

ty considerations. The catalytic utilization of these reactions for the production not only of benzenoid trimers but also of novel and otherwise difficult of access dimers and tetramers is being pursued.

I thank all my collaborators, in particular, Drs. P. M. Bailey, H. Dietl, B. E. Mann, K. Moseley, H. Reinheimer, D. Roe, and T. Hosokawa, for their expert work in disentangling this very knotted skein.

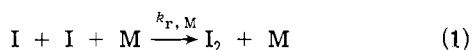
## Why Atoms Recombine More Slowly as the Temperature Goes Up

Huw O. Pritchard

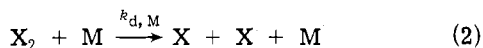
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It is now a little over 20 years since a series of experiments using flash-photolysis techniques<sup>1-3</sup> showed decisively that the reaction



went more slowly as the temperature was increased. At about the same time, it was becoming evident from many shock-tube dissociation experiments that the reverse reactions, i.e.



probably had Arrhenius temperature coefficients considerably less than the known spectroscopic dissociation energies ( $D_0$ ), and it is now generally accepted that this is the case.<sup>4,5</sup> By Arrhenius temperature coefficient we mean

$$"E" = -R^{-1}d(\ln k_{d,M})/d(1/T) \quad (3)$$

Since the rate quotient law

$$k_{d,M}/k_{r,M} = K_c \quad (4)$$

holds virtually exactly even for these systems,<sup>6,7</sup> this means that to a good degree of approximation

$$E_{d,M} - E_{r,M} = D_0 \quad (5)$$

where  $E_{d,M}$  and  $E_{r,M}$  are the Arrhenius temperature coefficients of  $k_{d,M}$  and  $k_{r,M}$ , respectively, and  $K_c$  is the equilibrium constant of the dissociation at the temperature in question. Thus, since  $E_{d,M}$  is less than  $D_0$ , these shock-tube data also imply a negative temperature coefficient (i.e.,  $E_{r,M}$  negative) for the recombination reaction, but a much more severe one than was found in the flash-photolysis experiments, as shown in Figure 1.<sup>8-11</sup>

There is no one single explanation of this behavior, and over the last 20 years at least half a dozen different ideas have been proposed,<sup>5</sup> all of which are probably valid to some extent, but which can only ex-

plain the magnitudes of the trends shown in Figure 1 with difficulty. However, it has recently become apparent that a very simple form of collision theory gives recombination rate constants for all diatomic molecules *similar in form* to those found in practice. The principal feature of this treatment is that it takes account of the rotational motion of the recombining atoms in a way which is already commonplace in molecular-beam or ion-reaction work,<sup>12-14</sup> and as such is rather similar to the orbiting resonance theory,<sup>15</sup> but without tunneling.<sup>16</sup> Of course, rotational effects have been included in previous discussions of this problem<sup>5</sup>—typical is the work of Palmer and Hornig,<sup>17</sup> which is a form of Hinshelwood-Lindemann theory, but can only account for the observed behavior of some systems by assuming more degrees of rotational freedom than the molecule can possess.

Another approach to the problem is the chaperon mechanism which invokes the pre-equilibrium



followed by



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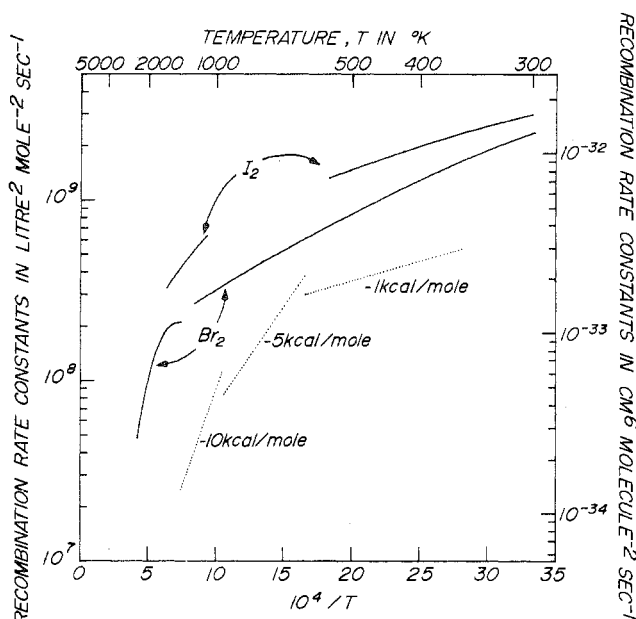
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Huw Pritchard was born in Bangor, Wales, in 1928. He studied chemistry in Manchester toward the end of the M. Polanyi and M. G. Evans era, and obtained his Ph.D. in 1951, working on the thermochemistry of mercury alkyls with H. A. Skinner. He remained as Lecturer in Manchester until 1965, when he moved to York University as Professor of Chemistry.



