

Estimate of the barrier to and rate of dissociation of dense nitrogen under shock conditions

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(Received 30 March 1987)

A simple method is introduced to estimate the barrier to dissociation of nitrogen under shock conditions. A free-energy curve is constructed from quantum-mechanical calculations of the ground-state potential well for N_2 , the model exponential-six potential for the dissociated state, and the additional chemical potential (due to the surrounding dense media) in the hard-sphere approximation. The curves are adjusted to yield behavior in agreement with equilibrium thermodynamic calculations. The barriers are several electron volts, decreasing with pressure. Estimates for the prefactor in an Arrhenius rate expression are based on the recent computer simulations of nitrogen vibrational relaxation [B. Holian, *J. Chem. Phys.* **84**, 3138 (1986)]. Time scales for reaction vary from microseconds to tenths of nanoseconds with increasing shock pressure.

INTRODUCTION

The dissociation of molecular nitrogen under high densities is an intriguing phenomenon. The evidence for the dissociation is the observed (unexpected) "softening" of shock pressures in liquid nitrogen above 30 GPa.¹ The purpose of this paper is to present an estimate of the barrier to this dissociation and hence the rate of dissociation. In doing so we have introduced a simple calculation method which should be of utility in other systems.

The Hugoniot data for N_2 has an unusual kink or "shoulder" at 30 GPa. This feature is difficult to reproduce in an equilibrium calculation that allows dissociation.^{2,3} Our calculation was motivated by the suggestion that there may be a kinetic effect retarding the dissociation, and hence it is important to understand the nature of the thermodynamic barrier to dissociation.

We are also motivated by the desire to understand chemical kinetics at extremely high densities and temperatures. There are few available detailed experimental investigations on simple molecular systems under these conditions from which we can extract dynamic information. Understanding simple systems is seen as a prelude to the study of complex systems, such as explosives.

The N_2 bond has a strength over 9 eV. It is the release of this energy that drives most of the organic compounds used as explosives. The temperatures at which the softening in shock pressure begins are less than 0.6 eV (with densities two to three times higher than the normal liquid). Such conditions can occur in the product states of detonating reactive solids. High-temperature, low-density nitrogen (shocked gas) is known to show dissociation,⁴ but it is still surprising that the high-density liquid, where excluded-volume effects would seem to encourage association, should show dissociation.

It has been predicted that the zero-temperature molecular solid should undergo a (possibly) related transition from a "molecular" solid to an "atomic" solid⁵ at pressures on the order of 80 GPa. Experimentally, this is

not observed,⁶ and it has been suggested that there may be a large kinetic barrier to the process. This suggests that a sizable barrier may be present for the high-temperature, condensed-phase process also.

A complete determination of the relevant many-body potential surface for this process is clearly unfeasible. Although we may define a one-dimensional reaction coordinate as the separation of the two nitrogen nuclei; the real energy surface has a very high dimension because the surrounding atoms and molecules must be playing an important role. For this reason, we prefer to call our calculation an "estimate" of the barrier. Our "estimation" procedure is based on what is known as the Marcus theory for relating the free-energy change during the course of a reaction to the barrier. Marcus first proposed this method in the context of electron transfer reaction, where it has a firmer scientific basis.⁷ Other workers have found the method to be of utility for a wider range of kinetic processes;⁸ it is in the latter spirit that we use the name here. It is the introduction of this highly simplified procedure that is the major contribution of this work.

To connect the barrier to the dissociation rate, a value for the prefactor, A (in $k = Ae^{-\Delta F^\ddagger/k_B T}$) is necessary. As we explain in greater detail shortly, we have assumed that this value will be related to the time scale for vibrational relaxation. We then used the results of recent computer simulations⁹ to complete our estimation of the rate.

METHOD OF CALCULATION

Our calculations for a kinetic barrier make use of the theoretical Hugoniot computed by the chemical equilibrium (CHEQ) code.¹⁰ Namely, the CHEQ code evaluates thermodynamic properties of N_2 -N mixtures by minimizing the Gibbs free energy $G(P, T, \{n_i\})$ with respect to the compositions $\{n_i\}$ ($i = N$ and N_2) at fixed T and P . Computation of $G(P, T, \{n_i\})$ employs an accurate statistical mechanical model of mixtures, together with exponential-6 (exp-6) potentials (Table I) for N-N, N_2 -N,

TABLE I. Exponential-6 parameters for the N₂-N₂, N-N₂, and N-N interactions. (exponential-6 potential: $\phi(r) = \epsilon/(\alpha - 6)[6e^{\alpha(1-\gamma/\gamma^*)} - \alpha(\gamma^*/\gamma)^6]$).

	r^* (Å)	ϵ/k_B (K)	α
N ₂ -N ₂ ^a	4.09	101.9	13.0
N-N ^b	2.496	20.0	15.0
N ₂ -N ^b	3.293	45.14	14.0

^aReference 14.

