

Thermal desorption of argon and neon from solid xenon. I. Transition state theory rate constants

John E. Adams and Jimmie D. Doll

Citation: *The Journal of Chemical Physics* **77**, 2964 (1982); doi: 10.1063/1.444218

View online: <http://dx.doi.org/10.1063/1.444218>

View Table of Contents: <http://scitation.aip.org/content/aip/journal/jcp/77/6?ver=pdfcov>

Published by the AIP Publishing

Articles you may be interested in

[Dynamics and mechanism of the non-adiabatic transitions from the ungerade \$I_2\(D_0 + u\)\$ state induced by collisions with rare gas atoms](#)

J. Chem. Phys. **133**, 244304 (2010); 10.1063/1.3517503

[Transition from single-file to Fickian diffusion for binary mixtures in single-walled carbon nanotubes](#)

J. Chem. Phys. **133**, 094501 (2010); 10.1063/1.3469811

[Four-component relativistic theory for nuclear magnetic shielding constants: Critical assessments of different approaches](#)

J. Chem. Phys. **126**, 214101 (2007); 10.1063/1.2736702

[Many-body interactions and high-pressure equations of state in rare-gas solids](#)

Low Temp. Phys. **33**, 545 (2007); 10.1063/1.2746249

[Transition of window breakdown from vacuum multipactor discharge to rf plasma](#)

Phys. Plasmas **13**, 123506 (2006); 10.1063/1.2403782



Thermal desorption of argon and neon from solid xenon. I. Transition state theory rate constants

John E. Adams^{a)} and Jimmie D. Doll

University of California, Los Alamos National Laboratory, Los Alamos, New Mexico 87545^{b)}
(Received 17 July 1982; accepted 10 June 1982)

Rate constants for thermal desorption of physisorbed argon and neon from a xenon(111) crystal face have been calculated using a generalization of Slater's unimolecular reaction rate theory, with a particular emphasis being placed on an investigation of the dependence of these rates upon the degree of surface coverage and upon the lattice motion of the solid. For argon our Monte Carlo results show a non-negligible coupling between adatom dynamics and the thermal vibration of the crystal surface which leads roughly to a 20% enhancement of the desorption rate. The increase is, however, only half as great for neon, with a static-solid description becoming appropriate as the system temperature is decreased. The adatom concentration effect on the kinetics also appears to be more dramatic for adsorbed argon than for neon, presumably as a consequence of the longer range and greater strength of the argon-argon potential.

I. INTRODUCTION

It is well known that desorption from solid surfaces represents one of the fundamental component processes of heterogeneous catalysis. An understanding of the dynamics of these events may consequently lead to an ability to forestall catalyst poisoning, or to an improvement in catalytic selectivity. From yet another point of view, one might also deduce from dynamical information those features of microscopic retention kinetics which would contribute to a more rigorous characterization of gas chromatographic separations. Even though the desorption problem is, therefore, clearly one which appears frequently in the study of a variety of important phenomenology, only in very recent years has some measure of insight into these processes been gained.¹

We have recently reported² the calculation of rate constants for the thermal desorption of helium from solid xenon via a generalization of Slater's theory³ for treating unimolecular processes. That formalism, which essentially describes transition state theory (TST), was shown to be particularly versatile in that it permits one to include effects of adatom-adatom interactions as well as concurrent diffusive motion. When coupled with a procedure for dynamically correcting the TST results⁴ so as to generate "exact" rate constants, such an approach to the study of desorption phenomena provides, we feel, a means for computing kinetic data that are comparable in accuracy with that derived from "state-of-the-art" experimental measurements.

In the present work, we extend our previous study² (hereafter, I) by including the motion of the lattice atoms, thereby completing the dynamical picture of the desorption process. Again the substrate is chosen to be a perfect xenon crystal. However, in this study we examine desorption of heavier rare gas atoms, specifically neon and argon, which are expected to exhibit a kinetic behavior analogous to that seen in the preliminary helium-xenon results and which are likely to

be described quite adequately by classical mechanics. Since one of our principal interests lies in exploiting the particular advantages of the Monte Carlo TST formalism we also include in Sec. III a consideration of the effects that lateral adatom interactions have on the observed desorption rate constants.