**Figure 1.** Rate constants for recombination of bromine atoms and of iodine atoms with argon as third body, plotted in Arrhenius form. The low-temperature points are direct measurements using flash photolysis<sup>8,9</sup> and the high-temperature points are calculated, using eq 4, from shock-wave dissociation rates.<sup>10,11</sup> It is much more common to plot these results in the form  $\log k_r$  vs.  $\log T$ , which gives almost featureless lines, but the Arrhenius form is useful when discussing some aspects of the problem, e.g., eq 5, 6, and so on. Three dotted lines shown on the diagram have slopes corresponding to  $-1$ ,  $-5$ , and  $-10$ , kcal/mol, respectively. Note that there is an intentional mismatch of a factor of two between the right-hand and left-hand ordinates, due to differences in the definition of the meaning of the recombination rate constant.

whence the binding energy of MX appears as a negative (Arrhenius) temperature coefficient in the expression for the overall recombination process.<sup>18</sup> The difficulties are twofold: that many MX pairs, e.g., ArH, do not have large enough binding energies, and that these binding energies, where they exist, e.g.,  $I_2$ -I, do not increase with temperature as would be required if this theory alone were to have to explain the behavior shown in Figure 1; furthermore, in the full nonequilibrium treatment of the chaperon mechanism, the kinetics of formation of the MX pairs are also governed by angular momentum restrictions,<sup>19</sup> of the kind discussed below.

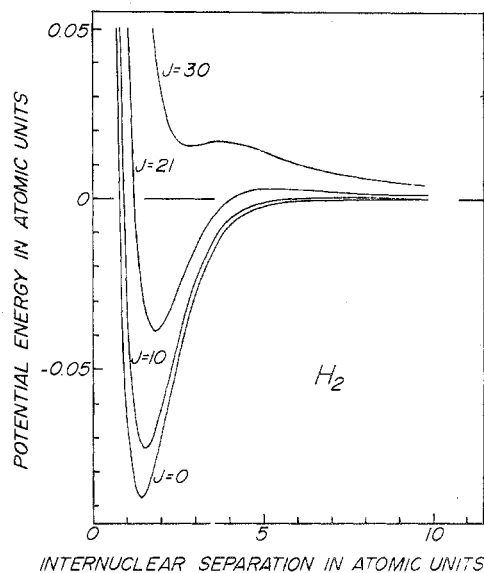
A third approach to the problem has been to consider departures from equilibrium, which have the general property of reducing the rates, and becoming more serious at high temperatures.<sup>4,5</sup> These nonequilibrium effects are the most severe for  $H_2$ , but much less so for  $D_2$ , and appear to be related to the density of energy levels in the molecule: thus, they might well be rather unimportant for heavier molecules, particularly at low temperatures.<sup>5,16</sup> There is, however, disagreement between the nonequilibrium calculations of Dove and Jones<sup>20</sup> and of my own group<sup>5,16</sup> on the one hand and those of Johnston<sup>4</sup> and of Kiefer<sup>21</sup> and their co-workers on the other, and in fact the latter calculations<sup>4,21</sup> do yield results quite similar to the experimental results. The essential difference between these two types of calculation is that the for-

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**Figure 2.** Effective potential energy curves for  $H_2$  for four values of  $J$ . For  $H_2$  the maximum value of  $J$  which gives rise to the existence of a quasi-bound vibrational level is  $J = 38$ , and for  $D_2$  it is  $J = 54$ , using the Kolos and Wolniewicz adiabatic potential.<sup>29</sup> For  $I_2$ , depending upon the exact choice of the form of the potential, there are some 800–900 allowed values of  $J$ . N.B.: 1 au of energy =  $219\,475\text{ cm}^{-1}$  and 1 au of distance =  $0.529\text{ \AA}$ .

mer authors use probabilities for dissociation which are very small for all but the topmost few vibrational levels whereas the latter authors use much larger transition probabilities for the more strongly bound states, and allow a lot of direct dissociation from almost all the vibrational states of the molecule. For  $H_2$ , at least, quantum mechanical calculations of these transition probabilities<sup>22</sup> are more in accord with the former approach, and classical trajectory calculations on  $Br_2$  and  $I_2$  suggest that the dissociation flux arises almost exclusively from molecules already having internal energies within  $kT$  of the dissociation limit.<sup>23</sup> There is also some experimental support, both direct<sup>24,25</sup> and circumstantial,<sup>26</sup> that a significant fraction of the critical energy for reaction must come from internal energy of the reacting molecule(s) and that only a relatively small fraction of the total critical energy comes from the relative translational motion of the reacting collision. Thus it seems likely that vibrational disequilibrium alone is insufficient to account for these experimental results.