^bPreliminary values. Our final result will be reported in the future (Ref. 3).

and N₂-N₂ molecular interactions. The present model employs spherical potentials for nonspherical molecules. This assumption is accurate for shocked fluids in the pressure and temperature region of interest here.^{11,12} We use a combination rule¹³ to obtain the N-N₂ exp-6 parameters from the N₂-N₂ and N-N parameters. The N₂-N₂ exp-6 parameters (Table I) have been shown to satisfactorily describe the shock data in the undissociated regime below 30 GPa.¹⁴ The N-N parameters (Table I) are obtained so that their use, together with N₂-N₂ and N-N₂ parameters, in CHEQ will reproduce the shock-wave data as closely as possible. Details on the fitting procedure and comparisons with experiment will be described in a later publication.³ One characteristic feature of the N-N interaction in Table I is that its repulsive range (2.496 Å) is much shorter than that (4.09 Å) of the N₂-N₂ repulsion. Therefore, in the presence of shock pressures (hence, shock compression), N₂ molecules can dissociate if the net internal energy (including the bond dissociation energy) exceeds that of dissociated N atoms. In addition to the aforementioned “pressure” dissociation, very high temperatures attained by shock heating further promote dissociation, as in the low-density gas.⁴

The picture that emerges from the equilibrium calculation is that of a pressure-induced electronic transition—a transition from the diatomic (N₂) electronic ground state to a dissociated monatomic electronic state favored by the interactions (predominantly repulsive) between the N nuclei and the surrounding atoms and molecules. The transition is marked by an *increase* in the mean distance between the two nitrogen nuclei. For this reason, we take the N-N internuclear spacing as a reasonable reaction coordinate. We then focus, or project onto, this coordinate, averaging over the remaining degrees of freedom. Formally, this yields a (complicated) one-dimensional equation of motion for the reaction coordinate, from which a rate constant can be calculated. The result for the rate will essentially be of the Arrhenius form, $k = Ae^{-\Delta F^\ddagger/k_B T}$, where ΔF^\ddagger is the barrier height and A is a very complicated function of environmental parameters. We will focus on ΔF^\ddagger since this term usually dominates the rate expression. We will return to the question of the prefactor in the discussion.

Our calculation proceeds by constructing effective N-N potentials wells for the two electronic states. These are really “free-energy” wells because they are calculated by freezing the internuclear spacing and averaging over the positions of the surrounding atoms and molecules. If

the two nitrogen atoms are labeled 1 and 2, the probability of finding them at a distance r apart is

$$p(r) = \frac{1}{Z} \int e^{-H/k_B T} \delta(r_{12} - r) d\Gamma, \quad (1)$$

where H is the full Hamiltonian of the system, the integration $d\Gamma$ is over all the degrees of freedom, and

$$Z = \int e^{-H/k_B T} d\Gamma. \quad (2)$$

From this we can define an effective potential V_e ,

$$e^{-V_e(r)/k_B T} = p(r). \quad (3)$$

This can also be written as

$$V_e(r) \equiv u(r) + \mu(r), \quad (4)$$

where $u(r)$ is a two-body (nitrogen atom) potential energy in the absence of the (repulsive) interactions of the surrounding atoms and molecules, and the chemical potential $\mu(r)$, given by

$$e^{-\mu(r)/k_B T} \equiv y(r), \quad (5)$$

where $y(r)$ is the “cavity distribution function”,¹⁵ essentially the probability of finding two “holes” at a distance r apart in the condensed phase. Recent interest in the frequency shifts and linewidths of molecular vibrations at high densities have focused attention on the chemical potential for overlapping hard-sphere cavities.¹⁵ We evaluate the effective diameter of the hard spheres (for both atoms and molecules) from the chemical equilibrium calculations using the Mansoori-Canfield-Rasiah-Stell-Ross form of perturbation theory. We use that hard-sphere diameter as the effective hard-sphere diameter for μ_{HS} , using the computationally convenient form of $\mu_{HS}(r)$ given by Zakin and Herschbach.¹⁶

From the equilibrium calculations, we extract two pieces of information: the degree of dissociation and the approximate shape of the interaction potential (or well) between two nitrogen atoms in the dissociated state. Our model treats the dissociation as the partitioning between two states. From the degree of dissociation we calculate the free-energy difference between the associated and dissociated states

$$\Delta F_{\text{reaction}} = k_B T \ln \left[\frac{x}{1-x} \right], \quad (6)$$

where x is the degree of dissociation. We allow the CHEQ code to do that part of the calculation, and adjust relative heights of the minima of the effective-potential-well depths to be $\Delta F_{\text{reaction}}$. This free-energy difference is taken to be the difference in height of the bottoms of the two wells. This is not precisely the difference that would be calculated by using Eq. (1), because the entropy along the reaction coordinate has effectively been included. As long as the entropy (or curvature) does not vary rapidly with separation in this region on either curve, this should be an acceptable approximation.

