Lattice influence on gas–solid desorption: RRKM model

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Transition state theory is frequently employed in the interpretation of gas–solid desorption kinetics.[1] The transition state is conventionally chosen to include all configurations in which the adatom is located at the onset of the exit plateau (exit barrier) or at the exit maximum (no exit barrier) of the gas–solid potential energy function. This choice leads to the following transition state thermal desorption rate constant

$$k_{TR}(T) = (\beta h)^{-1} [Z^+(\beta)/Z(\beta)] e^{-\beta D}. \qquad (1)$$

In Eq. (1), $\beta = (k_B T)^{-1}$, $Z^+(\beta)$, and $Z(\beta)$ are, respectively, the free solid and adatom plus solid partition functions, and D is the barrier height for desorption of the gas atom from the solid. Notice we have assumed the transmission factor is unity.

$Z^+(\beta)$ may be computed in the harmonic approximation from the solid normal mode spectrum $\rho(\omega)$. We expect that $\rho(\omega)$ will only be weakly perturbed by the adatom. Thus we compute $Z(\beta)$ from the approximate mode density

$$\rho_A(\omega) = \rho(\omega) + \delta(\omega - \omega_0), \qquad (2)$$

where ω_0 is the harmonic frequency of the adatom (computed from the curvature of the gas–solid potential function at its minimum). Eq. (1) with the approximation Eq. (2) reduces to

$$k_{TR}(T) \cong (\beta h)^{-1} (1 - e^{-\beta \hbar \omega_0}) e^{1/2 \hbar \beta \omega_0} e^{-\beta D},$$
$$\cong (\omega_0/2\pi) e^{-\beta(D - 1/2\hbar\omega_0)}, \qquad (3)$$

where the last equality in Eq. (3) holds in the classical ($\beta\hbar\omega_0 \to 0$) limit. This simple classical approximation is often employed in the interpretation of desorption experiments.[1]

Notice that Eq. (3) contains no lattice dynamical information; e.g., $k_{TR}(T)$ computed from Eq. (3) is independent of the solid Debye frequency ω_D. Equation (3) describes the thermal desorption of an ensemble of adatoms maintained at a temperature T but bound to a fictitious rigid solid. While a more realistic treatment of $\rho_A(\omega)$ than Eq. (2) would lead to a dependence of $k_{TR}(T)$ on ω_D, we expect that the dependence will be rather weak.

The insensitivity of $k_{TR}(T)$ to lattice motion is somewhat surprising given the great sensitivity of gas–solid collisional energy transfer processes to lattice or many-body effects.[2–5] Apparently the strong dependence on lattice motions of individual dynamical events is largely suppressed by thermal averaging.

To test this notion and to gain a clearer understanding of the desorption rate constant $k(T)$, we have examined the microcanonical rate constant $\tilde{k}(\overline{T})$ appropriate to an adatom–solid system of fixed energy per particle $k_B\overline{T}$. The rate constants $\tilde{k}(\overline{T})$ and $k(T)$ are related by

$$k(T) = Z^{-1}(\beta) \int_{E_0+D}^{\infty} N(E) e^{-\beta E} \tilde{k}(\overline{T}) dE, \qquad (4)$$

where E_0 is the zero-point energy of the solid, assumed to contain N_a atoms, and $N(E)$ is the density of states of the adatom–solid system at energy $E = (N_a + 1)k_B\overline{T}$. Since $\tilde{k}(\overline{T})$ contains more detailed information than $k(T)$ we expect $\tilde{k}(\overline{T})$ will display more sensitivity to lattice motion than $k(T)$.
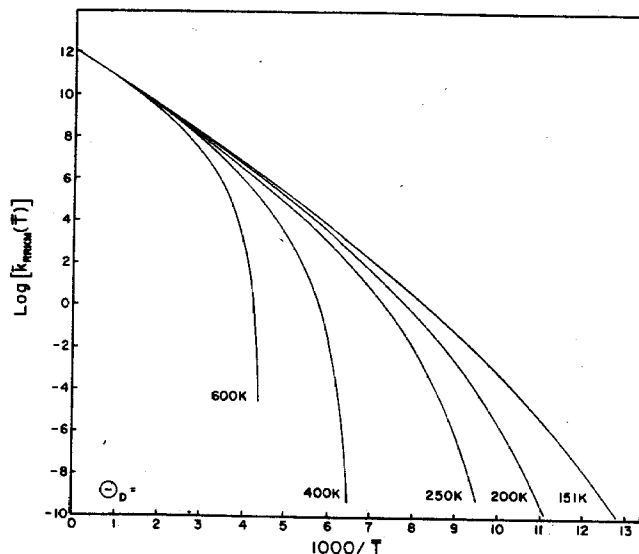

FIG. 1. $\text{Log}_{10}(\tilde{k}_{RRKM}(\overline{T}))$ vs $1000/\overline{T}$ for various Debye temperatures θ_D.

We employ the RRKM (Marcus–Rice) approximation[6] for $\tilde{k}(\overline{T})$ given by

$$\tilde{k}_{\text{RRKM}}(\overline{T}) = W^{+}(E-D)/h\,N(E) , \qquad (5)$$

where $W^{+}(x)$ is the total number of solid quantum states with energy less than x.

The RRKM model, Eq. (5), is simply a microcanonical form of transition state theory; thus the approximate $k(T)$ found by inserting Eq. (5) into Eq. (4) is just the transition state result $k_{TR}(T)$, Eq. (1).

