

Rate Expression Incorporating Interaction between Reactants: Application to the Zero-Order Desorption Spectra

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A new and simple rate expression incorporating mutual interaction between reactants is presented within the framework of absolute-reaction-rate theory. The expression is derived by applying a simplified model of the lattice-gas Hamiltonian and working with it in the molecular-field approximation. Applications to the results of zero-order desorption spectra occurring in isothermal- and thermal-desorption measurements are discussed. Direct extension of the present results to the general inhomogeneous reactions suggests that the reaction rate would be zero order whenever an adsorptive reactant system is in the two-phase or multiphase coexistence region.

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At the present status of theoretical development in the reaction-rate theory, the conventional rate formula that one can use in analyzing experimental results has been confined to the simple Arrhenius one.¹ And in almost all the cases, disagreement between the experimental and theoretical values has been rendered to the neglect of interaction between reactants.^{1,2} The initial theoretical attempt to take the interaction faithfully into account was devised by Toya.³ Subsequently, many attempts have been made to treat his formulation as applicable to a variety of systems.⁴ However, none of them could derive a simplified rate expression nor could they formulate expressions in a form as compact as that of the Arrhenius equation. Hence, these expressions are too unwieldy to apply to experimental situations directly and therefore have not gained wider acceptance.¹ In the present paper, a new and very simple rate expression is derived which explicitly incorporates the interaction between reactant particles, and applied for the simple case of unimolecular desorption as an example.

Consider the system composed of mutually interacting particles adsorbed on the surface of a substrate, which provides a potential well for the adsorbates. We specify a coordinate of surface normal z , with $z=0$ at the substrate surface. At some distance $z=z^{\ddagger} > 0$ from the surface, we assume that the potential energy becomes maximum (or attains its flatness) and the local density of particles becomes minimum, i.e., the plane usually called the activated complex or the transition state.^{1,5}

According to absolute rate theory, the rate of desorption R per unit time and unit area is given by the density at the transition state, n^{\ddagger} , and is written as

$$R = \nu n^{\ddagger}, \quad (1)$$

where ν is the frequency factor of desorbing particles at the transition state. Starting from the original equation for desorption (1), we then calculate the density

n^{\ddagger} , applying the idea of the grand canonical ensemble.⁶ It is well known that the inclusion of interaction becomes much easier in a treatment of the grand canonical ensemble than that of the canonical ensemble which has been usually used in the conventional reaction-rate theory.^{5,6}

To simplify the modeling, we take only two layers of the two-dimensional (2D) lattice-gas system^{7,8} into account, i.e., the first layer of adsorbates (adsorbate layer) residing mostly at the bottom of the potential well and the one at the transition-state layer (transition layer).

The Hamiltonian for this lattice-gas system is

$$-\frac{H}{k_B T} = \frac{1}{\tau} \left[e \sum_{\langle i,j \rangle} \hat{n}_i \hat{n}_j + e^{\ddagger} \sum_{\langle i,j \rangle} \hat{n}_i \hat{n}_j^{\ddagger} - v \sum_i \hat{n}_i - v^{\ddagger} \sum_i \hat{n}_i + \mu \sum_i (\hat{n}_i + \hat{n}_i^{\ddagger}) \right], \quad (2)$$

where τ is temperature, and e , v , and μ are the nearest-neighbor interaction energy, potential energy, and chemical potential, being multiplied by a minus sign, respectively; the double-dagger superscript distinguishes quantities in the transition layer from those in the adsorbate layer; the occupation operator \hat{n}_i is equal to 1 (0) when site i is occupied (empty); the summation $\sum_{\langle i,j \rangle}$ extends over the first nearest-neighbor pairs of sites in each layer. With the use of the simplest molecular-field (or Bragg-Williams) approximation,^{6,8} one can derive the self-consistent equations for layer density n and n^{\ddagger} as follows:

$$[aen - v + \mu]/\tau = \ln[n/(1-n)], \quad (3)$$

$$[aen^{\ddagger} - v^{\ddagger} + \mu]/\tau = \ln[n^{\ddagger}/(1-n^{\ddagger})], \quad (4)$$

where a is the coordination number of the nearest neighbors in each 2D lattice-gas layer, and is equal to 6 for the triangular lattice which is considered in this paper.

