COLLISION-INDUCED GAS PHASE DISSOCIATION RATES

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SUMMARY

The Landau-Zener theory of reactive cross sections has been applied to diatomic molecules dissociating from a ladder of vibrational states. The result predicts a dissociation rate that is quite well duplicated by an Arrhenius function having a preexponential temperature dependence of about $T^{-1/2}$, at least for inert collision partners. This relation fits experimental data reasonably well.

The theory is then used to calculate the effect of vibrational nonequilibrium on dissociation rate. For Morse oscillators, the results are about the same as given by Hammerling, Kivel, and Teare in their analytic approximation for harmonic oscillators, though at very high temperature a correction for the partition function limit is included. The empirical correction for vibration nonequilibrium proposed by Park, which is a convenient algorithm for CFD calculations, is modified to prevent a drastic underestimation of dissociation rates that occurs with this method when vibrational temperature is much smaller than the kinetic temperature of the gas.

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INTRODUCTION

Rate coefficients have been measured experimentally over a limited range of temperature for most of the reactions that occur in high temperature air flow about hypersonic vehicles. These measurements are typically fit to an Arrhenius expression for the rate coefficient assuming that the activation energy is the heat of reaction and then empirically fitting a preexponential term with the size and temperature dependence which best fits the data. These expressions reproduce the data satisfactorily over the range of experiment; the question is whether they extrapolate correctly far outside this range.

Rates for collision-induced vibrational excitation, dissociation, atom exchange, and ionization have been measured in shock tubes at temperatures from a few thousand to about ten thousand degrees K. These data now need to be extrapolated to temperatures about 40,000°K to apply to the new generation of space vehicles which are designed to decelerate at much higher velocity and at much higher altitude in the atmosphere, where flow conditions can be far out of equilibrium. Experimental confirmation at these temperatures and over a range of nonequilibrium conditions is unlikely. Thus in order to extrapolate reaction rates with more confidence, a theoretical framework is needed to evaluate the proper activation energy and the temperature dependence of the preexponential factors in the Arrhenius expressions. The heat of reaction establishes a minimum value for the activation energy, but an additional barrier to the rate process is possible if the transition occurs at a potential crossing that lies above the energy of the products of reaction. In addition, the effects of nonequilibrium need to be assessed, particularly the effects of nonequilibrium between the vibrational and kinetic modes.

The present paper will focus on the collision induced dissociation of diatomic molecules such as O_2, N_2, and NO. Collision cross section theory will be used which incorporates a realistic functional form for the reaction cross sections, and the total rate coefficient for dissociation will be the sum of rates from all vibrational levels. This procedure will be shown to fit experimental measurements reasonably well with a minimum of empiricism. Then the correction to the dissociation rate for vibrational nonequilibrium will be assessed. The results will be extended to 40,000°K and compared with the extrapolation of single-term Arrhenius functions which empirically fit lower temperature data.

DISSOCIATION RATE EXPERIMENTS AND ARRHENIUS FUNCTIONS

The Arrhenius function normally used to fit the exothermic rate coefficient of a reaction to experimental data is

$$k_f=CT^{-n}\exp(-E^{\star}/kT) \qquad \text{Eq. (1)}$$

where C is a constant, T is the temperature, n is a constant coefficient which gives the temperature dependence of the preexponential term, and E^* is the activation energy. The data can define the activation energy reasonably well, if the scatter is not severe, but do not determine the exponent n very precisely. For example, the dissociation of O_2 by collisions with Ar has been measured by Camac and Vaughan[1], with perhaps greater accuracy than any other high temperature dissociation process, over a temperature range from about 3500° to 8000°K. Their data is shown on Fig. 1 along with three different Arrhenius functions where n = 1/2, 1, and 3/2. The activation energy shown, $(E^*/k) = 59400°K$, allows for a very slight barrier above the dissociation energy from the ground vibrational level $(D_o/k) = 58970°K$. This value of E^*, was used by Camac and Vaughan to fit their data, and is the value recommended by Bortner[2], along with n = 1. The Arrhenius equation with C = 3.61 x 10^{18} cc/mol sec and n = 1 has probably been more widely used in CFD calculations of flow containing dissociating O_2 than any other, and is suggested as a probable rate coefficient by Blottner[3] and by Gupta, Yos, Thompson, and Lee[4] for all collision partners, N_2, O_2, NO, N, and O as well as Ar. The value of the constant C = 3.74 x 10^{18} cc/mol-sec shown on Fig. 1 is the least mean squares value when n = 1 which was obtained here, but this small difference is probably due merely to slight differences in reading data points from the graph published by Camac and Vaughan.

The slope of the data is so strongly determined by the exponential factor that it matters very little which value of n is chosen to represent the preexponential temperature variation. The slope of the Arrhenius function depends on n only at very high temperatures where kT is the order of E^* and the exponential factor approaches unity. When $(E^*/k) = 59400°K$, the coefficient n = 1 gives the best least mean squares fit to the data with a standard deviation in $\ln(k_f)$ equal ± .22. However when n = .5 the standard deviation is only increased to ± .24, and when n = 1.5 the standard deviation is only increased to ± .23. This near equality of the standard deviation can more or less be appreciated by eye as one views the fit of the three functions to the data on Fig. (1).

Although one can judge that the activation energy will be very close to the dissociation energy from the slope of the data, E^* cannot be evaluated precisely. An increase in E^* will increase the slope and would push the best least mean squares fit of the data toward the n = 3/2 function; a decrease in E^* will similarly push the best fit toward n = 1/2.

The lack of precision in fitting an Arrhenius function to data becomes much more severe for dissociation reactions such as those resulting from N_2+N_2, O_2+O_2, and NO+NO collisions, where much greater scatter in data is found. Because of these uncertainties, a theoretical model which would reduce the empiricism in fitting an Arrhenius function to data would be useful.

RATE COEFFICIENT THEORY

The rate coefficient k_f for a reaction such as

$$O_2+M \rightarrow O+O+M \qquad \text{Eq. (2)}$$

gives the number of reactions R per unit volume

$$R = k_f n n' \qquad \text{Eq. (3)}$$

where n is the density of the reacting specie and n′ is the density of the collision partner. The rate coefficient is rigorously the cross section S for the reaction averaged over the distribution of collision energies in center of mass coordinates. Generally this distribution becomes Maxwell-Boltzmann like so very quickly, requiring only a few collisions per molecule, that an accurate expression for k_f is

$$k_f = \frac{\bar{u}}{s}\int_o^\infty S(x)xe^{-x}dx \qquad \text{Eq. (4)}$$

where ū is the mean collision velocity in center of mass coordinates, s is the symmetry number (unity if the colliding species are dissimilar, two if they are the same), x is the dimensionless collision energy in units of kT ($x = E/kT$), and S(x) is the reactive cross section expressed as a function of x.

Very little data exists for reactive cross sections near threshold, but the general form of the function is known. For an endothermic reaction like dissociation, the cross section vanishes below a threshold energy E* which is equal to or greater than the heat of reaction. The cross section then increases rapidly as collision energy increases beyond E*, tops out at some fraction of the total scattering cross section (which is the order of 10^{-15} cm^2 for most light diatomic molecules), and eventually decreases again as collision energy increases further[5],[6]

$$\begin{aligned} S &= o \qquad & x < x^* \\ S &= S(x-x^*) \qquad & x^* < x \end{aligned} \qquad \text{Eq. (5)}$$

thus

$$k_f = \frac{\bar{u}}{s}\int_{x^*}^\infty S(x-x^*)xe^{*}dx = \frac{\bar{u}S_o}{s}e^{-x^*}\int_o^\infty \left(\frac{S}{S_o}\right)(x^*+y)e^{-y}dy \qquad \text{Eq.(6)}$$

where x* is the activation energy in units of kT.

Eq. (6) has the usual Arrhenius form which depends on the exp (-x*). This factor is a consequence of the Maxwell-Boltzmann distribution of collision energies and must be present no matter what nonequilibrium exists in energy modes other than kinetic. The preexponential factor varies as the mean velocity ū and the integral, which is a function only of x*. This integral takes a rather different temperature dependence at the limits. At very low and very high temperatures (x* > > 1 and x* < < 1 respectively), the rate coefficients take the forms

$$\lim_{x^* \to \infty} k_f = \frac{\bar{u} S_o}{s} \left[x^* \int \frac{S}{S_o} e^{-y} dy \right] e^{-x^*} \qquad \text{Eq. (6a)}$$

$$\lim_{x^* \to 0} k_f = \frac{\bar{u} S_o}{s} \left[\int \frac{S}{S_o} y e^{-y} dy \right] e^{-x^*} \qquad \text{Eq. (6b)}$$

To proceed further, the form of the cross section S must be estimated. At low temperatures relative to E*/k, the important part of the cross section is just above threshold. The higher energy end of the cross section function is relatively unimportant because the contribution there is nullified by the Maxwell Boltzmann distribution. However at high temperature relative to E*/k, the shape of the cross section at the peak and eventually at the tail becomes important.

According to the Landau-Zener quantum treatment of transition probability[5,6], transitions occur within a narrow interval of internuclear distance around a constant value r_0 where the potential functions for the reactive and reactant species either cross one another or come very close. The collision system crosses this critical reaction surface twice when the kinetic energy associated with the velocity between the centers of mass exceeds the intermolecular potential at the distance r_0; once during the approach to collision and again when the partners recede from one another. Thus the total probability that the system ultimately follows the reactant potential surface after the collision event is

$$P = p(1-p) + (1-p)p = 2p(1-p) \qquad \text{Eq. (7)}$$

where p is the probability of transition during a single crossing of the reaction surface. In other words, p(1-p) is the probability that transition occurs during the approach state and does not occur during the escape, while (1-p)p is the probability that transition does not occurring in approach but instead occurs during the escape. Similarly $p^2+(1-p)^2$ is the probability that collision does not result in reaction, even if energetic enough to cross the reaction surface.

