tau=0$. [$\psi_{(\bar{I}', j)}(t)$ is called the waiting-time density function which relates to the *potential characteristics at a site*. Specific sites on the lattice, such as active sites, defects, and their neighbors, would be assigned different $\psi(t)$'s.] $p_{ij}(\bar{I}, \bar{I}')$ is the probability that given the jump occurs, it is from (\bar{I}', j) to (\bar{I}, i) . When we express all quantities as matrices of dimension $m \times m$ (where m is the number of internal states) the equation of motion for the propagator can be solved¹⁴ in Fourier and Laplace (denoted by tilde) space yielding

$$\bar{R}(\bar{k}, u) = [\bar{I} - \bar{p}(\bar{k})\bar{\psi}(u)]^{-1} \exp(i\bar{k} \cdot \bar{I}_0), \quad (8)$$

where \bar{I}_0 is the initial position of the particle.

$$\bar{R}(\bar{I}', u|\bar{I}, 0) = \sum_{k_x=0}^{\alpha-1} \sum_{k_y=0}^{\beta-1} [1 - \psi(u) p(k_x, k_y)]^{-1} \exp[-i\bar{k} \cdot (\bar{I}' - \bar{I})], \quad (9)$$

where $2p(k_x, k_y) = \cos(2\pi k_x/\alpha) + \cos(2\pi k_y/\beta)$ and $\psi(u) = A/(A+u)$. The propagator $P(\bar{I}', u|\bar{I}, 0)$ is obtained by multiplying the right-hand side of Eq. (9) by $(A+u)^{-1}$ [see comments following Eq. (8)]. In terms of the above, the denominator in Eq. (6) is given by the Laplace transform of the product $R(0, t|0, 0)P(0, t|0, 0)$. With use of Eqs. (7), (6), and (4) the resulting expression for the rate $K(t)$

To obtain \underline{P} [Eq. (7)], the elements of \underline{R} [Eq. (8)] are multiplied by the elements of the diagonal matrix $\underline{\tilde{\Phi}}$ given by $\tilde{\Phi}_{ii} = u^{-1} [1 - \tilde{\psi}_{(\bar{I}, i)}(u)]$, which accounts for events where the particle reached site (\bar{I}, i) at a time earlier than t and paused there. Substituting the above in Eq. (7) and assuming random initial occupation probabilities, we obtain an expression for $C(u)$.

The denominator in Eq. (6) can also be expressed in terms of the propagators \underline{P} and \underline{R} corresponding to paths of two particles which both begin and later coincide at the active site, \bar{I}^* . The resulting expression is in the form of a finite-lattice (periodic boundary conditions) Green's function which depends upon the structure of the lattice.¹⁵ Consequently, $F(t)$ and thus the rate $K(t)$ are determined by both the potential characteristics of the system [transition rates via the site waiting-time distribution function $\psi_{(\bar{I}, j)}(t)$] and by the surface structure.

To illustrate the method consider migrating particles on triangular, hexagonal, and square lattices with a concentration of active sites Ω , and the unit cell chosen such that the active site is located at the origin. The particles are assumed to be structureless and are assigned a characteristic function $\psi(t) = A \exp(-At)$ with A being the local transition rate from a site and all nearest-neighbor transitions are weighted equally. By use of the above in Eq. (8), the Laplace-transformed propagator R is obtained:

can be used to obtain the "effective reaction time" $\theta(t)$ [Eq. (4)] which completes the determination of $\langle N(t) \rangle$. While the evaluation of $K(t)$ for all times is possible (though complicated) it is instructive to analyze it at times sufficiently long for the initial transient behavior of $K(t)$ to decay. Such an analysis employs a result due to Montroll¹⁵ for the asymptotic behavior of $R(0, u)$

$\equiv R(0, u | 0, 0)$,

$$R(0, u) = \Omega [1 - \psi(u)]^{-1} c_1 \log \Omega + c_2 + c_3 \Omega + c_4 \Omega^2 + \dots + O(1 - \psi(u))^{1/2}, \quad (10)$$

where the c_i 's are constants dependent upon the lattice structure, for example $c_1 = 1/\pi$, $3^{3/2}/4\pi$, and $3^{1/2}/2\pi$ for square, hexagonal, and triangular lattices, respectively.¹⁵ In using Eq. (10) we note that $\psi(u) \rightarrow 1$ as the Laplace variable $u \rightarrow 0$, i.e. for large t . Employing an asymptotic analysis, we obtain for the rate a constant value given by