Since the density at the transition layer, n^\ddagger , is very small as a result of the basic assumption of absolute rate theory, Eq. (4) is approximated as

$$[-v^\ddagger + \mu]/\tau = \ln(n^\ddagger). \quad (5)$$

Inserting it into Eq. (1), we obtain a rate expression

$$R = \nu \exp[(-v^\ddagger + \mu)/\tau], \quad (6)$$

and further eliminating μ between Eqs. (3) and (6), which means that the two layers are in equilibrium, we finally obtain the objective formula

$$R = \nu [n/(1-n)] \exp[-(aen + E_0)/\tau], \quad (7)$$

where $E_0 = v^\ddagger - \nu$ is the activation energy for desorption. If the interaction between the particles in the adsorbate and transition layers is added through the term $\epsilon \sum_{\langle i,j \rangle} n_i n_j$ to the Hamiltonian, Eq. (1), then the factor ae in Eq. (7) is replaced by $(ae - b\epsilon)$, where ϵ and b are the interaction energy and the coordination number of nearest neighbors between the two layers.

It should be noted that the effect of interaction appears through the variation of the chemical potential μ of the whole system, as seen from Eq. (6). Toya,³ however, considered that the short-range correlation at the transition state might be more effective for the complex behavior of the thermal-desorption spectra of hydrogen molecules from W(100), and treated the lattice-gas Hamiltonian in the Bethe-Peierls approximation, which is a better approximation than the present molecular-field approximation. However, he could not deduce a rate expression as simple and explicit as that of Eq. (7). It should be noted that Eq. (7) may be understood as a modified form of the regular Arrhenius-type formula with the activation energy being increased by the amount aen , and also with the preexponential factor divided by the factor $(1-n)$.

In the low-density limit, $n \rightarrow 0$, where the adsorbates can be viewed as a noninteracting ideal lattice gas, Eq. (7) reduces to the Arrhenius-type first-order rate expression,

$$R = \nu n \exp(-E_0/\tau), \quad (8)$$

which is a reasonable limiting form for our lattice-gas system.

In the high-density limit, $n \rightarrow 1$, Eq. (7) diverges because of the presence of the term $1/(1-n)$, which illustrates the fact that in that limit the particles are crammed most heavily in the first layer and which reflects in the divergence of chemical potential, $\mu \rightarrow \infty$, and ultimately causes the divergence of the density at the transition layer. The appearance of this kind of term is always expected to occur in the reaction system whereby the density of adsorptive reactants is confined from reaching the uppermost value. From the derivation presented above, it is clear that the rate expression, Eq. (7), is not valid in the higher-density region

near $n=1$, where multilayer adsorption⁸ would be present. This restriction of the validity is a shortcoming of the simplified two-layer model employed. Extension to the multilayer lattice-gas model can be readily made, however, at the cost of the simplicity of the rate expression.

The kinetic rate equation for the desorption is written as

$$-dn/dt = \nu [n/(1-n)] \exp[-(aen + E_0)/\tau]. \quad (9)$$

In the following examples, I integrate Eq. (9) numerically, and obtain isothermal-desorption spectra (ITDS), and thermal- (or flash) desorption spectra (TDS).