Landau and Zener find that the transition probability during a single crossing of the reaction zone can be approximated

$$p = 1 - \exp\left\{ -2\pi \; H_{12}^2 \; / \; u \frac{d}{dx} \left(H_{22} - H_{11} \right) \right\} \qquad \text{Eq. (8)}$$

where H_{ij} is the matrix element representing the average of the total Hamiltonian operator when the system's wave functions ϕ are in state i and j respectively

$$H_{ij} = \left\langle \phi_j^* \tilde{H} \phi_i \right\rangle \qquad \text{Eq. (9)}$$

The velocity of the system crossing the reaction zone is u, and $d(H_{22}-H_{11})/dx$ is the difference in slope between the product and reactant potential functions at that point. Generally the matrix elements and the potential surfaces are not available, but the probability p is obviously a strong function of the crossing velocity u; unity at u = 0 when the collision is barely energetic enough to reach the reaction configuration and vanishing at large u where the collision velocity is so high that transition does not have time to occur and the system remains on the same potential surface throughout the collision.

The Landau-Zener model is based on a number of approximations which comprise its precision, but it does serve to suggest the kind of shape reaction cross sections should have. See Hansen[7] for a discussion of the limitations and usefulness of the model. Whatever the exact shape, the total reaction probability P vanishes at either extreme, either very low or very high relative velocity, and becomes a maximum of 1/2 at whatever the velocity which produces a single crossing transition p of 1/2.

REACTION CROSS SECTION SHAPE

If the collision potential is spherically symmetric, conservation of angular momentum requires that of the collisions that initially have a miss distance equal to r_o, the radius of the reaction surface, only a fraction $(1-E^*/E)$ will reach r_o or closer. See Hansen[7] for the proof of this relation. Thus the reactive cross section can be expressed

$$\frac{S}{S_o} = 2p(1-p)\ (1-E^*/E) \qquad \text{Eq. (10)}$$

where S_o is πr_o^2. The rate of increase in p above threshold is generally not known since so few reactive cross sections have been measured there; we assume that p increase as some power m of the excess collision energy

$$p(1-p) = \left(1-\frac{E^*}{E}\right)^m \left\{1-\left(1-\frac{E^*}{E}\right)^m\right\}, \quad E > E^* \qquad \text{Eq. (11)}$$

We expect that the experimental m will be somewhere in the range near unity; at least this is the case for the ionization reactions measured by Utterback and Van Zyl[8,9]. Although we cannot be sure that the nonionizing dissociation reactions will be that similar, the Landau-Zener model suggests that the probability should increase rapidly as collision energy exceeds E* and it would be surprising to find a slower increase than when m equals 2. The faster increase near threshold as m approaches unity seems more realistic.

The total cross section can be expressed in terms of the dimensionless energies x*

$= E^*/kT$ and $x = E/kt$

$$\frac{S}{S_o} = \left(1 - \frac{x^*}{x}\right)^{m+1} \left\{1 - \left(1 - \frac{x^*}{x}\right)^{m}\right\} \qquad \text{Eq. (12)}$$

and the rate coefficient is then

$$\begin{aligned} k_f &= 2\bar{u}S_o \int_{x^*}^{\infty} \left\{ \left(1 - \frac{x^*}{x}\right)^{m+1} - \left(1 - \frac{x^*}{x}\right)^{2m+1} \right\} x e^{-x} dx \\ &= 2\bar{u}S_o e^{-x^*} \int_0^{\infty} \frac{(y+x^*)^m - y^m}{(y+x^*)^{2m}} y^{m+1} e^{-y} dy \\ &= \bar{u}S_o \, F_m(x^*) \, e^{-x^*} \end{aligned} \qquad \text{Eq. (13)}$$

The preexponential factor $F_m(x^*)$ is twice the integral expressed in Eq. (13). In the limits of very low and very high temperatures, where $x^* >> 1$ and $x^* << 1$ respectively

$$\lim_{x^* \to \infty} F_m(x^*) = \frac{2(m+1)!}{(x^*)^m} = 2(m+1)! \left(\frac{kT}{D}\right)^m \qquad \text{Eq. (14a)}$$

$$\lim_{x^* \to 0} F_m(x^*) = 2mx^* = 2m\left(\frac{D}{kT}\right) \qquad \text{Eq. (14b)}$$

Thus we can see that the preexponential factor in the Arrhenius equation should be a changing function of temperature, and not a constant function as usually assumed. The factor becomes small at very low and very high temperatures with a maximum in between. These integrals have been evaluated by numerical quadrature for $m = 1$, $3/2$, and 2; the results are shown in Fig (2). F_m peaks at about .42 near $x^* = 1$ for all three values of m and has a slightly skewed Gaussian-like shape about this peak.

At temperatures low compared with D/k, these results do not agree very well with the observed rate coefficients. For example the preexponential factor which fits the O_2 + Ar dissociation rate data varied about as T^{-1}, whereas the low temperature limit given by Eq. (14a) suggests that the preexponential factor should vary as $\bar{u}(kT/D)^m$ or as $T^{(m+1/2)}$. The explanation for this discrepancy is that very few dissociations occur from the ground vibrational state of the molecule; most dissociations occur from states that are about kT from the dissociation limit where the factor $F(x^*)$ is the order of one-half and less dependent on temperature. It is not correct to compare the expression for dissociation from the ground state to the experimental rate where the dissociation from higher excited states are primarily measured.

Interestingly, the simplest possible model for reaction, the available energy theory proposed long ago by Fowler and Guggenheim[10], fits the experimental data in a reasonable way. The problem with the available energy theory is that the number of internal degrees of freedom of the collision partners which contribute to the reaction is unknown, so this parameter is adjusted empirically to agree with data. However Hansen[7] suggests that this number be chosen as the number of degrees of freedom which disappear in the reaction, which for the dissociation of a diatomic molecule is 4. Then the preexponential term in the Arrhenius equation derived varies as T^{-1}, just as the best fit to Camac and Vaughan's O_2 + Ar dissociation data. Although the N_2+N_2 dissociation is generally taken[4] to vary as $T^{-1/2}$ in the preexponential factor while the NO+NO dissociation preexponential term varies as $T^{-3/2}$, these discrepancies are not serious in view of the insensitivity of the slope of the data to the temperature variation of the preexponential term. As we observed in the discussion of the O_2 + Ar dissociation data, a change in the temperature exponent n in Eq. (1) can be compensated by changing the constant C, and any mismatch in slope of the data can be corrected by changing the effective activation energy E^*. The point is that, at least over the range of experimental data, the Arrhenius preexponential term should vary inversely as some power of temperature, not as a direct power of temperature as given by Eq. (14a). The simple available energy theory arrives at a reasonable temperature dependence for the reaction by taking into account the contribution from the excited states, whereas the reactive cross section expression of Eq. (13) assumes that all the reactions occur from a single state where the activation energy is constant. The reactive cross section theory will only give a correct answer when the multiplicity of excited states is taken into account as will be shown next.

EFFECTS OF EXCITED STATES ON REACTION

When a ladder of excited states is present which provides multiple paths to the product state, the total rate of reaction can be expressed

$$R = \left[\sum_i k_{fi} \frac{n_i}{n} \right] n n' = k_f n n' \qquad \text{Eq. (3a)}$$

where the sum extends over all populated states i, n_i is the density of reactive particles in state i, n is the total density of reactive particles, and n' is the total density of collision partners as before. The single sum over excited states of the reactive partner of Eq. (3) applies strictly only when the collision partner is inert and does not change its internal energy during collision. For inert partners the effective total rate coefficient k_f is

$$k_f = \sum k_{fi} \frac{n_i}{n} = \frac{1}{Q(T_v)} \sum_i k_{fi} g_i e^{-\epsilon_i/kT_v} \qquad \text{Eq. (15)}$$

where T_v is a temperature which describes the distribution of reactive molecules over the excited states i. $Q(T_v)$ is the partition function for the reactive species and e_i is the energy of the ith state. At equilibrium, which we consider first, T_v equals the kinetic gas temperature T, of course.

Now we assume that all excited states have the same form for the reactive cross section given by Eq. (13). This is not certain, of course; the different states may have different matrix elements and different slopes of their potential surfaces at the reaction point in Eq. (8) and could presumably lead to somewhat different forms for the transition probabilities given by Eq. (11). However in the absence of better knowledge we proceed to use the assumption of equivalent forms

$$k_{fi} = \frac{\bar{u} S_i}{s} F(x_i^*)\, e^{-(E^*-\epsilon_i)/kT} \qquad \text{Eq. (16)}$$

where

$$x_i^* = \left(E^*-e_i\right)/kT$$

The total rate coefficient then becomes

$$k = \frac{\bar{u} S_o}{sQ} e^{-E^*/kT} \sum_i g_i \left(\frac{S_i}{S_o}\right) F\left(x_i^*\right) \qquad \text{Eq. (17)}$$

Certainly the exponential factor in Eq. (16) is correct, if E* does not change with the state i, and as observed in Fig. (2) the factor $F(x_i^*)$ is not highly dependent on the parameter chosen for m.