The N-N potential $u(r)$ in the dissociated state is taken to be the exp-6 potential, with the parameters given in Table I. This is one of the major assumptions in this

calculation. In the absence of any detailed calculations of the structure of the dissociated phase, calculations which are not currently feasible, we are forced to use the empirical potential. The potential is realistic in that it was chosen to reproduce the shock data and the functional form has been used in a variety of other shock experiments, but it is the uncertainty in the use of this potential that has caused us to call our calculation an "estimate" of the barrier.

For the N-N potential $u(r)$ in the diatomic state, we use the quantum-chemical calculation of Ermler, McLean, and Mulliken.¹⁷ To this we add $\mu_{\text{HS}}(r)$ to obtain $V_e(r)$. We again use the hard-sphere diameter taken from the equilibrium calculation. Although this is not exactly the appropriate diameter, the N-N potential is sufficiently steep in the region of interest that the change in $V_e(r)$ in that region is small, and hence the error introduced is small.

To construct a reaction surface from these effective potential wells, we essentially graph the two curves on a single plot, and adjust the relative height of the well minima to agree with the equilibrium degree of dissociation. The location of the curve crossing is identified as the transition state. At this crossing, real adiabatic potential curves will be "split," causing an avoided crossing. We assume that the splitting at the curve crossing is small compared to the height at the barrier crossing, so that the barrier is not dramatically lowered by the splitting. Given the height of the barriers, this is probably a safe assumption. These curves were calculated for the thermodynamic states listed in Table II. A sample curve is shown in Fig. 1. Both $u(r)$ and $u(r) + \mu_{\text{HS}}(r)$ are shown for the associated and dissociated state, for the highest pressure given in Table II. This clearly shows the effect of $\mu(r)$ is smaller on the associated curve than the dissociated curve. On the relatively more compressible dissociated state, the curve is pushed in considerably, with only small modifications on the N₂ well. The energy is plotted in units of electron volts, so the "small" effect of $\mu(r)$ can actually amount to lowering the transition state by half an electron volt or several thousand degrees kelvin.

The curves calculated are summarized in Fig. 2. Here we have plotted the free energy as a function of reaction coordinate for the various pressures given in Table II. The lowering of the kinetic barrier can clearly be seen.

The procedure outlined above can be regarded as a

generalization of the Marcus relation. In essence, what is usually referred to as the Marcus relation estimates the change in barrier height for a change in free energy of reaction assuming both wells are harmonic. With these assumptions, there is a simple quadratic relation between free energy of reaction and activation free energy. Our application constructs the relation between free energy of reaction and activation free energy for anharmonic wells. Inspecting ΔF^\ddagger as a function of $\Delta F_{\text{reaction}}$, a nearly linear dependence is found. It is not unusual, even within Marcus theory, to find linear behavior over a range of free energies; it is, in fact, the basis of many physical-organic-chemical relationships.

DISCUSSION AND CONCLUSIONS

The rate of dissociation, or barrier crossing, will be the product of a thermodynamic factor $e^{-\Delta F^\ddagger/k_B T}$ and a prefactor A . The theoretical analysis of the prefactor for barrier-crossing problems has been an active area of research for the last several years; the temperature and pressure dependence of even simple model processes can be very complicated.¹⁸ Because we are demonstrating a simple procedure to *estimate* the rate, and because in most cases the largest contribution to the temperature and pressure dependence is in the thermodynamic factor, we will regard the prefactor as simply the *time scale* for the process.

In view of both the approximate nature of our free-energy surface and the complicated nature of the prefactor, we have chosen to estimate the prefactor using information from computer simulations of vibrational relaxation. In essence, we view the relaxation of vibrational excitation as measuring the rate at which energy is being taken in and out of the reaction coordinate. Holian has performed classical molecular dynamics for N₂ vibrational relaxation under conditions of very high pressures and temperatures.⁹ At a density of 2.3 g/cm³ and a temperature of 4000 K, he finds vibrational relaxation occurring on the order of 200 psec. Using this information, we estimate the prefactor as $A = 1/(200 \text{ psec}) = 5 \times 10^9 \text{ sec}^{-1}$. In the absence of any detailed information on the temperature and pressure dependence of this factor, we will assume this prefactor is independent of environment in the density temperature range we are probing. The error involved could easily be an order of magnitude, but this is small compared to the many-

TABLE II. The thermodynamic states discussed and the resulting free energies and rates.