In the case of attractive interaction ($e > 0$), two-phase coexistence occurs in the low-temperature region $\tau < \tau_c$, where $\tau_c/e = \frac{3}{2}$ is the critical temperature for the 2D triangular lattice-gas system.⁶ In the two-phase coexistence region, the chemical potential remains constant,^{5,8} given by

$$\mu^* = -ae/2 + \nu \quad (10)$$

where the asterisk denotes the quantity at the two-phase coexistence. From Eq. (6), the constancy of the chemical potential $\mu = \mu^*$ during two-phase coexistence reflects the constant desorption rate, i.e., the zero-order desorption kinetics which are observed experimentally.⁹⁻¹¹ If one extends the above discussions directly, one can arrive at the universal rule that the reaction rate would be zero order whenever the system remains in the region of two-phase or multiphase coexistence of adsorptive reactants, the situation expected to occur frequently in inhomogeneous catalytic reactions. The densities at the boundaries of two-phase coexistence in the τ vs n phase diagram are given by solution of the following equation for n^* ,^{6,8}

$$ae(n^* - \frac{1}{2})/\tau = \ln[n^*/(1-n^*)]. \quad (11)$$

The relevance of the theory developed is examined by applying it to the experimental ITDS for Xe/CO/W(110)¹⁰ shown in Fig. 1(a). In the nearly flat part A-B indicated in the figure, the zero-order desorption operates, and outside of the flat part the quasi-first-order one does. Calculations of ITDS's using Eq. (9) are performed for various fixed temperatures with the initial density $n_{\text{init}} = 0.98$ and are illustrated in Fig. 1(b). Comparing overall shapes of the calculated ITDS's [Fig. 1(b)] with the experimental ones [Fig. 1(a)], we can determine the fitted parameters of $\tau = 1.25e = 55.3$ K, which gives the values of interaction energy $e = 0.088$ kcal/mol, and the critical temperature $\tau_c = 66.4$ K. Furthermore, equating the experimental and calculated times when zero-order desorption terminates (the point B in Fig. 1), we obtain $0.775t_0 = 43.0$ sec, where the scaling factor for the

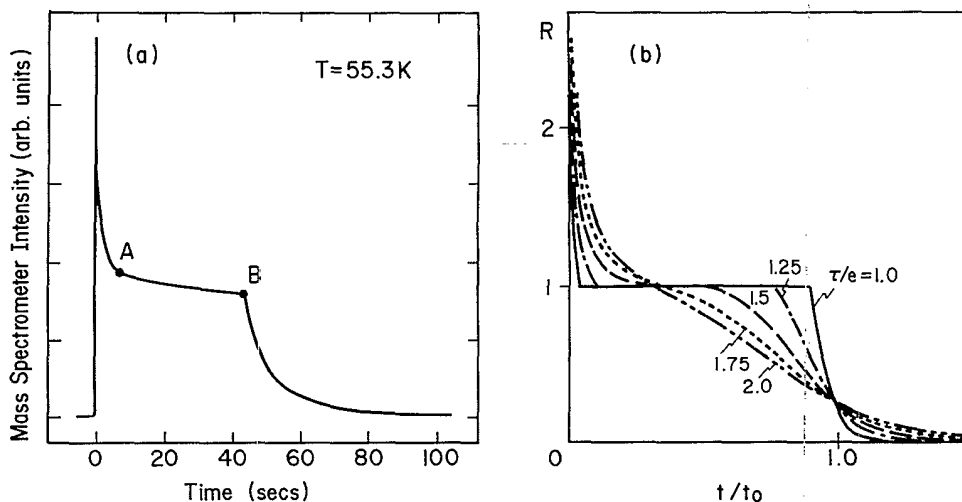


FIG. 1. (a) Experimental ITDS for Xe/CO/W(110) by Opila and Gomer (Ref. 10). The nearly flat part A-B indicates the zero-order desorption regime. (b) Calculated ITDS's for the various temperatures indicated. The unit of desorption rate R is set at $n = \frac{1}{2}$ and time is scaled by the unit of $t_0 = \exp[-(E_0 + a/2)/\tau]$. The flat part at $R = 1$ indicates zero-order kinetics given by Eqs. (6) and (10).