II. OUTLINE OF THE METHOD

Inasmuch as the transition state theory formulation used herein has been described previously,^{2,6} we shall only display the principal results at this point. For a stationary process $x = x(t)$ and some particular value of interest q ,⁷ one finds the number of "upzeros" of the function $x - q$ per unit time to be given by the expression

$$L(q) = \frac{1}{2} \left\langle \delta(x - q) \left| \frac{dx}{dt} \right| \right\rangle. \quad (2.1)$$

In the present case $x(t)$ describes the motion of an atom in the vicinity of a solid surface, with the assumption being that the species is adsorbed if $x(t) < q$, and unbound if $x(t) \geq q$. Thus, $L(q)$ becomes just the rate at which the adatoms desorb from the surface. We also note that Eq. (2.1) may be further simplified in the event that $x(t)$ describes a thermal process (for which the average is performed over a canonical ensemble):

$$L(q) = \frac{1}{2} \left(\frac{2k_B T}{\pi m} \right)^{1/2} \langle \delta(x - q) \rangle.$$

As in I, the remaining equilibrium average may be obtained via a Monte Carlo procedure that employs the Metropolis sampling algorithm. The usefulness of this method becomes particularly evident upon the inclusion of substrate dynamics inasmuch as one avoids the task of integrating the equations of motion for a large number of solid atoms over a long time interval. We are also able to take advantage of well-defined importance sampling techniques^{8,9} which allow us to compute results for a range of system temperatures in a single Monte Carlo calculation. It should be recognized, however, that since importance sampling introduces a weighting factor of the form

$$\exp \left[- \left(\frac{1}{k_B T} - \frac{1}{k_B T_0} \right) V(x) \right],$$

^{a)}Present address: Department of Chemistry, University of Missouri-Columbia, Columbia, MO 65211.

^{b)}Work supported by the U.S. Department of Energy.

TABLE I. Lennard-Jones 6-12 potential parameters.

| Rare gas pair | ϵk_B^{-1} (K) | σ (Å) |
|---------------|-------------------------|--------------|
| Ne-Ne | 42.3 | 2.74 |
| Ar-Ar | 119.8 | 3.405 |
| Xe-Xe | 281.0 | 3.89 |
| Ne-Xe | 75.0 | 3.34 |
| Ar-Xe | 171.0 | 3.69 |

[here $V(x)$ is the total potential energy and T_0 is some reference temperature at which the Metropolis sampling is actually performed] which varies more rapidly at lower temperatures, the practical utility of such a shortcut is likely to be realized only in a relatively high temperature regime.

Using the result obtained in Ref. 9, namely that within this TST framework the activation energy for thermal desorption is given by

$$E_a^{\text{TST}} = \frac{1}{2} k_B T + \frac{\langle V(x) \delta(x-q) \rangle}{\langle \delta(x-q) \rangle} - \langle V(x) \rangle,$$

we have, in addition, obtained Arrhenius activation energies via the same calculations in which the rates are determined.

III. RESULTS

Much of the computational scheme adopted in the present work is a direct carryover from the approach taken in I. All rare gas interactions are assumed to be modeled adequately by Lennard-Jones 6-12 potentials, with periodic boundary conditions being assumed. We cannot, of course, retain the Fourier expansion of the adatom-surface potential summation used previously, inasmuch as thermal motion breaks the surface's spatial symmetry. Consequently, a direct summation of two-body interactions must be employed in order to correctly reproduce distortions of the xenon crystal. The