$$K = A/(1 + 2\eta), \quad (11)$$

where $\eta = -(c_1/\Omega) \ln \Omega + (c_2/\Omega) + c_3 + c_4 \Omega + \dots$. The rate diminishes as the concentration of active sites Ω is decreased since reaction occurs exclusively at these sites. The dependence of the rate K (Eq. 11) upon the structure of the substrate reflects the sampling of lattice sites by the propagating reactants prior to achieving a binary encounter, resulting in a reaction, on an active site. In general it is found that the rate constants order as $K_{tr} > K_{sq} > K_{hex}$, which is the same ordering as the coordination of these lattices and the structural effect is more pronounced for low active-site concentration Ω (e.g., for $\Omega = 10^{-1}$, K_{sq} and K_{tr} are larger by 7% and 16% than K_{hex} , and for $\Omega = 10^{-4}$ by 23% and 39% respectively). Furthermore, the rate of reactions of the type discussed above can be affected by defects which may inhibit or promote the migration of the reactants. These effects can be incorporated in the theory via the internal-state formalism¹⁴ or through a defect renormalized propagator method.¹⁶ When the influence of the defects or active sites extends to neighboring sites a further dependence on lattice structure is introduced.¹⁶ At short times the rate is time dependent. However, a measurement of the mean number of reactants on the surface, $\langle N(t) \rangle$ in Eq. (3), as a function t would allow a determination of the rate $K (= -N_0^{-1} d \ln \langle N(t) \rangle / dt)$.

Finally, calculations for a system of two-state reactants (mobile and immobile states), and where a bimolecular reaction occurs on active sites when both particles are in their mobile states, show similar structural dependence of the rate constant as well as variation due to the mechanism governing internal-state population.

The rate equation (2) provides a general description of bimolecular reactions of N particles. Different reactions are distinguished by the rate K whose calculation incorporating characteristics

of the system is of fundamental importance. For certain active-site catalyzed surface reactions we have related K to the underlying stochastic process, Ψ , which governs single-particle transitions. This was achieved by proceeding through a sequence of relations, employing single-particle probability propagators, to calculate the probability of reactive coincidences. The above results coupled with kinetical experiments (controlled measurements of reaction evolution on single-crystal surfaces) and data about the migration of adsorbed species (rates, structural and compositional dependencies) from field-ion microscopy¹⁴ and other methods could provide quantitative estimates of structural and potential surface parameters which control the rates of migration and active-site catalyzed bimolecular reactions.

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Has Two-Dimensional Superfluidity Been Seen in Real ⁴He Films?

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The theory of two-dimensional superfluidity by Nelson and Kosterlitz is examined in the context of ideal interacting ⁴He films. It is shown that superfluid onset in a film on a uniform surface would have a critical-temperature gap due to phase condensation. No experiments on uniform or heterogeneous substrates have disclosed any gap, indicating that superfluid onset in experimental films may have another origin.

In a recent Letter Nelson and Kosterlitz¹ predict that, if recent theories of phase transitions in the planar XY model are applicable to uniform two-dimensional ⁴He films, the areal density of superfluid will undergo a universal jump ρ_s as the critical temperature T_c is approached from below. The predicted relation is a linear dependence, with theoretical slope independent of the wall potential, coverage, and other details:

$$\lim_{T \rightarrow T_c^-} \left(\frac{\rho_s}{T} \right) = 2m^2 k_B / \pi \hbar^2 = 3.49 \times 10^{-9} \text{ g/cm}^2 \text{ K.} \quad (1)$$

Recent experiments by Bishop and Reppy² using a torsional oscillator and re-examination of third-sound experiments by Rudnick³ are in quantitative agreement with Eq. (1). In addition Bishop and Reppy cite third-sound results obtained by Mochel and by Hallock which are consistent with Refs. 2 and 3. The correspondence appears to confirm the theory and, at the same time, the judgment that the experimental films were indeed uniform two-dimensional (2D) systems. However, in this Letter I cite contrary evidence that makes it extremely unlikely that the films in question could have been uniform. On this basis, we are faced with (at least) two alternative explanations: (a) 2D superfluidity is not strongly affected by the kind of heterogeneity present in the experimental films, or (b) the agreement is fortuitous and an explanation of the data must be sought elsewhere.

Virtually all solid surfaces are heterogeneous in adsorption except for atomically clean and well-ordered crystals having a single class of crystal facet exposed to the adsorbed gas.⁴ Un-

less the uniformity of the substrate is demonstrated for the particular gas, physical property, coverage, and temperature conditions in question, then it is prudent to suspect it as heterogeneous. There are no reported studies demonstrating that the several substrates Mylar,² glass,³ argon-coated glass,³ and polished CaF₂³ used in the torsional oscillator and third-sound experiments are uniform in adsorption, and therefore the uniformity of the films has to be doubted. But even in the event that all of the substrates were ideal, the ⁴He films themselves would be nonuniform *in the plane*. This nonuniformity arises from the interactions between the He atoms themselves, which causes monolayers adsorbed on uniform surfaces to condense into 2D liquid phase at low temperature and, if the density is sufficiently high, to form 2D solid. In the following I discuss the experimental results for ⁴He on uniform surfaces, and explore the consequences of the theory of 2D superfluidity applied to such films.

Monolayer and multilayer films of ⁴He have been studied for many years. During the earlier period the substrates were typically heterogeneous adsorbents, and on these surfaces the films showed little evidence of any layer structure or phases within layers. The absence of structure is now understood to result from strong lateral fields due to substrate heterogeneity. However, since 1970 film studies on more uniform substrates have disclosed a succession of distinct regimes within the first and second adsorbed layers of ⁴He, ³He, and ⁴He-³He mixtures.⁵⁻¹² These adsorbents have been various high-area basal-plane graphite substrates and basal-plane graphite plated with monolayers of noble gases. The