The simplification will now be made that the dissociation rate depends primarily on the vibrational state of the molecule and not on its rotational state. This is not strictly so, though it has often been assumed in dissociation rate studies. Typically the rotational states are completely in equilibrium with the kinetic temperature and the characteristic rotational temperature B/k is orders of magnitude smaller than T. If we assume that the rotational partition function is separable from the vibrational, this factor of Q largely cancels the similar factors in the sum over states in Eq. (17). The remaining degeneracies of the vibrational states are all unity. We also take the ratios (Si/So) in Eq. (17) to be unity; this also is not strictly so as we expect cross sections for higher vibrational states probably increase, but the increase should be small for stiff molecules like O_2 and N_2 until very close to the dissociation limit when the factors $F(x_i^*)$ cancel the importance of these terms anyway. For dissociation, the activation energy E* is taken as the dissociation energy D. Then the simplified expression for the total rate coefficient is

$$k_f = \frac{\bar{u} S_o e^{-D/kT}}{s Q_v} \sum_i F(x_i^*) \qquad \text{Eq. (18)}$$

where the summation now extends only over the vibrational levels and Q_v is the vibrational partition function.

The summations of $F(x_i^*)$ and the partition function Q_v have been determined numerically for a Morse oscillator series of energy levels where the energy above the ground state is

$$e_i = \left(\frac{\hbar\omega}{kT}\right)\left[i - \left(\frac{\hbar\omega}{4D}\right) i(i+1)\right] \qquad \text{Eq. (19)}$$

for N_2, O_2 and NO. The summation of $F(x_i^*)$ is remarkably independent of temperature since it essentially sums only levels where $x_i^* = (D-e_i)/kT$ is close to unity. Thus the preexponential term of the rate coefficient in Eq. (18) varies about as $\bar{u}/Q_v$. For harmonic oscillators Q_v varies about as T and a little bit faster than this for the Morse oscillator, so the total variation in the preexponential is roughly $T^{-1/2}$.

ENDOTHERMIC RATES WITH VANISHING REVERSE REACTION

Rates of reaction are never observed under equilibrium conditions when forward and reverse reactions are unbalanced, only when they are out of balance. In a shock tube the rate of reaction is measured at the inception of reaction caused by a sudden discontinuity of kinetic temperature when the gas is heated by a passing shock wave. Under these conditions the reverse exothermic reaction is absent because the concentration of reactants is zero, and this is the situation that should be analyzed when comparing a theoretical model with experimental data.

Under these highly nonequilibrium conditions, the population of excited states is depleted in the upper levels. The reaction proceeds from a pseudo-steady distributions that is like a truncated Boltzmann distribution as shown by solutions to the Master Equations which allow for shuffling between all the excited levels as well as for reaction. Hansen[7] shows that as a first approximation a Boltzmann distribution of vibrational states truncated about kT below the dissociation limit, or perhaps a bit more, will duplicate the rate of dissociation that is predicted to occur from a pseudo steady distribution according to solutions of the Master Equations, even considering a rather wide variation in reactive cross sections. Park[11] has suggested that more realistic distributions of vibrational states should be bi-model. The lower and upper vibrational levels do not exchange vibrational quanta easily because of anharmonicity; thus lower levels can be in a Boltzmann distribution at a temperature T_v that is far out of equilibrium with the kinetic temperature T, while upper levels tend toward a Boltzmann distribution described by the temperature T, because the vibrational states then become so closely spaced they act more like a classical continuum which the high energy collisions shuffle back and forth more easily. However that may be, for the conditions of interest here the problem is somewhat moot since the upper states are missing due to their rapid escape to the dissociated state. To model the typical experimental condition, the summation over all $F(x_i^*)$ and of terms in the vibrational partition function Q_v in Eq. (18) is truncated kT below the dissociation limit. This truncation of states introduces an extra temperature dependence at high temperature that reduces both the sum of $F(x_i^*)$ and of Q_v, though these reductions compensate to a large extent.

Figure 3 shows the comparison between the predictions of Eq. (8) and the best single term Arrhenius functions which have been recommended[4] to represent experimental data. Fig (3a) shows the O_2-Ar dissociation rate coefficient from Eq. (18) (solid curve) and for Blottner's Arrhenius equation (dashed curve) along with Camac and Vaughan's data mentioned previously. Blottner's formula agrees with the O_2-Ar data and has been recommended without modification for all collision partners including N_2, O_2, NO, N, and O as well as Ar. The slope of the function given by Eq. (18) has been made as small as possible by reducing the effective activation energy as far as possible to the value of $D_o = 5.117 eV$. However this reduction in the slope is only about 1% which is relatively meaningless. The present theory is slightly more in accord with a $T^{-1/2}$ preexponential dependence than the T^{-1} dependence given by Blottner's equation; however again this difference is rather insignificant in view of the scatter in data, excellent data though it is. The first appreciable difference between the two appears at high temperatures near 40000°K where the present calculations suggest a greater rate coefficient might occur by a factor of about 2.5. Again this difference has questionable significance in view of all the approximations involved, and for practical purposes the use of Blottner's equation seems quite justified.

Fig (3b) shows the comparison between the present calculations for N_2-N_2 dissociation and Blottner's Arrhenius equation. In this case Blottner decided that a $T^{-1/2}$ preexponential dependence best described the data and the agreement between the two is almost perfect. However the data for N_2-N_2 dissociation shows considerable scatter, even on the logarithmic Arrhenius plot, so the assignment of this temperature dependence is far from certain.

Fig. (3c) shows the same comparison between the present calculations and Blottner's recommended equation for NO-NO collision dissociation. In this case a $T^{-3/2}$ dependence has been assigned to the preexponential term of the Arrhenius equation,and the fit between the two suffers accordingly, although the worst discrepancy occurring at 40,000°K is only a factor of 5. The NO-NO dissociation data is even more widely scattered than the previous cases, so the temperature dependence assigned by Blottner is not necessarily precise. However it represents the best estimate of an Arrhenius function based on available data.

DISSOCIATION WITH RECOMBINATION

As dissociation proceeds in the gas and the free atom concentration builds up, the recombination reaction subtracts from the observed forward rate. Usually this is treated by calculating separately the reverse reaction using the recombination rate coefficient k_r, which is related to k_f by the equilibrium constant $K_{eq}(T)$

$$\frac{k_f}{kr} - K_{eq}(T) - \frac{Q_a^2}{Q_m} e^{-D/kT} \qquad \text{Eq. (20)}$$

where Q_a and Q_m are the total partition functions of the atoms and molecules respectively. However, if the process is modelled reasonably well by the pseudo-steady distributions obtained in solution of the Master Equations, we can simply subtract the fraction of dissociation events which are in balance with the atom concentration. The fraction of the total number of reactive molecules which is in pseudo equilibrium with the atom concentration a is (a/a*), where a* is the atom concentration which would be in equilibrium with the total molecule density n.

$$(a*)^2 = n\,K_{eq}(T) \qquad \text{Eq. (21)}$$

then the effective forward rate coefficient which gives the net rate of dissociation is

$$k_f(net) = \left[1-\left(\frac{a}{a*}\right)^2\right]\frac{\bar{u}\,S_o e^{-D/kT}}{sQ_v}\sum_i F(x_i^*) \qquad \text{Eq. (22)}$$

Because the correction involves the square of the product concentration in the case of dissociation, the observed forward rate is quite insensitive to the back reaction until rather close to full equilibrium. When free atom concentrations are 30% of their equilibrium value, the observed dissociation rate has only decreased about 10%.

DISSOCIATION WITH VIBRATIONAL NONEQUILIBRIUM

When the vibrational temperature T_v has not relaxed to equilibrium with the translational temperature T, the population distribution in the lower states is assumed to be Boltzmann

$$\frac{n_i}{n} = \frac{e^{-E_i/kT_v}}{Q_v(T_v)} \qquad \text{Eq. (23)}$$

then the dissociation rate coefficient of Eq. (18) becomes

$$k_f = \frac{\bar{u}S_o}{s}\sum_i \frac{e^{-\left(\frac{D-E_i}{kT}\right)}e^{-E_i/kT_v}}{Q_v(T_v)}\,F_i\left(x_i^*\right)$$
$$k_f = \frac{\bar{u}\,S_o e^{-D/kT}}{sQ_v(T_v)}\sum F_i\left(x_i^*\right)e^{-E_i/kT^*} \qquad \text{Eq. (24)}$$

where the temperature T* is

$$\frac{1}{T^*} = \frac{1}{T_v} - \frac{1}{T} \qquad \text{Eq. (25)}$$

This is the same effective temperature proposed by Hammerling, Kivel, and Teare[12] for their vibrational non-equilibrium correction factor, which was based on a harmonic oscillator model.

The ratio of the dissociation rate coefficient for non equilibrium, $k_f(T,T_v)$, to the coefficient for full equilibrium, $k_f(T,T)$ is according to Eq. (24)

$$\frac{k_f(T,T_v)}{k_f(T,T)} - \frac{Q_v(T)}{Q_v(T_v)} \frac{\sum_i F_i\left(x_i^*\right) e^{-E_i/kT^*}}{\sum_i F_i\left(x_i^*\right)} \qquad \text{Eq. (26)}$$

Fig. (4) shows the ratio $k_f(T,T_v)/k_f(T,T)$ based on the Morse oscillator ladder of vibrational states for T_v/T equal 0.9, 0.6, and 0.1; all for the limiting case where atom concentration is zero and there is no recombination reaction. Curves are shown for O_2 dissociation and for N_2 dissociation. The correction is somewhat larger for N_2 principally because the characteristic vibrational temperature $\hbar\omega/k$ is much larger.

As gas temperature increases, the dissociation occurs more readily from lower levels on the vibrational ladder. Then the vibrational nonequilibrium becomes a less important factor in determining the dissociation rate and the rate coefficients approach the equilibrium value more closely as shown in Fig. (4).