abscissa is $t_0 = \exp[-(E_0 + a/2)/\tau]$. The value of the activation energy E_0 deduced is 3.22 kcal/mol, which is in good agreement with the estimated value of 3.1 kcal/mol, obtained from the first-order desorption spectra of Xe/CO/W(110).¹⁰

Using these parameters, we next compute the TDS. Figure 2(a) shows the calculated TDS's starting with various initial coverages for a typical heating rate of $\beta = 25$ K/sec, and a frequency factor of $\nu = 1 \times 10^{13}$ sec⁻¹. Figure 2(b) shows the corresponding TDS trajectories in the temperature versus density phase diagrams.¹¹ "The common leading edge," one of the

characteristic features of zero-order desorption kinetics, in which spectra starting with different initial densities all coincide in the ascending portion of the TDS's, is seen in the figure.^{9,11} Within the two-phase coexistence region in Fig. 2(b), the zero-order desorption kinetics dominates, but outside, the quasi-first-order one does. When each trajectory in Fig. 2(b) crosses the phase boundary out to the single-phase region, the corresponding ITDS in Fig. 2(a) starts to deviate from the common leading edge; the crossing points are denoted with arrows. Inclusion of interaction gives rise to the variation of peak temperature

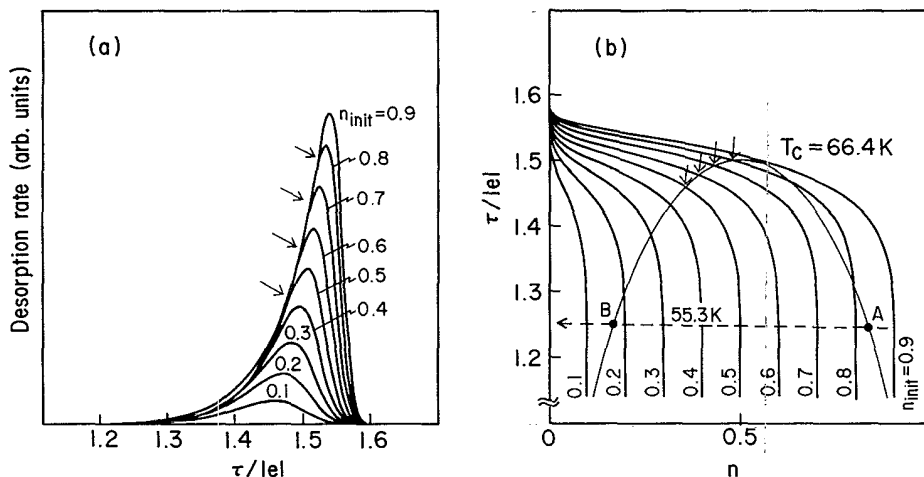


FIG. 2. (a) Calculated TDS's and (b) their trajectories in temperature vs density phase diagram, with initial densities n_{init} (the arrows indicate the crossing points from the zero-order to the quasi-first-order desorption kinetics). The parameters used are $e = 0.088$ kcal/mol, $E_0 = 3.22$ kcal/mol, and $a = 6$. Thin lines, the boundary of two-phase coexistence; dotted line, the ITDS trajectories of Fig. 1(a).

with initial coverage as clearly seen in Fig. 2(a), which is the feature usually observed in experiments¹² but not explained in the simple Arrhenius-type first-order expression.⁹

In summary, a simplified rate expression for unimolecular desorption of interacting adsorbate particles is reported on the original basis of the absolute rate theory. The resultant desorption rate reduces to the Arrhenius one in the low-density limit, and diverges as density approaches the upper-limit value. The relevance of this expression is examined by applying it to the zero-order desorption. The conclusion derived that the constant chemical potential in the two-phase coexistence region brings about zero-order desorption kinetics is expected to hold in more general cases. Extension to more complex reactions will be the subject of future communications.

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