Estimates for Collision-Induced Dissociation Rates

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Collision-induced dissociation rates for diatomic and triatomic molecules are estimated from a version of the available energy theory. The collision is assumed to excite one mode of internal momentum in an unbounded Boltzmann distribution, and the number of energy modes used in the dissociation process is taken to be the number of internal modes that disappear when the molecule breaks apart. This simple model is found to deviate from available experimental data generally no more than a factor of 10 over a wide range of temperature and for a wide variety of collision partners.

Introduction

THE dissociation of molecules is often a major heat sink that establishes the level of kinetic energy in thermal plasmas of interest in aerospace problems. This occurs, for example, in calculations of the profiles behind normal shock waves in air, such as those made by Duff and Davidson,[1] or in the blunt-nose inviscid flow-field calculations published by Hall, Eschenroeder, and Marrone.[2] The kinetic energy level, in turn, establishes the rates of ionization and electronic excitation which determine the microwave and optical observables produced by the plasma.

Since reaction rate theories have not been highly successful, it generally has been necessary to resort to experiment for each specific reaction and temperature involved. It is obviously desirable to correlate these experimental results with a single unifying model, if possible, which can then be extended to predict dissociation rates for molecular species and for temperatures where data are lacking. Such a need was emphasized recently by Howe, Viegas, and Sheaffer,[3] who, stimulated by problems associated with space probes entering the atmospheres of Venus or Mars, calculated profiles behind shock waves in CO_2. Because dissociation rate data for CO_2 were not then available, parallel profiles were calculated in which the rate constants were varied about three orders of magnitude in order to bracket the range of uncertainty. It appeared from these results that, if the rate constants could be estimated within a factor of 10, this might be sufficient for some engineering needs. Accordingly, it is the purpose of this paper to describe some simple, order-of-magnitude estimates for dissociation rates that are suitable for both diatomic and triatomic molecules and to compare the results with available experimental data.

A number of theoretical models have been proposed for the dissociation rate problem. One of these is the activated-complex model described by Glasstone, Laidler, and Eyring.[4] Without going into detail, the problem here is that one is left with an undetermined transmission coefficient that seems difficult to evaluate except for the case of three hydrogen atoms. A very simple model for dissociation of diatomic molecules was proposed by Rice,[5] in which it is assumed that only the fraction of molecules with vibrational energy within kT of the dissociation limit are capable of being atomized by collision. The modern version of this theory, developed by Benson and Fueno,[6] considers the recombination process as a cascade sequence of single vibrational quantum jumps from the top vibrational levels. This is probably a valid model

for low velocity collisions, but Shuler and Zwanzig[7] and Mies and Shuler[8] have shown that at high energies transitions with multiple quantum jumps occur. In this case, it should be justifiable to use a classical model.

Where classical mechanics is valid, perhaps the most rigorous approach is to calculate the flux of three-body recombination systems across a given surface in phase space:

$$F = \int \rho \, \frac{dS/dt}{\mathrm{grad}S} \, d\sigma \qquad (1)$$

where ρ is the density of points in phase space, S is a surface defined by a function of the coordinates and their conjugate momenta, and $d\sigma$ is the surface element. The concept "surface" means here a $2m$-1 dimensional subspace in $2m$-dimensional phase space. The derivative dS/dt divided by $\mathrm{grad}S$ is the velocity with which the phase points cross the surface. Wigner[9] shows that, if such a surface is properly chosen, namely so the flux across the surface is a minimum, then the recombination rate is rigorously determined. Keck[10] has recently improved Wigner's calculations by using variational methods to find minimum values for surfaces having plausible functional forms. However, it is clear that the calculations must become increasingly intricate as one attempts to define this surface more rigorously and particularly as the method is extended to triatomic molecules. Another classical approach is taken by Light[11] and Light and Arnstein,[12] who solve the Liouville equation for diatomic dissociation assuming that collisions are adiabatic. Once again the solutions become so intricate that they must be found by numerical calculation, and the problem of polyatomic molecule dissociation does not appear tractable when approached by this method.