The principle feature of importance is that vibrational temperature of the oscillators does not enter the exponential factor of the Arrhenius function; T_v can at most influence the summation effect of dissociation from the excited states and thus modify the preexponential term of the Arrhenius function. Thus any scheme which weights the temperature in the exponential factor with the vibrational temperature, as proposed by Park[11], is theoretically incorrect in principle, though it may provide an approximate correction in an empirical way if the vibrational temperature is not depressed too far. Park proposed an effective temperature T_a for use in the Arrhenius expressions which are fitted to experimental data

$$T_a - T_v^{.3}\, T^{.7} \qquad \text{Eq. (27)}$$

In this case, for the Arrhenius function defined in Eq. (1), the correction factor for vibrational nonequilibrium becomes

$$\frac{k_f(T,T_v)}{k_f(T,T)} = \left(\frac{T}{T_v}\right)^{.3n} e^{-D/kT\left[\left(\frac{T}{T_v}\right)^{.3}-1\right]} \qquad \text{Eq. (28)}$$

The problem with this correction is that if it is pushed far enough, to very low T_v, it will greatly underestimate the true dissociation rate because of the extreme sensitivity of the exponential term in Eq. (1) to the temperature used, which as we have shown theoretically should be the kinetic gas temperature without modification. This factor appears because the Boltzmann distribution of kinetic states is truncated at the dissociation energy, without regard to the internal states of the collision partners.

Hammerling, Kivel, and Teare[12], using a harmonic oscillator approximation, derive a correction factor for dissociation rates when vibrational nonequilibrium is present

$$\frac{k_f(T_v,T)}{k_f(T,T)} = \frac{1}{N}\,\frac{1-e^{-N\theta/T^*}}{1-e^{-\theta/T^*}}\,\frac{1-e^{-\theta/T_v}}{1-e^{-\theta/T}} \qquad \text{Eq. (29)}$$

where $\theta = \hbar\omega/k$, the characteristic vibrational temperature, and N is the total number of vibrational levels considered.

As a first approximation a slightly modified form of Eq. (29) can be derived from Eq. (26). The sum of $F_i(x_i^*)$ is found to be rather constant, more or less independent of temperature. Thus the Gaussian-like function of Fig. (2) can be approximated by a square function having the maximum value about f_o and a width truncated at a specified number of vibrational levels N. Since the vibrational levels are approximately equally spaced about this maximum, even for a realistic model like the Morse oscillator, with vibrational levels spaced $\hbar\omega^* = k\theta^*$

$$\sum F_i\left(x_i^*\right) \approx N f_o \qquad \text{Eq. (30a)}$$

$$\sum F_i\left(x_i^*\right) e^{-i\theta^*/T^*} \approx f_o\,\frac{1-e^{-N\theta^*/T^*}}{1-e^{-\theta^*/T^*}} \qquad \text{Eq. (30b)}$$

Also, since we may wish to treat very high temperatures where kT is the order of the dissociation energy D, the cutoff in the vibrational partition function becomes more important. Then

$$Q_v(T) \approx \frac{1-e^{-D/kT}}{1-e^{-\theta/kT}} \qquad \text{Eq. (31a)}$$

$$Q_v(T_v) \approx \frac{1-e^{-D/kT_v}}{1-e^{-\theta/kT_v}} \qquad \text{Eq. (31b)}$$

and the approximation for Eq. (26) becomes

$$\frac{k_f(T,T_v)}{k_v(T,T)} \approx \frac{1}{N}\;\frac{1-e^{-N\theta^*/T^*}}{1-e^{-\theta^*/T^*}}\left(\frac{1-e^{-\theta/T_v}}{1-e^{-\theta/T}}\right)\left(\frac{1-e^{-D/kT}}{1-e^{-D/kT_v}}\right) \qquad \text{Eq.(26a)}$$

$$\xrightarrow[T_v,T>>\theta]{} \frac{1}{N}\;\frac{1-e^{N\theta^*/T^*}}{1-e^{-\theta^*/T^*}}\left(\frac{T_v}{T}\right)\left(\frac{1-e^{-D/kT}}{1-e^{-D/kT_v}}\right)$$

This has the same form as the correction given by Hammerling et al[12], except that the number of levels N is adjusted to a partial number of vibrational levels, θ^* is $\hbar\omega^*/k$ with ω^* the average frequency spacing between vibrational states at the level i where E_i is about kT, and the last factor in Eq. (26a) has been added to account for the finite limit in the vibrational partition function sum. One could also consider changing the characteristic temperature θ to an average value between the ground vibrational states and states where E_i is about kT, to account for anharmonicity in the molecule, but as T_v and T both become large compared with θ the ratio of partition functions approaches (T_v/T) without regard to the value of θ anyway.

Fig. (5) shows comparisons between the correction factors for vibrational nonequilibrium given by Eq. (26), Eq. (28), and Eq. (26a). For the latter, the number of levels N is chosen to be 34 for both O_2 and N_2 dissociation. As expected, there is reasonable equality between Eq. (26) and the approximation of Eq. (26a) derived from that expression. When T_v/T is about ½ or greater, the empirical correction of Eq. (28) is not too bad; however as T_v becomes very small compared with T, this correction becomes very small due to the sensitivity of the modified exponential term in the Arrhenius rate coefficient. Probably these small values are unrealistic in view of the fact that they have no theoretical justification. Nevertheless Park's correction has the advantage of being a very simple algorithm, and it could be a useful empirical approximation if care is taken that it not be used for T_v/T less than about ½ or so.

Although the effective temperature method of modifying an Arrhenius dissociation rate coefficient cannot be justified in a theoretical way, this algorithm is appealingly simple to use and is worth salvaging for CFD computations. Accordingly, the corrections to dissociation rate coefficient provided by the present theory were assumed valid, and the coefficient "a" in the effective temperature T_a

$$T_a = T_v^a\, T^{1-a} \qquad \text{Eq. (32a)}$$

was determined, which could be used in the Arrhenius expression

$$k = \frac{C}{T_a^n}\, e^{-D/kT_a} \qquad \text{Eq. (32b)}$$

to duplicate the results of Eq. (26).

The values of "a" obtained were somewhat scattered about a trend where "a" increases as a function of T_v/T

$$a \approx 0.1 + 0.4\ (T_v/T) \qquad \text{Eq. (32c)}$$

The comparison between the results given by Eq. (26) and by Eq. (32) are shown in Figure (6). Fig. (6a) is for the value n = ½, which has been used to duplicate experimental data for the dissociation rate of N_2; Fig. (6b) is for the value n = 1, which has been used to duplicate experimental data for the dissociation rate of O_2. The relation of Eq. (32c) provides a fair duplication of both cases over the range of T_v/T from 1 to 0.1.

As noted previously, the value a = .3 suggested by Park[11] is not a bad choice provided T_v/T is not too small. However, when vibrations are almost unexcited, as they are behind a shock wave moving into cold air, a smaller value of a is needed to avoid an excessive depression of the rate coefficient given by Eq. (32b). Clearly this occurs because of the sensitivity of the exponential term to any change in the effective temperature used, a change which increases as the vibrational temperature is weighted more strongly in Eq. (32a).

CONCLUDING REMARKS

An attempt has been made to apply collision cross section theory in a somewhat rigorous way, summing the rate of collision induced dissociation of diatomic molecules from each vibrational level, to obtain the total rate coefficient which is observed in experiment. The summed rate coefficient agrees quite well with the Arrhenius expressions which have been fit to data. The results explain the discrepancy that existed in the temperature dependence of the preexponential term of the Arrhenius equation when collision cross section theory was applied just to dissociation from the ground vibrational state; the effect of excited states on the rate process is an essential factor to obtaining the correct result.

The theory suggests that the forward rate coefficient for dissociation should be given by an Arrhenius function where the preexponential factor varies about as $T^{-1/2}$, at least for dissociations caused by collision with an inert partner that has no internal degrees of freedom to contribute to the process. This is indeed the variation that has been assigned for N_2-N_2 dissociation and the agreement there is very close; the agreement is not quite as good for O_2-O_2 where the variation T^{-1} has been assigned to the preexponential term, and the discrepancy becomes even greater for NO-NO collisions where the variation $T^{-3/2}$ has been assigned. This is shown in Figs. (3a), (3b), and (3c). However, the discrepancies are not very meaningful since the scatter in data is such that the mean square deviation of data from the Arrhenius formula is about the same no matter which temperature variation factor is chosen. Overall, the reaction cross section theory which sums the dissociation rate from a ladder of vibrational levels gives a reasonably good fit to data. Since the theory does assume the collision partner to be inert, some deviation from this theory might be expected where the collision partner contains unpaired electrons that would tend to form transient bonds with the reactive specie during the collision event. This may well be the case with NO and atomic collision partners, for example.

The collision cross section theory does not differ significantly from the Arrhenius expressions assigned to fit data, even when extrapolated to high temperatures around 40,000°K. The Arrhenius expressions all fit the data as well as possible in view of the data scatter, and they are simpler algorithms to use for extrapolation than the detailed theory. The results from the latter primarily provide confidence that these extrapolations are reasonable. However, the theory also provides a method of evaluating the effect of vibrational nonequilibrium on dissociation rates. This is an important factor in the calculation of flow about hypersonic space vehicles at high altitude. The results agree reasonably well with the correction developed by Hammerling, Kivel, and Teare[12]; small refinements for anharmonicity and truncation of the vibrational partition function become significant only at higher temperatures. The empirical modification of the Arrhenius function proposed by Park[11] to account for nonequilibrium vibration gives similar values so long as the ratio T_v/T is about 1/2 or more. Park's correction has the merit of being a very simple, quick algorithm to use in CFD calculations. However it should not be relied upon when the ratio T_v/T is much smaller than 1/2, since it uses the theoretically indefensible method of replacing the kinetic temperature, which properly belongs in the exponential factor of the Arrhenius function, with a lower temperature that has been empirically weighted with the vibrational temperature. Eventually at small enough T_v, the effective temperature must be weighted much more weakly with the vibrational temperature to avoid unrealistically small values of the dissociation rate coefficient.