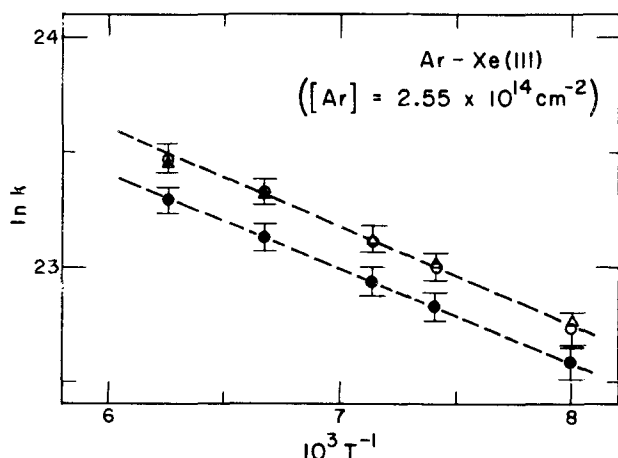


FIG. 1. Arrhenius plot for Ar-Xe(111), $[Ar] = 2.55 \times 10^{14} \text{ cm}^{-2}$. The curves correspond to calculations performed with (●) a static lattice, (○) 1 moving solid layer, and (Δ) 2 moving solid layers.

values of the potential parameters used in these calculations are given in Table I.¹⁰ Desorption was presumed to have occurred if an adatom moved to a position greater than 7.8 Å away from the surface plane.

We performed the Monte Carlo (minimum image) calculation for desorption from a rectangular crystal slab comprising 24 primitive lattice cells of (111) symmetry. The range cutoffs for the potential energy summations were then taken to be twice the nearest-neighbor internuclear separation for the solid, $2a = 8.68$ Å for fcc xenon. (The position of the counting surface indicated above was chosen so as to be compatible with this cutoff.) Adsorbate surface coverages could then be varied by changing the number of adatoms introduced onto the crystal slab. We should note that it will not be possible (as it was in I) to obtain "infinite dilution" results in the present calculation by setting the adatom-adatom potential to zero. Since the adatom-solid interactions are capable of inducing surface distortions, only by actually reducing the number of adatoms on the surface can one approach this limit.

A. Argon-xenon

In order to evaluate the effect of surface deformation upon the observed kinetics, we have generated Arrhenius plots for argon desorption ($[Ar] \approx 1/2$ monolayer) from a xenon crystal, the number of moving layers of which were varied from zero to two. (Two static layers were included in each case in order to anchor the crystal in space.) These results are displayed in Fig. 1. No statistically significant difference was found between the one and two moving layer rate constants, with both sets of results being roughly 20% larger than those obtained in the static solid limit. A rough calculation reveals that this rate difference arising as a result of lattice motion is merely a consequence of the potential interactions within this system. Briefly, the frequency of the desorptive motion perpendicular to the surface can be shown to be lower than the Debye frequency of the xenon crystal. One expects, therefore, that a coupling of the adatom motion to the thermal vibrations of the solid will drive the desorption process to a higher frequency, thus increasing the value of the associated rate constant. (This argument assumes that the pre-exponential frequency factor is the only contribution to the rate constant which changes appreciably upon the removal of the static-surface restriction. Values of the kinetic parameters listed in Table II lend support to just such an analysis.) The degree of coupling would, of course, be temperature dependent; however, the relatively narrow range of temperatures over which the Ar-Xe system was studied, does not appear to be large

TABLE II. Arrhenius parameters for Ar-Xe(111) $[Ar] = 2.55 \times 10^{14} \text{ cm}^{-2}$.

| Number of moving layers | $E_a k_B^{-1}$ (K) | A (s^{-1}) |
|-------------------------|--------------------|-------------------------|
| 2 | 457 (± 49) | 2.9×10^{11} |
| 1 | 477 (± 36) | 3.3×10^{11} |
| 0 | 427 (± 24) | 1.9×10^{11} |