	P (GPa)	T (eV)	ρ (g/cm ³)	N ₂ (mol %)	$\beta\Delta F_{\text{reaction}}$	$\beta\Delta F^\ddagger$	k_{reaction} (sec ⁻¹)
1	20	0.390	1.859	99.98	8.38	9.3	4.57×10^5
2	30	0.580	2.033	98.95	4.56	5.2	2.76×10^7
3	40	0.752	2.210	94.21	2.85	3.5	1.51×10^8
4	50	0.874	2.407	87.22	2.06	3.0	2.49×10^8
5	60	0.981	2.606	78.95	1.56	2.5	4.10×10^8
6	70	1.080	2.803	70.18	1.21	1.9	7.48×10^8
7	80	1.184	2.996	60.91	0.94	1.5	1.12×10^9
8	85	1.240	3.090	56.18	0.83	1.4	1.23×10^9

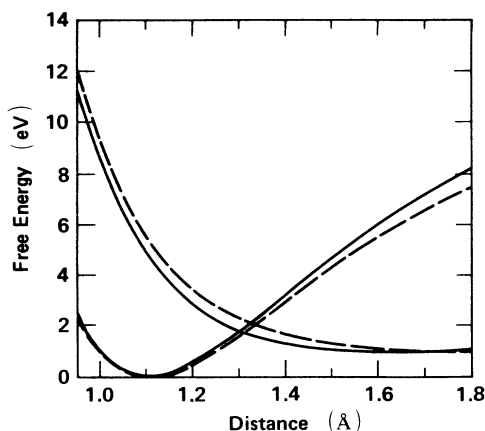


FIG. 1. The effective free-energy curves for N_2 at 8.5 GPa. The solid curves include μ_{NS} , the dashed curves do not.

order-of-magnitude change due to the change in the barrier height. Using this assumption, we arrive at the rates given in Table II. These rates are similar to the results of Ross, who scaled molecular dissociation rates for gases to liquid densities using hard-sphere collision rate theory.² The combined effects of decreased barrier heights and increased temperatures cause the very large changes in the estimated rate. At the lowest shock pressures, the process occurs on a timescale of microseconds. In a typical shock experiment, the material is observed over a time on the order of 100 nsec. The presence of the "shoulder" observed in the Hugoniot data can be explained by the reaction being too sluggish to occur on the timescale of the shock experiment for the weaker shocks. At higher pressures, the reaction becomes much more rapid and the shock experiment effectively sees an equilibrium mixture of molecular and atomic nitrogen. It should also be noted that the fraction of dissociated N atoms is very small at low pressures, so the thermodynamic properties are essentially identical to those of N_2 without dissociation.

On the basis of the present barrier calculations, we can comment on the inability to observe the predicted low-temperature phase change in a diamond-anvil experiment. Under those conditions, nitrogen is in a solid phase, whereas our results are for a high-temperature fluid phase, and so the reaction surface may be consider-

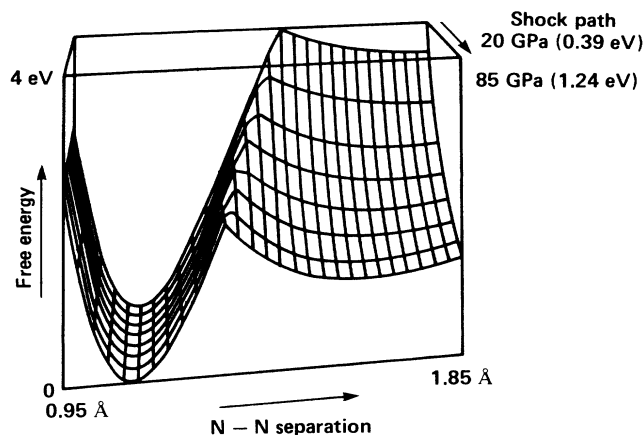


FIG. 2. The free-energy curves as a function of shock pressure.

ably different. We can argue that the rates in the solid phase would not be expected to be any faster than in a fluid phase at that density. This suggests at room temperature at a density of 2.4 g/cm^3 , for example, there will be a barrier of at least 3 eV, which corresponds to an Arrhenius factor in a rate expression of 10^{-48} . Combining that with any reasonable estimate of the prefactor, the timescale for the process becomes prohibitively long, and we would not expect to observe dissociation in a diamond-anvil experiment.

In conclusion, we have presented a simple procedure for estimating reaction rates for important physical processes in regimes that are difficult for traditional physical chemistry. This procedure was developed by combining ideas from statistical mechanics and physical organic chemistry. The results provide a picture consistent with the experimental observations, and have helped shed some light on the unusual behavior of nitrogen under extreme conditions.

ACKNOWLEDGMENT

This work was performed under the auspices of the U.S. Department of Energy by the Lawrence Livermore National Laboratory under Contract No. W-7405-ENG-48.

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