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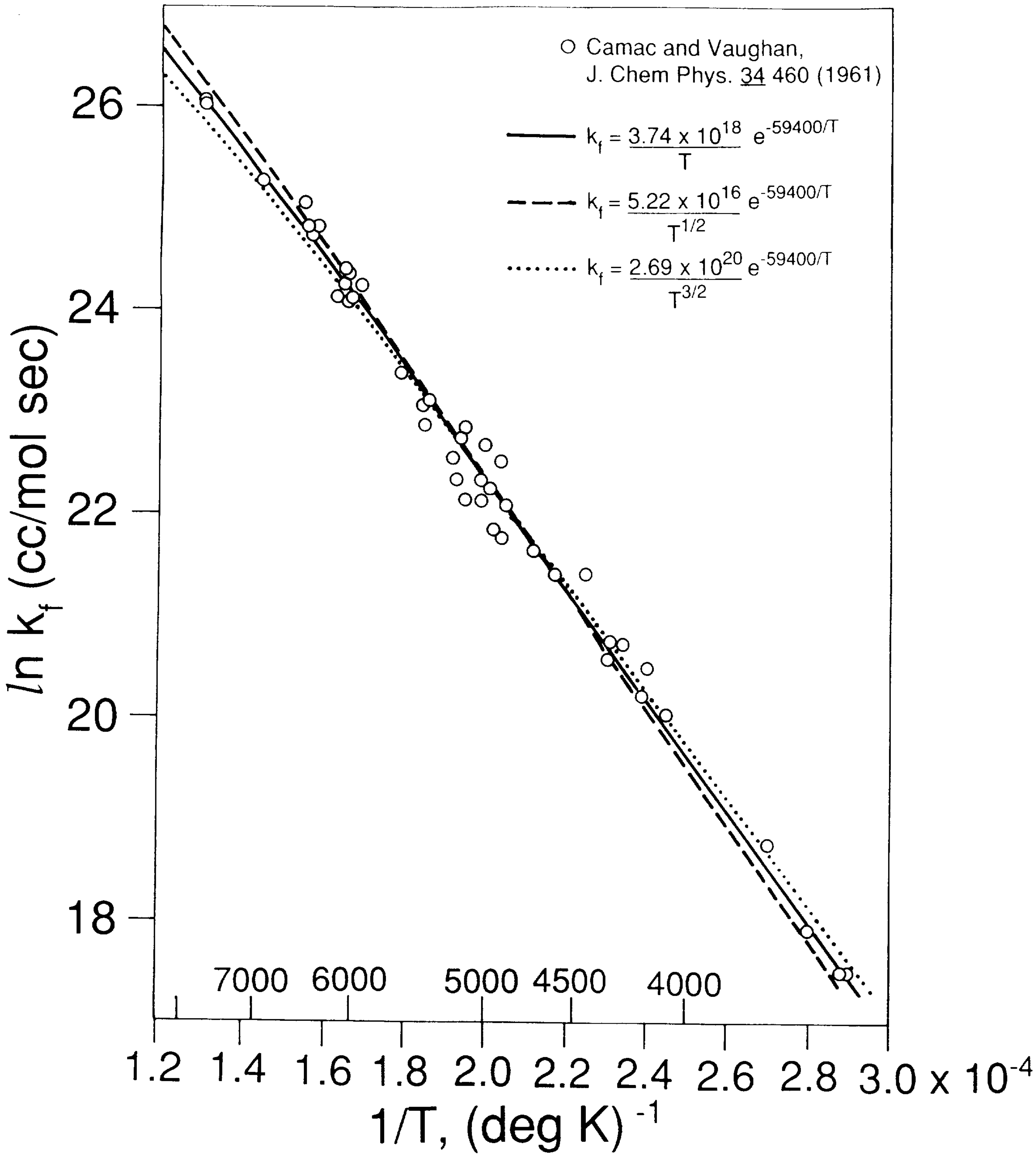


Figure (1). Comparison between Data and Different Arrhenius Expressions for Dissociation of O_2 by Ar Collisions

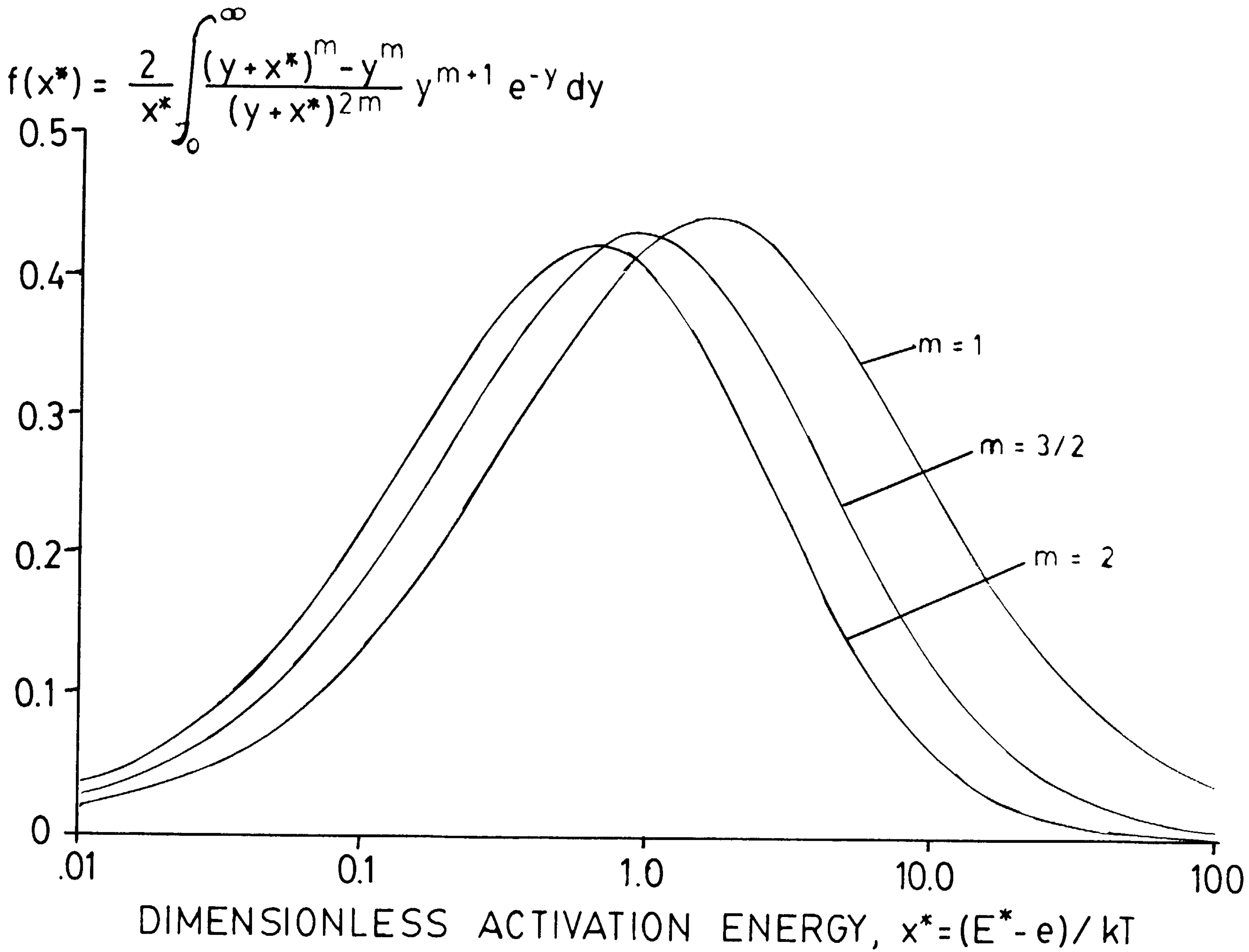


Figure (2). Integration of Reactive Cross Section Over a Boltzmann Distribution of Collision Energies as a Function of the Dimensionaless Activation Energy x* = E*/kT, Cross Section Increase with Collision Energy Above Threshold to the Power m