For the purposes of the present paper, the simple available-energy theory[13] has the advantage that the physical meaning is relatively clear at each step of the calculation. Moreover, it seems to give results that are almost as good as those derived from the more intricate theories. The basic difference between this model and the Wigner theory is that S is now taken to be a surface in phase space which all collision systems must cross, both the stable and unstable. Then the fraction of the flux F in Eq. (1) for which the systems have sufficient energy to be unstable is taken as the probability that a single collision excites dissociation.

Dissociation Rate Model

For the collision induced dissociation

$$AB + M \rightarrow A + B + M \qquad (2)$$
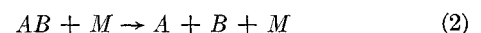
the rate coefficient α is defined by

$$d[AB]/dt = \alpha[AB][M] \qquad (3)$$

where the brackets denote concentrations. The rate coeffi-

Table 1 Cross-section parameters

Molecule	S_∞, $\times 10^{+16}$ cm^2	C, °K	D/k, °K
Cl_2	44.0	330	28,730
Br_2	42.7	533	22,860
I_2	58.3	568	17,880
N_2	33.0	104	113,200
O_2	29.2	125	58,900
NO	29.6	128	75,240
CO_2	27.2	213	63,290
He	11.8	80	. . .
Ne	17.7	56	. . .
A	28.0	142	. . .
Kr	32.5	188	. . .
Xe	39.7	252	. . .
N	16.5	1312	. . .
O	12.5	649	. . .

cient may be expressed as the product of a collision rate θ and the probability P that dissociation results from a single collision

$$\alpha = \theta P/s \tag{4}$$

The symmetry number s is unity, unless the molecules AB and M are identical, in which case it must equal 2 to avoid counting systems twice in Eq. (3).

For a gas in equilibrium, θ is given by

$$\theta = (2\pi\mu kT)^{-3/2} \int_0^\infty \frac{p}{\mu} S(p) \exp\left(-\frac{p^2}{2\mu kT}\right) 4\pi p^2 dp \tag{5}$$

where p is the momentum of the colliding particles in center of mass coordinates, μ is the reduced mass, and $S(p)$ is the collision cross section for both favorable and unfavorable events.

The cross section is not precisely known, but it is not difficult to estimate within a factor of about 2, sufficient for present purposes. The wave functions of outer electrons extend about the same range for all atoms and only slightly more for diatomic molecules, such that all cross sections are the order of 30×10^{-16} cm^2. As a next approximation, the cross section can be considered a weak function of momentum. For example, the cross section appropriate to viscosity may be expressed as

$$S = S_\infty(1 + 8k\mu C/\pi p^2) \tag{6}$$

where C is Sutherland's constant, the order of a few hundred degrees Kelvin for most atoms and molecules. In view of the fact that the cross section is not the crucial parameter, it will be considered adequate to use the viscous cross sections given in Table 1 in the calculations to follow. Then the collision rate given by Eq. (5) becomes

$$\theta = (8kT/\pi\mu)^{1/2}S_\infty(1 + 4C/\pi T) \tag{7}$$

The crucial problem is to evaluate the probability factor P in Eq. (4). Fowler and Guggenheim[13] consider the surface S to be any surface normal to the component of momentum between centers of the colliding particles which the system crosses prior to collision. The flux of systems across this surface [Eq. (1)] is just

$$F = \int e^{-E/kT}(p_1/\mu)dp_k dq_k \tag{8}$$

where the phase density has been taken as the exponential Boltzmann distribution, the velocity across the surface is p_1/μ, and the surface element is the element $dp_k dq_k$ involving all the momenta and their conjugate coordinates except q_1, the coordinate that is held constant over the surface. Then, if the energy that contributes to the dissociation of AB involves n terms with only momenta or coordinates squared,

the fraction of this flux where the energy is greater than D is given by

$$P = \frac{\int_D^\infty e^{-E/kT}E^{(n-1)/2}dE}{(kT)^{(n+1)/2}\Gamma[(n+1)/2]} \tag{9}$$

The momenta and coordinates involved have been transformed to the energy variable E, which is the total energy in the n modes considered, including the kinetic energy along the collision path. The factors in the denominator are just the normalization constants required so that the total probability goes to unity when both favorable and unfavorable collisions are considered.