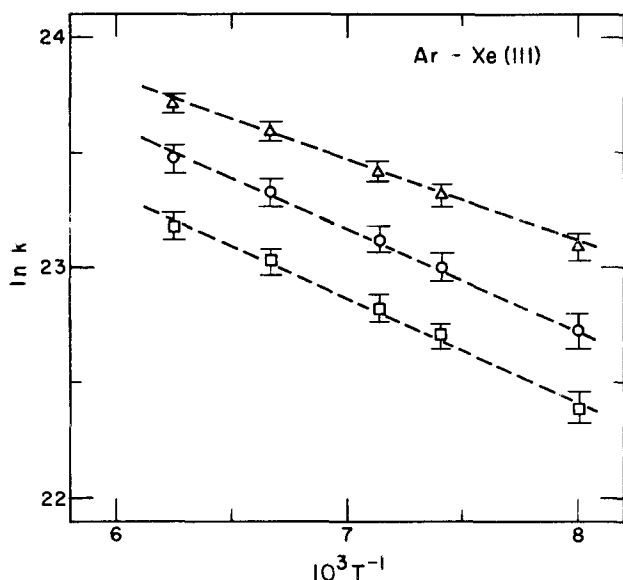


FIG. 2. Arrhenius plot for Ar-Xe (111), 1 moving solid layer. Argon concentration shown are (\square) $1.28 \times 10^{14} \text{ cm}^{-2}$, (\circ) $2.55 \times 10^{14} \text{ cm}^{-2}$, and (Δ) $3.83 \times 10^{14} \text{ cm}^{-2}$.

enough for a significant variation in the rate enhancement to be observed.

One might also guess that there should be a noticeable, albeit perhaps small, change in the rates upon "switching on" the motion of a second solid layer. The fact that we do not observe any appreciable change is to some extent an artifact of the Monte Carlo calculation scheme. Remember that the sampling techniques used herein are such that thermal equilibrium is imposed upon the system at each step. The real influence on desorption of the motion of additional layers would, on the other hand, be principally one of increasing the ability of the surface layer to accommodate energy transferred from the adatoms via the excitation of motion normal to the surface plane. Since artificial thermalization renders considerations of energy accommodation quite irrelevant, it is actually not surprising that a lack of sensitivity to the presence of a second moving layer is indicated. (A study currently in progress of energy transfer in this system suggests that, at least at low surface coverages, even a single moving layer can provide a reasonably good description of adatom energy dissipation.)

An indication of the dependence of the desorption rate upon surface coverage may be obtained from the results displayed in Fig. 2. There one finds Arrhenius plots

TABLE III. Arrhenius parameters for Ar-Xe (111) 1 moving solid layer.

| [Ar] (atoms cm^{-2}) | $E_a k_B^{-1}$ (K) | A (s^{-1}) |
|--------------------------------|--------------------|-------------------------|
| 1.28×10^{14} | 455 (± 36) | 2.1×10^{11} |
| 2.55×10^{14} | 477 (± 36) | 3.3×10^{11} |
| 3.83×10^{14} | 410 (± 35) | 2.8×10^{11} |

for three different concentrations of adsorbed argon, corresponding roughly to 1/4, 1/2, and 3/4 monolayer coverages. (In each case, movement of the outermost solid layer was permitted.) The kinetic parameters describing the curves are, in addition, given in Table III. Note first that increasing the argon coverage from 1/4–1/2 of a monolayer has little or no effect on the calculated activation energy. However, since at these lower coverages the adatoms do not approach each other sufficiently closely to feel the mutually repulsive interactions which lead to a decrease in E_a at higher coverages, it is hardly surprising that the only concentration dependence appears in the frequency prefactor. When the coverage is increased to 3/4 of a monolayer, the expected reduction in the activation energy does appear, presumably as a result of the dominance of close, repulsive Ar-Ar encounters over the longer range attractive interactions, although at this argon concentration the decrease is still fairly small.

B. Neon-xenon

From the potential parameters listed in Table I, one can make some general predictions concerning neon thermal desorption as compared with the corresponding argon results described above. In particular, the activation energy for desorption should be only a 1/3 to a 1/2 as great for neon as it is for argon. Coverage effects are also expected to be less marked for adsorbed neon inasmuch as the adatom-adatom interactions are much smaller in magnitude and shorter in range. Just such behavior does indeed appear in the high-temperature portion of the Arrhenius plots presented in Fig. 3. (The neon desorption rate constants can be reported for