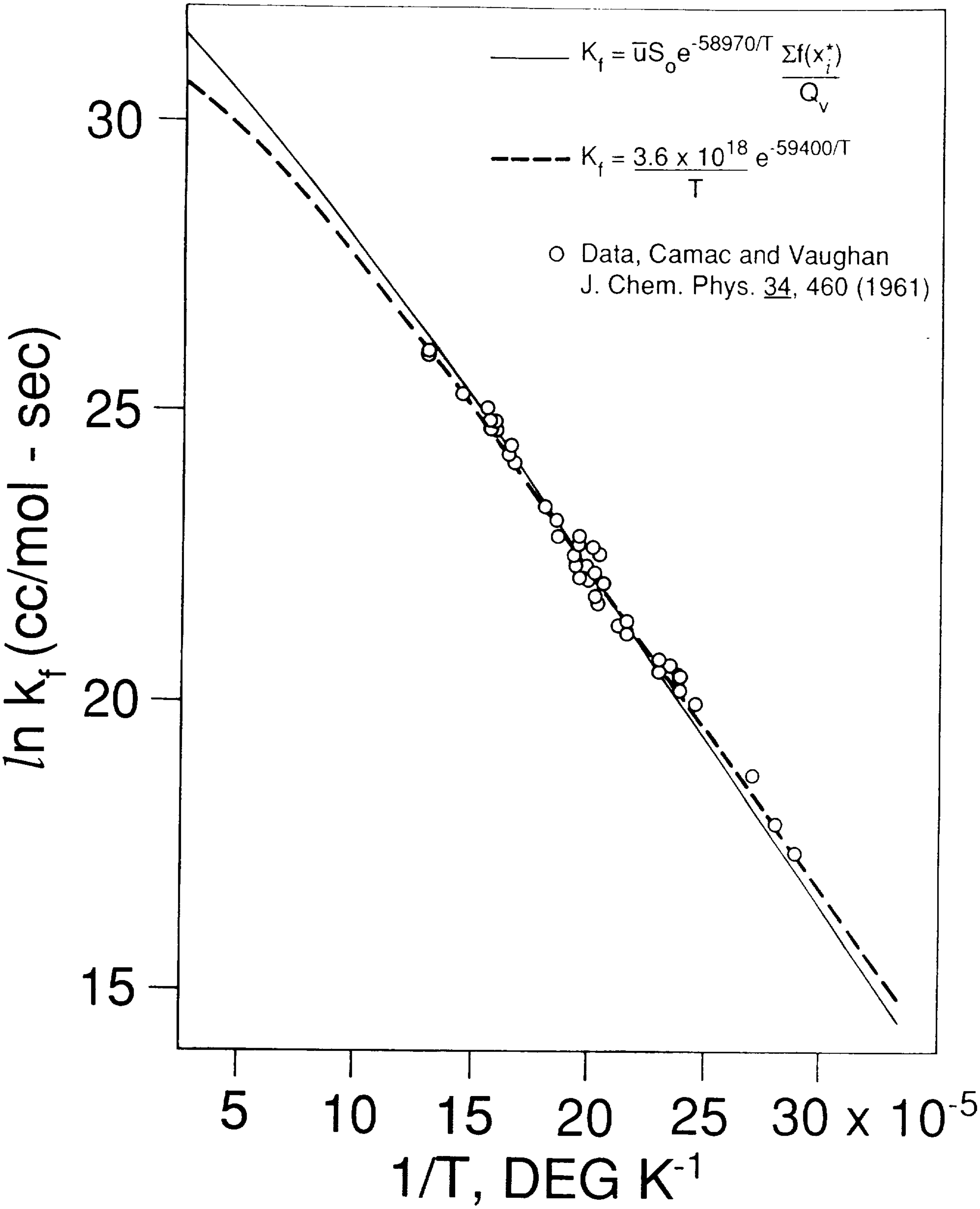


Figure (3a). Theory and Data for O_2-Ar Dissociation

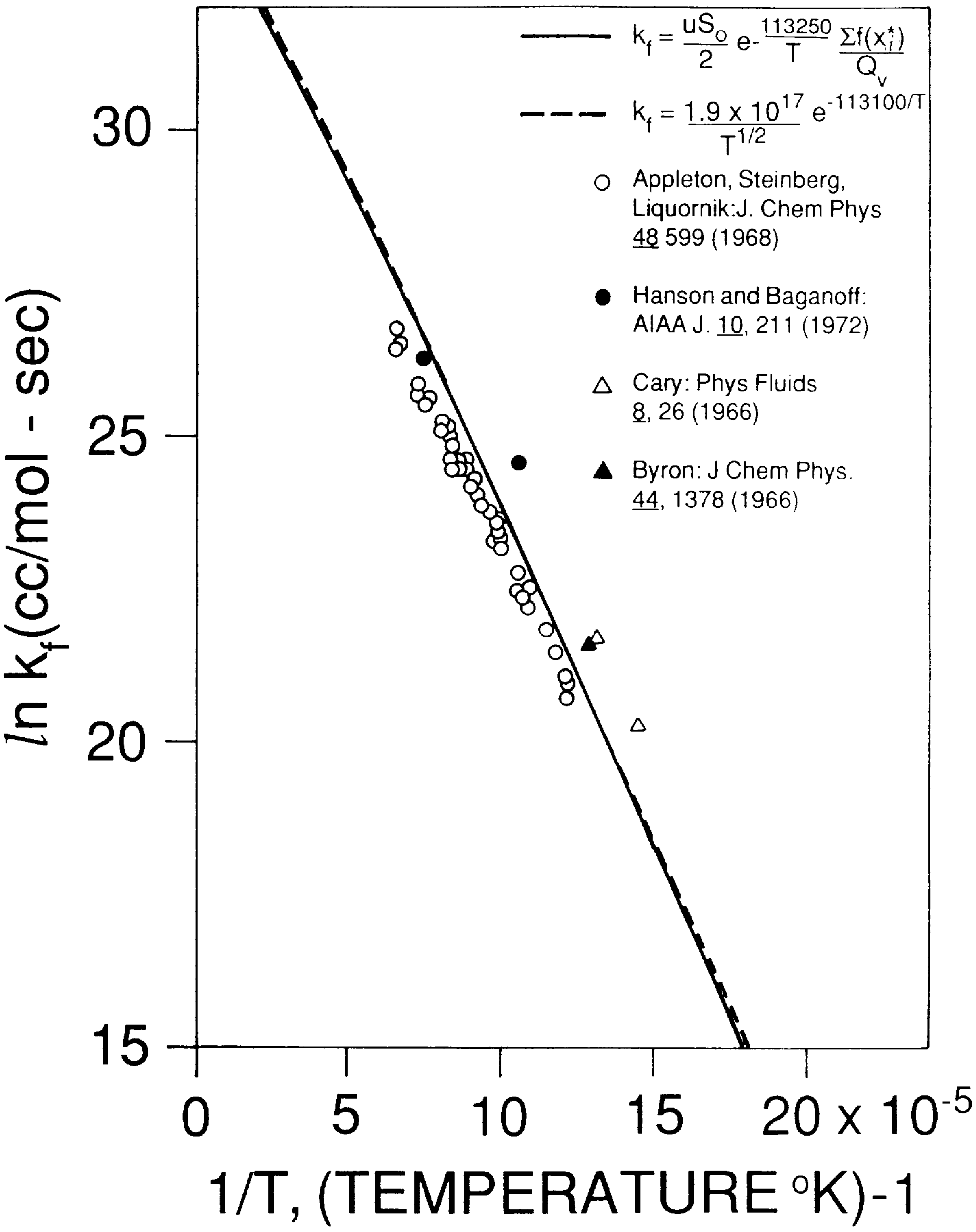


Figure (3b). Theory and Data for N_2-N_2 Dissociation