The problem remaining is that the number of degrees of freedom which should contribute to dissociation is undefined. If the total number of degrees of freedom involved in the two particles AB and M is used, the probability P turns out to be much too large. On the other hand, one degree of freedom gives a value for P which is too small. However, if it is assumed that the collision produces an activated complex, the energy that causes dissociation appears, at least momentarily, in the internal energy modes of this complex. Since energy is conserved, it seems reasonable to choose n as the number of these internal degrees of freedom which disappear when the activated complex breaks apart.

In the general case, the activated complex may include the collision partner, but only that limiting case will be considered here where this partner is perfectly inert. That is, the collision is assumed to be billiard-ball-like, approximating the case where the interaction potentials are very steep, short range, repulsive, and nearly spherically symmetric. Such an inert partner will normally interact with just one of the atoms in the molecule and transfer momentum to that atom only along the coordinate between centers at the moment of closest approach. The collision process is conceived as a sudden discontinuity in one component of the molecule's internal momentum, without change in the other momentum components or in the atomic position coordinates. The activated complex is just the original molecule in which one component of internal momentum has suddenly taken a new distribution independent of the energy residing in the other modes. As in the Eyring theory,[4] the activated molecule is assumed to have a Boltzmann-like distribution of internal energies. Certainly the momenta and position coordinates that are unchanged by the collision remain in the Boltzmann distributions with which they entered the collision event. Note that these distributions are bounded by the requirement that the molecule be stable before collision. The excited momentum should also have a Boltzmann-like distribution, at least at the low-energy end, since those excited molecules that remain stable become part of the equilibrium background. However, this distribution may be unbounded and independent of the energy residing in the other modes, since the molecule is not obliged to be stable after collision. It seems plausible that a Boltzmann-like distribution should extend to the unstable excited molecules as well.

After collision with the inert partner M, the subsequent history of the activated molecule may be described by the flux of phase points through a space involving just the position and momenta coordinates of the molecule's internal energy modes. (In this approximation, the Hamiltonian is independent of the position of the inert partner except at the instant of impact.) The reaction surfaces in this phase space will be chosen as the subspaces across which the flux suffers the maximum discontinuity, that is, the surfaces $S = q_k = $ const, where q_k is the coordinate conjugate to the excited momentum p_k at the instant of collision. This is not the only possible choice for S, and this particular set of surfaces is chosen merely because it makes the integrations easy to do. The probability that a single collision excites dissociation is then taken as the fraction of the flux which

crosses the surface with energy in the active modes greater than the dissociation energy, averaged over the manifold of all possible such surfaces.

Consider first a diatomic molecule with four internal energy modes that disappear when the molecule breaks apart into atoms. This is the familiar two-body escape problem; the two bodies will part when the total energy in the two rotational-momentum modes, the vibrational-momentum mode, and the vibrational-potential mode is greater than the dissociation (or escape) energy. Designate the excited momentum coordinate by p_1, the two residual momenta by p_2 and p_3, and the displacement of the interatomic distance from its equilibrium value by q_1. In general, the excited momentum p_1 will lie at some arbitrary angle φ with respect to the vector q_1. A rotated position coordinate system with direction vectors parallel to the three orthogonal components of momentum may be defined by

$$q_1{}' = q_1 \cos\varphi - q_2 \sin\varphi$$
$$q_2{}' = q_2 \cos\varphi + q_1 \sin\varphi \qquad (10)$$
$$q_3{}' = q_3$$