Using the Debye model for the solid density of modes and the approximation, Eq. (2), we have computed[7] $\tilde{k}_{\text{RRKM}}(\overline{T})$. The parameters $\omega_0 (9.233\times10^{12}\,\text{s}^{-1})$ and $D(3064$ K) are appropriate to the xenon–silver (111) system.[8] The solid Debye temperature $\theta_D = \hbar\omega_D/k_B$ is varied between 151–600 K. The results are displayed in Fig. 1. At high $\overline{T}$ values the microcanonical rates are independent of lattice effects, i.e., θ_D. This is physically understandable since at very high solid energies, the desorption occurs on a time scale short compared to the response time of the solid. At lower $\overline{T}$, however, $\tilde{k}_{\text{RRKM}}(\overline{T})$ displays a strong dependence on θ_D. For example, at $\overline{T} = 167$ K (or $1000/\overline{T} = 6$), $\tilde{k}_{\text{RRKM}}(\overline{T}) = 6.8\times10^3$ s^{-1} for $\theta_D = 151$ K and $\tilde{k}_{\text{RRKM}}(\overline{T}) = 2.8\times10^{-2}$ s^{-1} for $\theta_D = 400$ K. This is a change of over 5 orders of magnitude.

The insensitivity of $k(T)$ to θ_D does not arise because only $\tilde{k}(\overline{T})$ values at very high $\overline{T}$ contribute importantly to the integral in Eq. (4). Rather, the integrand in Eq. (4) is a sharply peaked function of $\overline{T}$ and the peak energy $\overline{T}_0$ is a strong function of T. For example, $\overline{T}_0 = 167$ for $\theta_D = 151$ and $T = 160$ K. Thus we can conclude that the lattice effects are large for the microcanonical rate constants $\tilde{k}(\overline{T})$ but are obliterated in a nontrivial way upon thermal averaging.

The thermally averaged rate constant of Eq. (3) or (4) can be used to predict a thermal desorption curve.[1] The desorption curve for Xe/Ag will peak at $T_p \sim 100$ K. This is in good agreement with the Xe/W data[9] where the attraction between the gas and solid is stronger, thus the desorption comes at a higher temperature ($T_p \sim 150$ K).

We thus conclude that solid lattice motion plays an important role in desorption dynamics. The lattice effects are, however, masked by thermal averaging and are thus largely unobservable in conventional experiments. This is origin of the simple rigid lattice picture implicit in the transition state theory rate constant.

Our conclusions, while based on an analysis of desorption kinetics, are suggestive for other condensed phase rate processes. It appears not unlikely that the many-body problems involved in computing condensed phase thermal rates will be largely static rather than dynamic. From experimental viewpoint, thermal rates may depend importantly upon only gross potential parameters (e.g., ω_0 and D) and may be rather insensitive to the detailed dynamics of the substrate.

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[1] For recent reviews of thermal desorption, see for example, L. A. Péterman, in *Progress in Surface Science*, edited by S. G. Davison (Pergamon, New York, 1972), Vol. 3, Pt. 1, p. 1; V. N. Ageen and N. I. Ionov, *ibid.*, Vol. 3, Pt. 1, p. 1; D. Menzel, in *Interactions on Metal Surfaces*, edited by R. Gomer (Springer, Berlin, 1975), Chap. 7; and D. A. King, Surf. Sci. 47, 384 (1975).

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[6] See P. J. Robinson and K. A. Holbrook, *Unimolecular Reactions* (Wiley-Interscience, London, 1972) and references therein, especially, R. A. Marcus and O. K. Rice, J. Phys. and Colloid Chem. 55, 894 (1951) and R. A. Marcus, J. Chem. Phys. 20, 359 (1952).

[7] The density of states $N(E)$ for the solid plus adatom and total number of solid states $W^{+}(E-D)$ are determined by the steepest descent method given by Robinson and Holbrook, Ref. 6, pp. 144–146. The partition functions $Z^{+}(\beta)$ and $Z(\beta)$ are the only quantities needed for $W^{+}(E-D)$ and $N(E)$, respectively, and are defined by

$$Z^{+}(\beta) = \exp\left[\int_0^{\infty} \rho(\omega)\ln\left(\frac{e^{-1/2\,\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right) d\omega\right] ,$$

$$Z(\beta) = \exp\left[\int_0^{\infty} \rho_A(\omega)\ln\left(\frac{e^{-1/2\,\beta\hbar\omega}}{1-e^{-\beta\hbar\omega}}\right) d\omega\right] ,$$

$$\rho_A(\omega) = \rho(\omega) + \delta(\omega - \omega_0) ,$$

$$\rho(\omega) = \rho_D(\omega) = (N_a 3\omega^2/\omega_D^3)\,\eta(\omega - \omega_D),$$

and where $\eta(x)$ is a step function. The rate $\tilde{k}_{\text{RRKM}}(\overline{T})$ appears to be a function of N_a, since both $W^{+}(E-D)$ and $N(E)$ are very strong functions of N_a. However, the ratio of $W^{+}(E-D)/N(E)$ becomes constant as N_a increases. The value of N_a used in these calculations is typically 10^6–10^8 depending on $\overline{T}$ and θ_D.

[8] The barrier height D is from R. Sau and R. P. Merrill, Surf. Sci. 34, 268 (1973) and the frequency ω_0 from a Morse potential of Y.-W. Lin and G. Wolken, Int. J. Quant. Chem. "Quantum Model for Gas–Solid Energy Transfer: Role of Phonon Polarization and Propagation Direction," (in press).

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