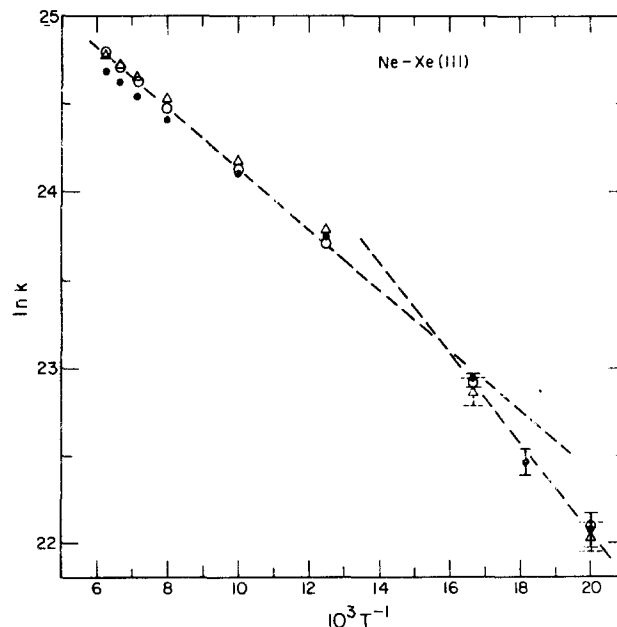


FIG. 3. Arrhenius plot for Ne-Xe (111). The points correspond to (\bullet) static lattice, $[\text{Ar}] = 2.55 \times 10^{14} \text{ cm}^{-2}$, (\circ) 1 moving layer, $[\text{Ar}] = 2.55 \times 10^{14} \text{ cm}^{-2}$, and (Δ) 1 moving layer, $[\text{Ar}] = 3.83 \times 10^{14} \text{ cm}^{-2}$. Unless indicated otherwise, the error bars (1 standard deviation) are of the dimension of the symbol or less.

TABLE IV. Arrhenius parameters for Ne-Xe(111).

| | [Ne] (atoms cm ⁻²) | $E_a k_B^{-1}$ (K) | A (s ⁻¹) |
|----------------|--------------------------------|--------------------|------------------------|
| $T_0 = 140$ K | | | |
| Static solid | 2.55×10^{14} | 154 (± 3.1) | 1.4×10^{11} |
| 1 moving layer | 2.55×10^{14} | 184 (± 11.0) | 1.8×10^{11} |
| | 3.83×10^{14} | 141 (± 8.8) | 1.4×10^{13} |
| $T_0 = 60$ K | | | |
| Static solid | 2.55×10^{14} | 174 (± 5.6) | 1.7×10^{11} |
| 1 moving layer | 2.55×10^{14} | 171 (± 8.6) | 1.6×10^{11} |
| | 3.83×10^{14} | 162 (± 14.0) | 1.3×10^{11} |

a considerably wider range of temperatures than can the argon results, simply because formal association of the adsorbed neon occurs at a much lower temperature. Although the Monte Carlo - TST formalism is easily adapted so that one may examine diatom desorption, in the present study we have considered only the monatomic process.¹ One finds the ratio of activation energies $E_a^{(\text{Ar-Xe})}/E_a^{(\text{Ne-Xe})}$ to be equal to 2.6 ± 0.4 (with E_a determined by a direct Monte Carlo calculation, $T_0 = 140$ K), a number which should be compared with the ratio of adatom-solid potential well depth $\epsilon^{(\text{Ar-Xe})}/\epsilon^{(\text{Ne-Xe})} = 2.8$. This comparison suggests that for two chemically similar species the relationship

$$\frac{E_a^{(1)}/\epsilon^{(1)}}{E_a^{(2)}/\epsilon^{(2)}} \approx 1$$

might be useful as a guide to estimating desorption activation energies. (However, sets of adatom-solid potentials having quite disparate ranges, this result would not, in general, be satisfactory.)

As anticipated, one finds that an increase in neon surface coverage from 1/2 to 3/4 of a monolayer leads to a quite small change in the rate constants. The major consequence of this adatom concentration change appears to be a decrease in the activation energy (see Table IV) since any difference in the frequency prefactors is probably not significant. Thus the qualitative temperature dependence predicted for neon desorption agrees well with that described above for argon over the same range of temperatures.