where q_2 and q_3 are orthogonal to q_1 and are rotated so that q_3 coincides with $q_3{}'$. The surface normal to p_1 in phase space is defined by

$$S = q_1{}' = q_1 \cos\varphi - q_2 \sin\varphi = \text{const} \qquad (11)$$

For a Boltzmann distribution of classical, rotating harmonic oscillators, the element of flux across S, whose outward normal lies in the element solid angle $2\pi \sin\varphi d\varphi$, is proportional to

$$dF \propto \exp\left(- \frac{p_1{}^2 + p_2{}^2 + p_3{}^2}{2\mu kT} - \frac{2\pi^2\mu\omega^2 q_1{}^2}{kT}\right) p_1 d\sigma \, \sin\varphi d\varphi \qquad (12)$$

where ω is the vibrational frequency, and μ is now the reduced mass of the diatomic molecule. The surface element may be expressed

$$d\sigma = dp_1 dp_2 dp_3 dq_2{}' dq_3{}' =$$
$$dp_1 dp_2 dp_3 (\cos\varphi dq_2 + \sin\varphi dq_1) dq_3 \qquad (13)$$

The integration over q_2 may be transformed to an integration over q_1 in accordance with Eq. (11), and the flux element then becomes proportional to

$$dF \propto \exp\left(- \frac{p_1{}^2 + p_2{}^2 + p_3{}^2}{2\mu kT} - \frac{2\pi^2\mu\omega^2 q_1{}^2}{kT}\right) p_1 (\cos^2\varphi +$$
$$\sin^2\varphi) dp_1 dp_2 dp_3 dq_1 \qquad (14)$$

The differential elements dq_3 and $d\varphi$ are dropped in Eq. (14) because q_3 and φ do not appear in the Hamiltonian, and the integration over these variables contributes only an arbitrary constant that does not affect the fraction of the flux with energy exceeding a given value.

Transform to the energy coordinates

$$\epsilon = [(p_2{}^2 + p_3{}^2)/2\mu] + 2\pi^2\mu\omega^2 q_1{}^2 \qquad (15a)$$
$$\epsilon^* = p_1{}^2/2\mu \qquad (15b)$$

and it follows that

$$\epsilon^{1/2} d\epsilon \propto dp_2 dp_3 dq_1 \qquad (16a)$$
$$d\epsilon^* \propto p_1 dp_1 \qquad (16b)$$

Then the fraction of the flux crossing S, with energy in the excited mode between ϵ^* and $\epsilon^* + d\epsilon^*$, and with the residual energy in the remaining three modes between ϵ and $\epsilon + d\epsilon$, is given by

$$dP = \frac{e^{-\epsilon/kT} \epsilon^{1/2} d\epsilon}{\Gamma(\tfrac{3}{2})(kT)^{3/2}} \frac{e^{-\epsilon^* kT} d\epsilon^*}{kT} \qquad (17)$$

The denominators in Eq. (17) are again the normalization constants required. Actually, the energy ϵ has an upper bound of the order of the dissociation energy D, whereas the normalization constant $\Gamma(\tfrac{3}{2})(kT)^{3/2}$ is for an unbounded Boltzmann distribution. However, for the temperatures of greatest interest, the ratio D/kT is appreciably greater than unity, in which case the correction required is small. It will be neglected here for simplicity.

Integrating Eq. (17) over all combinations of internal energy greater than D, with ϵ^* unbounded but with the restriction $\epsilon \leqslant D$, one obtains

$$P = \frac{\int_0^D e^{-\epsilon/kT} \epsilon^{1/2} \left[\int_{D-\epsilon}^\infty e^{-\epsilon^*/kT} d\epsilon^*\right] d\epsilon}{\Gamma(\tfrac{3}{2})(kT)^{5/2}} \qquad (18a)$$

$$P = (4/3\pi^{1/2})(D/kT)^{3/2} e^{-D/kT} \qquad (18b)$$

This is the same result as obtained by Fowler and Guggenheim when $n = 4$ (i.e., three internal energy modes plus the kinetic energy along the collision path), neglecting the lesser-order terms in D/kT which arise when the energy in each mode is considered unbounded and independent.