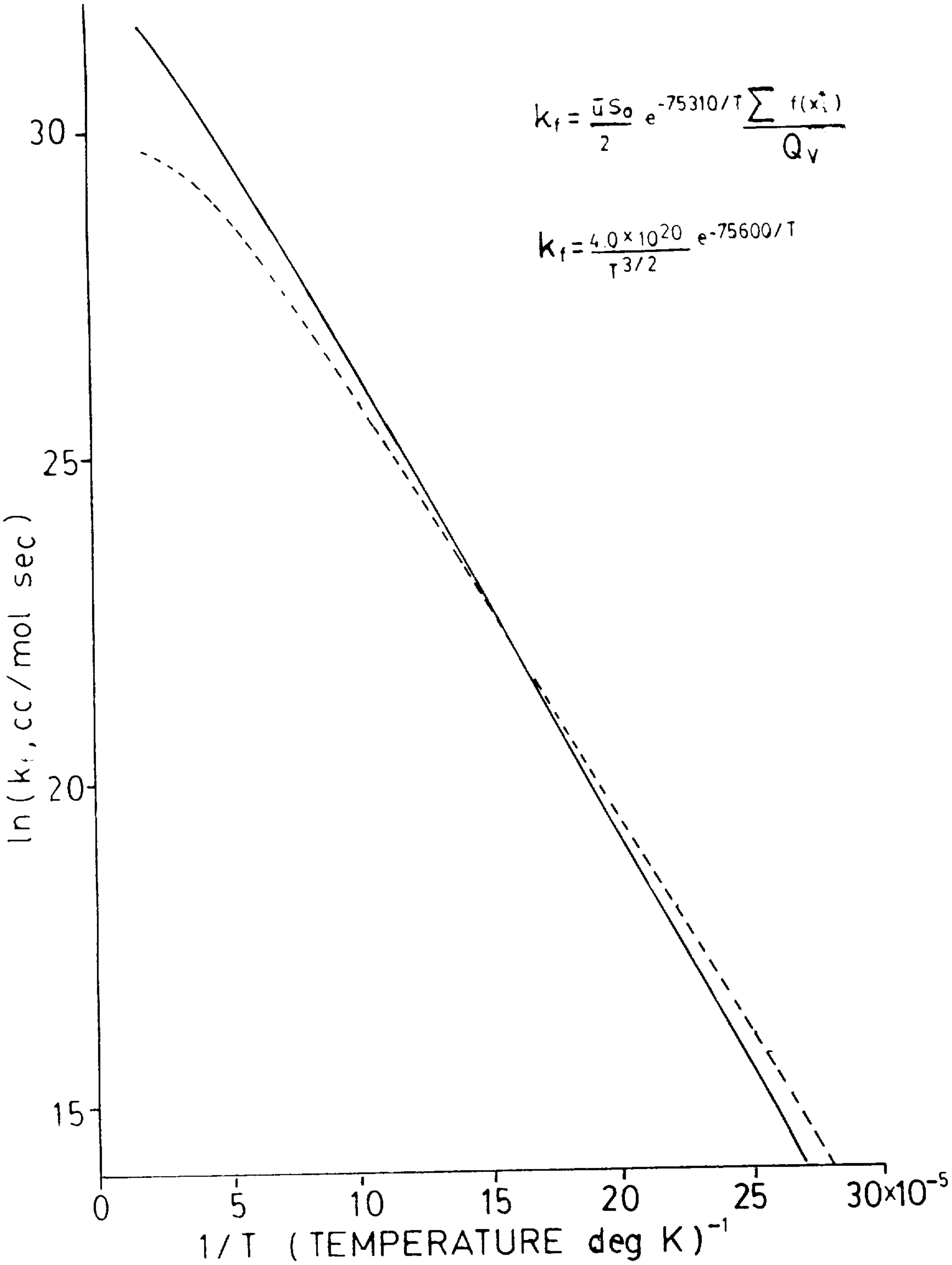


Figure (3c). Theory for NO-NO Dissociation

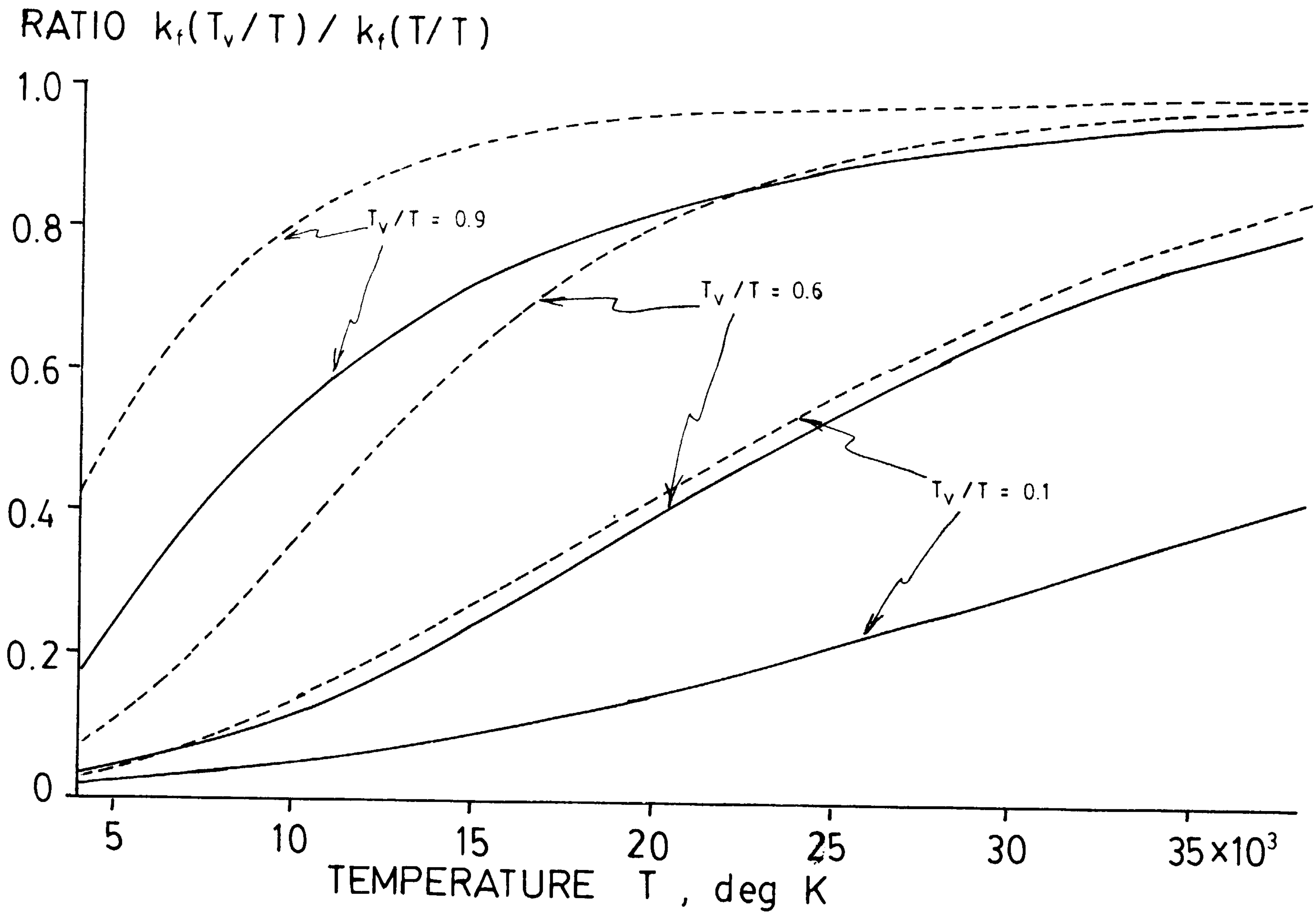
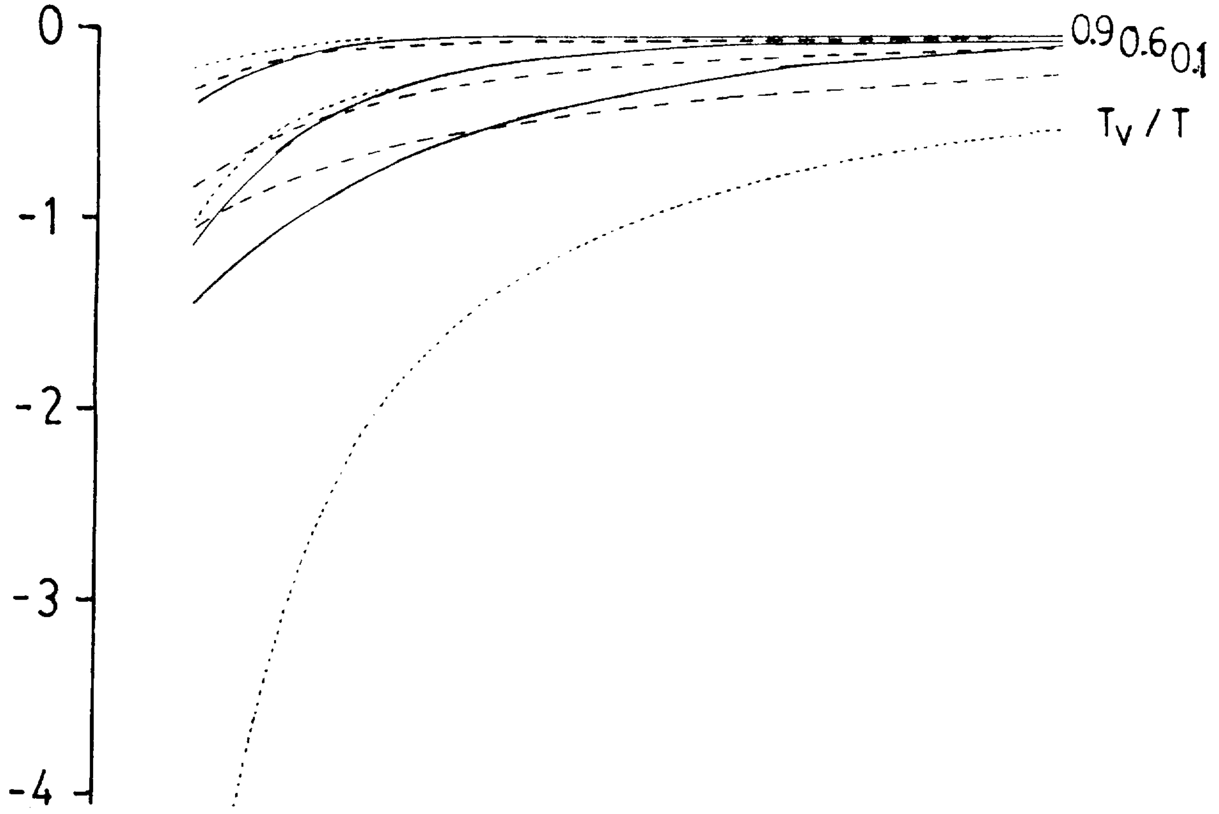
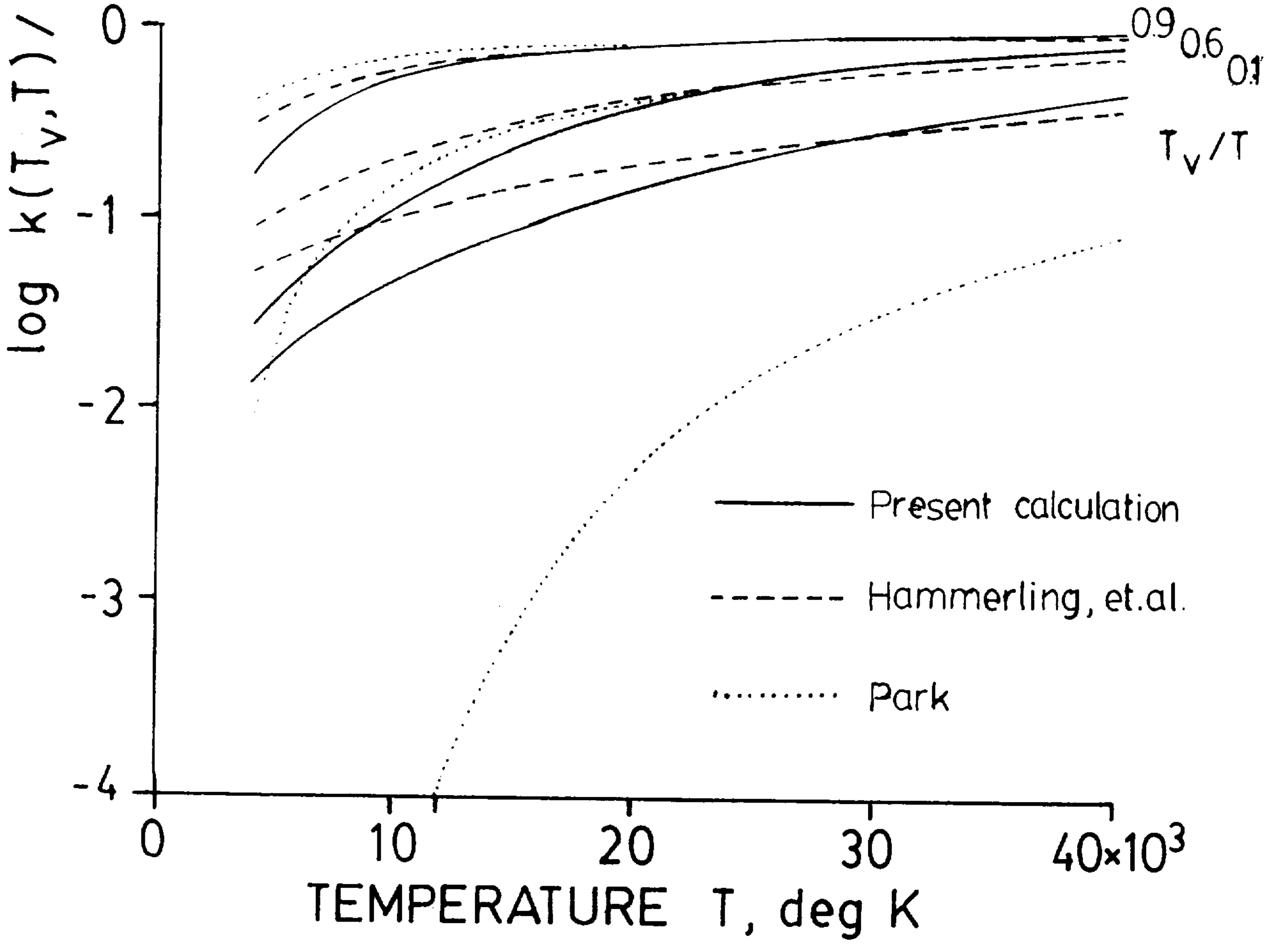