It is, though the low temperature regime which reveals a particularly interesting kinetic behavior for the neon-xenon system. One notes that at temperatures below 65 K a single Arrhenius parameterization provides an adequate description not only of both static and moving surface results but also of rate constants corresponding to differing surface coverages. This rate invariance occurring at low temperatures suggests that in this temperature regime the amplitudes of thermal vibrations of the crystal have become small enough that the periodicity of the surface potential is not seriously distorted. Hence, a model of the surface that incorporates a static-lattice approximation will yield a quite satisfactory picture of the desorption dynamics. With the surface symmetry essentially unbroken, it then becomes possible for the neon adatoms to find themselves locally "trapped" in surface potential wells

sufficiently isolated from one another, that even at 3/4 of a monolayer a concentration dependence cannot be discerned. We are led, therefore, to interpret the neon-xenon results in much the same way as we did our earlier ones which described helium desorption,² namely that the appearance of distinct high- and low-temperature kinetics reflects the presence of barriers to adatom diffusion along the surface.

IV. SUMMARY

By extending our previous Monte Carlo - TST calculation so as to include the thermal distortions of the substrate, we have obtained rate constants for the thermal desorption of argon and neon from a xenon (111) crystal face. Our calculations indicate that the coupling of the surface vibrations to desorptive motion can be fairly important for certain systems (e.g., argon), although it does not appear possible to make many general statements concerning the overall significance of the interaction since it may, for other systems or for other temperature regimes, be relatively inconsequential. It is particularly encouraging that a Monte Carlo approach requires that, at most, only a single moving layer of surface atoms need be considered in order to recover the effect of lattice dynamics on the TST results. Thus, inasmuch as the calculations remain manageable upon the introduction of surface motion, one may, by a simple extension of the present work, begin to look at more interesting systems, such as diatomics adsorbed on metals.

¹See, e.g., T. J. Lee, *Surf. Sci.* **44**, 389 (1974); J. T. Yates, Jr., P. A. Thiel, and W. H. Weinberg, *ibid.* **84**, 427 (1979); G. S. De, U. Landman, and M. Rasolt, *Phys. Rev. B* **21**, 3256 (1980); S. Efrima, K. F. Freed, C. Jedrzejek, and H. Metiu, *Chem. Phys. Lett.* **74**, 43 (1980); H. Ibach, W. Erley, and H. Wagner, *Surf. Sci.* **92**, 29 (1980); R. J. Behm, K. Christmann, G. Ertl, and M. A. Van Hove, *J. Chem. Phys.* **73**, 2984 (1980); H. J. Kreuzer, *Surf. Sci.* **100**, 178 (1980); Z. W. Gortel, H. J. Kreuzer, and R. Teshima, *Phys. Rev. B* **22**, 5655 (1980).

²J. E. Adams and J. D. Doll, *J. Chem. Phys.* **74**, 1467 (1981).

³N. B. Slater, *Theory of Unimolecular Reactions* (Cornell University, Ithaca, 1959).

⁴J. E. Adams and J. D. Doll, *Surf. Sci.* **103**, 472 (1981).

⁵For an analogous (but computationally different) approach see E. K. Grimmlmann, J. C. Tully, and E. Helfand, *J. Chem. Phys.* **74**, 5300 (1981).

⁶J. D. Doll, *J. Chem. Phys.* **73**, 2760 (1980).

⁷Desorption may be viewed as a stationary process if the system is artificially bounded at $x \geq q$.

⁸For a recent review of Monte Carlo methods see J. P. Valleau and S. G. Whittington in *Statistical Mechanics, Part A*, edited by B. J. Berne (Plenum, New York, 1977).

⁹J. E. Adams and J. D. Doll, *J. Chem. Phys.* **74**, 5332 (1981).

¹⁰J. M. Parson, T. P. Schafer, P. E. Siska, F. P. Tully, Y. C. Wong, and Y. T. Lee, *J. Chem. Phys.* **53**, 3755 (1970); J. A. Barker, R. O. Watts, J. K. Lee, T. P. Schafer, and Y. T. Lee, *ibid.* **61**, 3081 (1974); G. Scoles, *Annu. Rev. Phys. Chem.* **31**, 81 (1980); J. O. Hirschfelder, C. F. Curtiss, and R. B. Bird, *Molecular Theory of Gases and Liquids* (Wiley, New York, 1954), p. 1110.