Two correction terms can be accounted for in the preceding model rather simply. The rotation of the diatomic molecule contributes a term $l^2/2\mu r^2$ to the effective interatomic potential,[10] where l is the angular momentum vector. Thus, instead of integrating throughout a domain bounded by a simple surface of constant energy, one should integrate throughout an ellipsoid-like domain in energy space. Also, the upper limit of the outer integral, Eq. (18a), should be reduced by the initial energy in the excited mode, and this result averaged over the distribution of this initial energy. For purposes of estimating the magnitude of these effects, it seems sufficient to add an average rotational barrier equal to $kT(kT/2$ for each of the two rotational modes involved) and assume that the initial energy in the excited momentum mode is the average value $kT/2$. Then Eq. (18) becomes

$$P = \frac{\int_0^{D+kT/2} e^{-\epsilon/kT} \epsilon^{1/2} \left[\int_{D-\epsilon+kT}^\infty e^{-\epsilon^*/kT} d\epsilon^*\right] d\epsilon}{\Gamma(\tfrac{3}{2})(kT)^{5/2}} \qquad (19a)$$

$$P = \frac{4}{3\pi^{1/2}} \left(\frac{D}{kT} + \frac{1}{2}\right)^{3/2} e^{-[(D/kT)+1]} \qquad (19b)$$

Still other corrections could be considered. For example, integrations over vibrational states should be replaced by quantum summations at low temperatures, but then the model of Benson and Fueno[6] would be more appropriate. Also, anharmonic effects could be important at high temperature, although the results of Light and Arnstein[12] suggest that the anharmonic model may yield poorer results than the harmonic oscillator model. In either case, the complexities added by these considerations seem inconsistent with the order of approximation inherent in the model. The principal concern here will be to examine how the simple model correlates with observed dissociation rate data, and the estimates given by Eq. (19) will be used for the comparisons with diatomic molecule dissociation rate data that follow.

Where polyatomic molecules are concerned, the number of modes which contribute to dissociation will again be taken as the number of internal energy modes which disappear when the molecule breaks into two fractions. These fractions are, by definition, a part of the equilibrium background with internal energy fully excited in a Boltzmann distribution ($kT/2$ average energy in each mode). Although a detailed analysis of the molecule's history might show that all of the internal modes participate in the dissociation process to some extent, still, the amount of energy that is used to break the bond and give the molecular fractions kinetic energy with respect to their center of mass is, on the average, just the energy contained in the vanishing internal modes. The
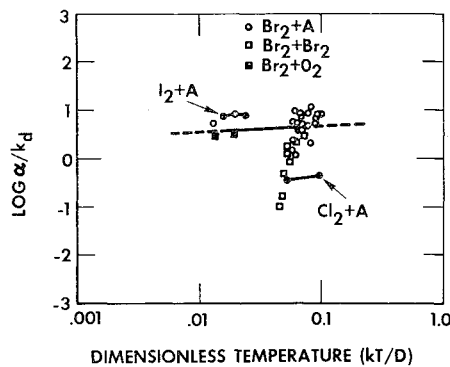
Fig. 1 Dissociation of halogens.

collision is assumed to excite but one mode of energy in these active internal degrees of freedom, and the remaining internal modes are presumed to be inactive.

Consider first the linear, triatomic molecule with a total of 10 degrees of internal freedom (two rotational modes, two vibrational stretching modes, two vibrational bending modes, and a potential mode associated with each of the vibrational momentum modes). The diatomic fraction formed has four degrees of internal energy, and so the number of active modes which contribute to dissociation is taken to be $n = 6$. Then the probability factor becomes

$$P = \frac{\int_0^{D+kT/2} \epsilon^{3/2} e^{-\epsilon/kT} \int_{D+kT-\epsilon}^{\infty} e^{-\epsilon^*/kT} \, d\epsilon^* \, d\epsilon}{\Gamma(\frac{5}{2})(kT)^{7/2}} \quad (20a)$$

$$P = \frac{8}{15\pi^{1/2}} \left(\frac{D}{kT} + \frac{1}{2}\right)^{5/2} e^{-[(D/kT)+1]} \quad (20b)$$

where again the two rotational modes have been considered to increase the effective potential along any stretching coordinates by the amount kT, and the five unexcited modes are bounded by $D + kT/2$.