Figure (4). Correction to the Dissociation Rate Coefficient as a Function of Temperature for Different Vibrational Temperatures, ——— N_2 , - - - - - - O_2



(5a) $O_2 - O_2$



(5b) $N_2 - N_2$

Figure (5). Comparison Between Various Methods of Correcting the Dissociation Rate Coefficient for Vibrational Non-Equilibrium

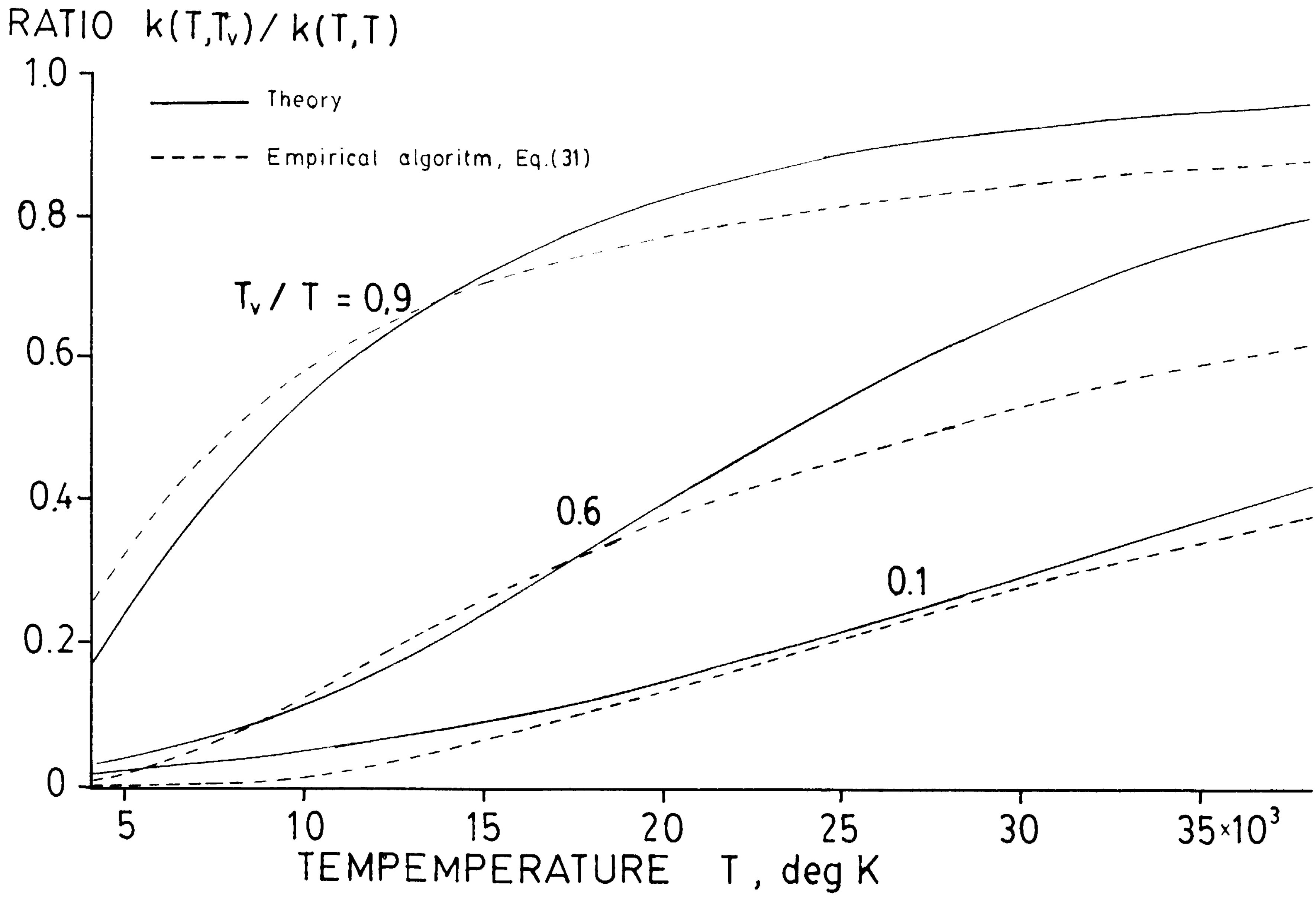


Figure (6a) Comparison Between the Theoretical and a Modified Empirical Method of Correcting the Dissociation Rate Coefficient for Vibrational Non-equilibrium in N_2, where the Equilibrium Coefficient $k = CT^{-1/2} \exp(-D/kT)$

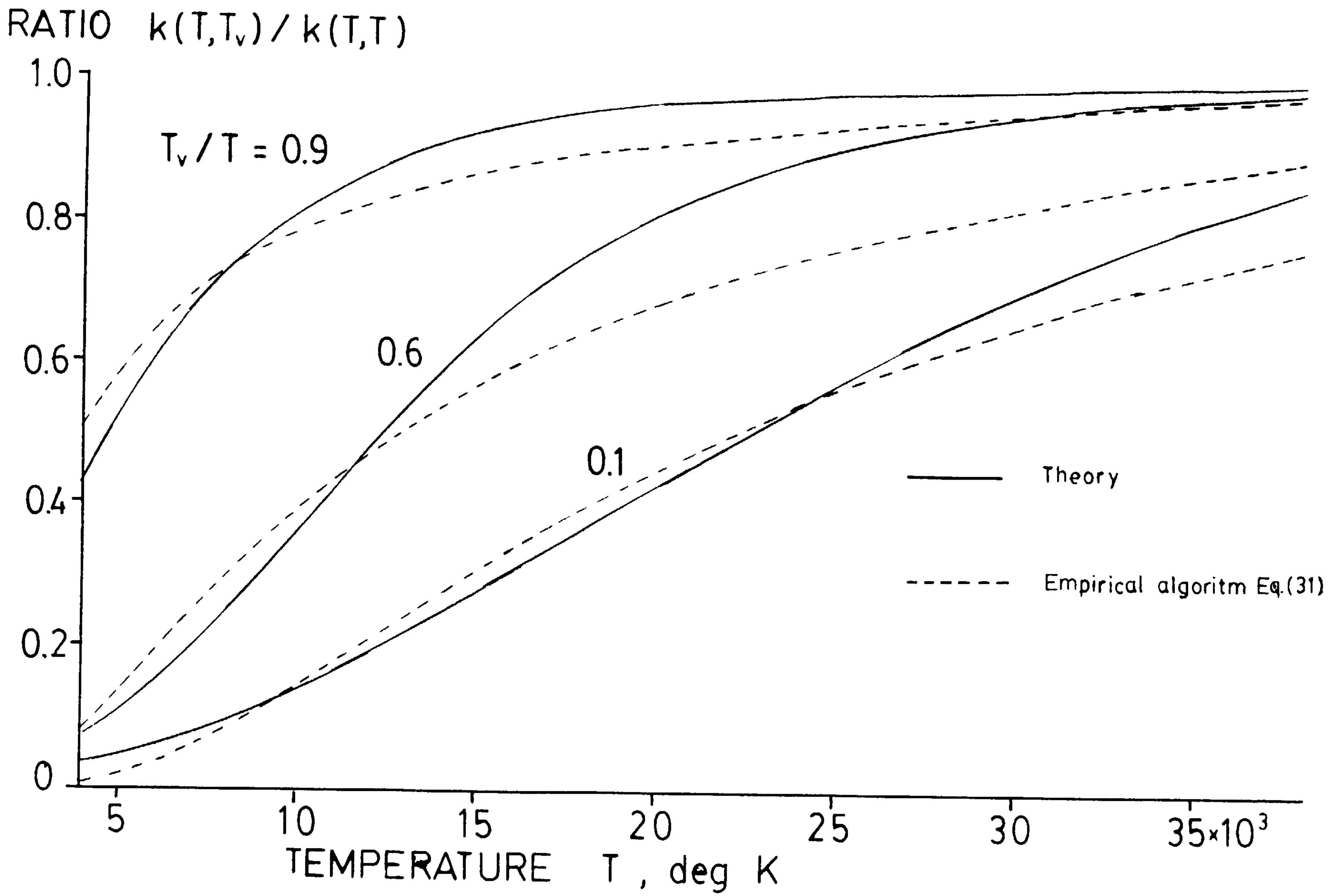


Figure (6b) Comparison Between the Theoretical and a Modified Empirical Method of Correcting the Dissociation Rate Coefficient for Vibrational Non-equilibrium in O2, where the Equilibrium Coefficient $k = CT^{-1} \exp(-D/kT)$