The nonlinear triatomic molecule has nine degrees of internal freedom (one more rotational mode than the linear triatomic molecule, but one less vibrational bending mode with its associated potential mode). Thus $n = 5$ for this case. The three rotational modes are considered to increase the effective potential along any stretching coordinate by $3kT/2$, and four unexcited modes are then bounded by $D + kT$. Accordingly, the probability factor becomes

$$P = \frac{\int_0^{D+kT} \epsilon e^{-\epsilon/kT} \int_{D+(3kT/2)-\epsilon}^{\infty} e^{-\epsilon^*/kT} \, d\epsilon^* \, d\epsilon}{\Gamma(2)(kT)^3} \quad (21a)$$

$$P = \frac{1}{2} \left(\frac{D}{kT} + 1\right)^2 e^{-[(D/kT)+(3/2)]} \quad (21b)$$

In the case of triatomic molecules, the collisions could excite at least two modes of internal energy. For example,
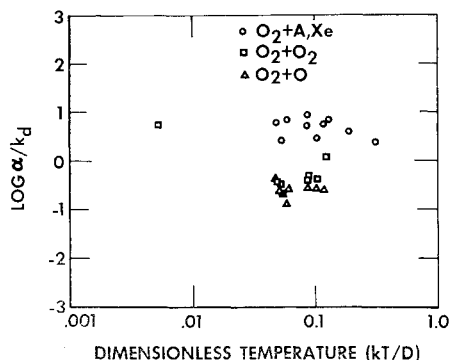
an end-on collision with the linear triatomic molecule could be expected to excite both the symmetrical and asymmetrical vibrational momentum modes. Similarly, a collision normal to the molecular axis could simultaneously excite one of the bending vibrational modes and one of the rotational modes. It is shown in Ref. 14 that, should two modes be excited, the leading terms in D/kT remain the same as before, and that the correction term is the order of $(D/kT)^{-3/2}$ smaller than the leading term. At the temperatures of interest, this is negligible relative to the accuracy of the present model, so that Eqs. (20) and (21) are considered adequate for estimates of dissociation of the linear and nonlinear triatomic molecules, respectively.

Comparison with Experiment

Experimental values of dissociation rates and recombination rates are now available for a number of diatomic molecules and a few triatomic molecules. Where recombination rates k_r are given, these have been transformed to dissociation rates k_d by use of the equilibrium constant K_c:

$$k_d = k_r K_c \quad (22)$$

Rice[15] discusses some of the questions concerning the validity of this procedure and concludes that, even if the gas is not in equilibrium, the ratio of the observable rates should still be the equilibrium constant. Therefore, the dissociation rate calculated from Eq. (22) is presumed to be the rate that would have been measured in the same experiment.

Figure 1 shows the ratio of theoretical to experimental dissociation rates α/k_d for the halogens as a function of the dimensionless temperature kT/D. It is seen that most of the data lie within a factor 10 of the predicted values. The figure illustrates another interesting point; the slope of the shock-tube data does not agree with the predicted temperature dependence. In general, the shock-tube rates increase more slowly with increasing temperature than the predicted rates. It is for this reason that the statement is frequently made that the available energy theory does not agree with experiment. For example, most of the high-temperature $Br_2 + A$ data shown are from Palmer and Hornig,[16] and a least-mean-squares fit to their data corresponds to a collision rate more than 100 times smaller than reasonable and 9 contributing degrees of freedom, which is clearly impossible.

However, in each similar case, the data span a very narrow temperature interval and, in view of the typical dispersion in the data, perhaps the slope should not be taken too seriously. Aside from this, there are reasons why the slopes should be different. For example, Treanor and Marrone[17] find that dissociation should depopulate the upper vibrational states behind strong shock waves, such that the observed dissociation rate is less than the equilibrium rate that would occur if the vibrational states were fully excited. This suggests that the data may be perfectly correct, but it is incorrect to interpret the measured rates as equilibrium
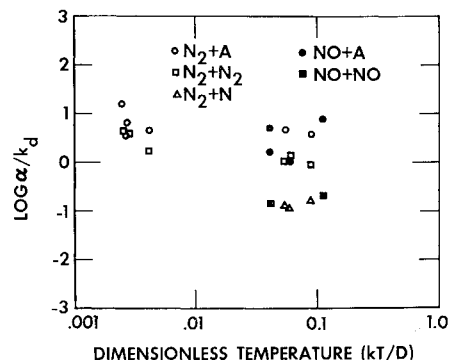

Fig. 2 Dissociation of oxygen.

Fig. 3 Dissociation of nitrogen and nitric oxide.

rates. In any case, where the data are anchored by additional low-temperature data (in the present case Strong, Chien, Graf, and Willard's[18] data for $Br_2 + A$) the least-squares coefficients then correspond to a reasonable collision rate and about four contributing energy modes. This was observed by Palmer and Hornig,[16] and the solid line in Fig. 1 is the equation that they fit by least-squares to both sets of data. It agrees well with the predicted values. Other data for halogens shown in this figure are from Britton, Davidson, Gehman, and Schott[19] and from Hiraoka and Hardwick[20] (Cl_2 data).

Figure 2 shows O_2 dissociation rate data from Matthews,[21] Byron,[22] Camac and Vaughan,[23] Rink, Knight, and Duff,[24] Marshall,[25] Schexnayder and Evans,[26] Wray,[27] and Anderson.[28] Again the data agree with the available energy model within a factor of 10. A typical feature observed here is that the ratio α/k_d is highest for the noble gas collision partners, lower for collisions with stable molecules, and lower yet for collisions with reactive atoms. These sets of data can be empirically superposed by modest adjustments of the collision cross sections chosen.

Figure 3 shows the results for N_2 and NO dissociation. Again the same general remarks apply. The N_2 rate data are primarily due to Byron[29] with a few points from Allen, Keck, and Camm.[30] Low-temperature N_2 data are from Herron and Franklin,[31] Harteck, Reeves, and Mannella,[32] and Marshall.[25] Data for NO dissociation are from Freedman and Daiber[33] and Wray and Teare.[34]

A considerable amount of data exists for dissociation of hydrogen and deuterium (see Ref. 35, for example) as well as for the heavier molecules considered previously. In this case, one would not expect a classical model to work as well for vibrational transitions, and the model developed by Benson and Fueno[6] would perhaps be more appropriate. Nevertheless, the hydrogen and deuterium dissociation rate data still lie close to the limits predicted by the available energy theory. If one of the factors kT in the denominator of Eq. (19a) is replaced by the quantum vibrational partition function, almost all of the data will lie within a factor of 10, as for the other diatomic gases. This does not, however, constitute a sufficient treatment of the quantum effects, and the agreement may be fortuitous.

Figure 4 shows results for triatomic gases. The H_2O vapor point is an estimate by Duff[36]; the NO_2 rates are from Ford and Endow[37] and Huffman and Davidson.[38] The O_3 rate is quoted by Bortner and Golden[39] and is about the same as deduced from a recombination rate published by Benson.[40] The low-temperature point for CO_2 dissociation is a group of measurements due to Brabbs, Belles, and Zlatarich[41] centered around $2700°K$. The two connected points at higher temperature cover data obtained by Davies[42] between $4000°$ and $6000°K$, and the remaining points are measurements made by Steinberg.[43] In general, these results for triatomic molecules all agree with the predicted values within the stated margins. The one exception is the high-tempera-
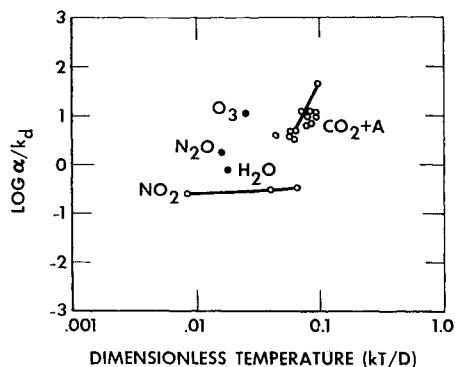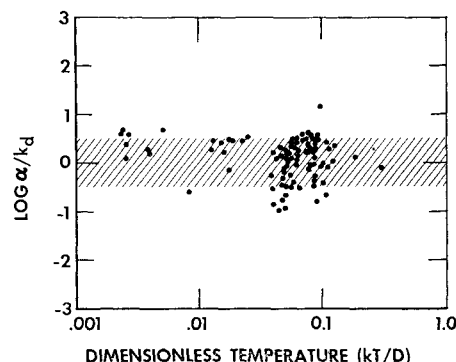

Fig. 5   Ratio of predicted to measured dissociation rates as a function of dimensionless temperature.

ture CO_2 data by Davies, and here the experimental rates are somewhat lower than those obtained by Steinberg.

The preceding is not necessarily a complete list of experimental dissociation rate results, but it seems extensive enough to provide a reasonable check on the available energy model. Figure 5 shows the total of all these results for both diatomic and triatomic molecules, where the effective cross sections have been arbitrarily taken three times smaller than the viscosity cross sections in Table 1 when inert gases are the collision partners, equal to the viscosity cross section when stable molecules are the collision partners, and three times larger than the viscosity cross sections when the collisions are with reactive atoms. In this case, most of the data scatters within a factor of 3 about the predicted values.

Concluding Remarks

The surprising thing about dissociation rate theories is that very different models yield approximately the same sort of correlation with experiment. The differences range from assumptions that optical quantum selection rules apply[6] the purely classical behavior,[9] from adiabatic[11] to impulsive-type collisions, and sometimes the more rigorous the model, the worse the correlation seems to become.[12] Thus, agreement with experimental data is not a sufficient test to differentiate one approach from another, though it is certainly a necessary condition that must be satisfied. In view of this, one might as well choose the simplest model consistent with the accuracy required. It is concluded that the available energy model is about as trustworthy as other existing theories, and it generally has the advantage of greater simplicity. A modest adjustment of total cross section is normally sufficient to bring about agreement with experimental data. Extrapolation to species and temperatures where data are lacking will probably not involve large uncertainties, even though many details of the dissociation process are obviously missing in the available energy model.

The temperature dependence of the equilibrium rate often does not agree with the experimental temperature dependence, and it is suggested that this occurs because the data are taken in gases that are out of equilibrium. Where upper vibrational states are depopulated by dissociation, the measured rate may be less than the equilibrium rate.[17] This trend is observed in much of the data taken behind strong shock waves, and the extrapolation of empirical fits to such data can be misleading if interpreted to represent equilibrium dissociation rates. It may be better to fit the theory to the data by adjusting the cross section and accept the theoretical temperature dependence as the correct relation for the equilibrium rate. Then, if the state of vibrational nonequilibrium is known, this rate can be corrected by the method of Treanor and Marrone.[17]

The available energy model seems attractive for use as a subroutine in calculating properties of dissociating gases or thermal plasmas, because the results are expressible in

Fig. 4   Dissociation of triatomic molecules.

terms of simple, analytic functions rather than in terms of integrals that need to be evaluated by time consuming numerical methods. For purposes of engineering approximation, it may remain useful even if a highly successful and rigorous theory of dissociation rates is eventually formulated.

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