Space does not permit discussion of many successful calculations using numerical theories<sup>27</sup>—suffice it to say that for the chemist, at least, a visual model is equally important as getting the right answer.<sup>28</sup>

### Formulation of the Minimum Equilibrium Dissociation and Recombination Rates

Figure 2 shows how the potential energy curves for a diatomic molecule depend on the rotational quan-

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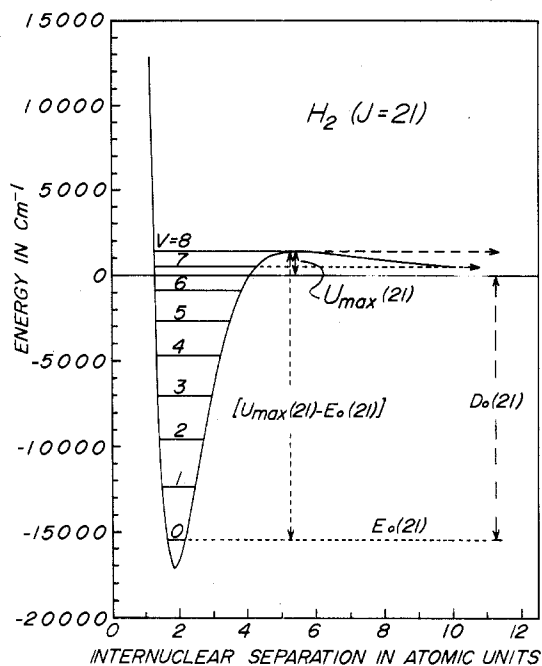
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**Figure 3.** Vibrational energy-level diagram for the  $J = 21$  state of  $H_2$ , showing two quasi-bound states,  $v = 7, J = 21$  and  $v = 8, J = 21$ ; the lifetimes of these states with respect to predissociation (tunneling) are about  $5 \times 10^{-4}$  sec and  $10^{-13}$  sec, respectively. In all,  $H_2$  has 349 rotation-vibration levels, of which 48 are quasi-bound, and  $D_2$  has 703 levels, of which 131 are quasi-bound,<sup>29</sup> the highest levels in each case being about  $7500 \text{ cm}^{-1}$  above the dissociation limit. However,  $I_2$  (again depending somewhat on the assumed form of the potential) has about 55 000 levels, of which about 11 000 are quasi-bound, but since rotational energy increases quadratically with  $J$ , some of these levels have exceedingly high energies, up to about  $14 000 \text{ cm}^{-1}$  above the dissociation limit. The density of levels peaks very strongly at or near to the normal spectroscopic dissociation limit ( $E = 0$ ), but the distribution is not symmetric, there being roughly five times the density of levels just below the normal dissociation limit as there is just above it.

tum number  $J$ ; for  $J > 0$ , centrifugal barriers occur and are usually sufficiently high to contain one or more states of the molecule which are metastable with respect to the normal dissociation limit ( $E = 0$ ), and which are called quasi-bound;<sup>29</sup> they can dissociate spontaneously by tunneling (predissociation) as shown in Figure 3, but it turns out<sup>5,16</sup> that this tunneling is of only secondary importance in recombination or dissociation, even for  $H_2$ .

Consider the dissociation of state  $J$  of the diatomic molecule  $XY$  with  $n(J)$  molecules distributed according to a vibrational Boltzmann distribution  $n_0(J), n_1(J), \dots, n_v(J), \dots$ , and a rotational barrier to dissociation of  $U_{\max}(J)$ ; cf. Figure 3. In principle, dissociation could take place whenever  $M$  and  $XY$  ( $v, J$ ) have between them more energy than  $[U_{\max}(J) - E_v(J)]$  along the line of centers. We may then write the rate of collisional dissociation of molecules in state  $J$  as

$$Z_{M,XY} N_M \sum_v k_v(J) n_v(J) e^{-[U_{\max}(J) - E_v(J)]/kT} \quad (8)$$

where  $N_M$  is the concentration of species  $M$ ,  $Z_{M,XY}$  is the appropriate collision number,  $k_v(J)$  is an efficiency factor for the conversion of relative translational kinetic energy into "critical" energy, and the summa-

tion is over all bound and quasi-bound vibrational levels of the rotational state  $J$ . But

$$n_v(J) = n_0(J) e^{-[E_v(J) - E_0(J)]/kT}$$

$$n_0(J) = n_0(0) (2J + 1) e^{-[E_0(J) - E_0(0)]/kT}$$

$$n_0(0) = N_{XY}/f_{\text{rot,vib}}$$

where  $f_{\text{rot,vib}}$  is the (unseparated) rotation-vibration partition function of  $XY$  (including quasi-bound levels). Thus, (8) becomes

$$\frac{Z_{M,XY} N_M N_{XY}}{f_{\text{rot,vib}}} (2J + 1) e^{-[U_{\max}(J) - E_0(0)]/kT} \sum_v k_v(J)$$

and summation over all  $J$  states capable of supporting vibrational levels gives the total rate of dissociation as

$$\frac{Z_{M,XY} N_M N_{XY}}{f_{\text{rot,vib}}} \times \sum_J \left[ (2J + 1) e^{-[U_{\max}(J) - E_0(0)]/kT} \sum_v k_v(J) \right] \quad (9)$$

Dividing through by  $N_M N_{XY}$  and rearranging slightly, we get the equilibrium rate constant<sup>30</sup> for dissociation

$$\tilde{k}_{d,M} = \frac{Z_{M,XY}}{f_{\text{rot,vib}}} e^{-D_0/kT} \times \sum_J \left[ (2J + 1) e^{-U_{\max}(J)/kT} \sum_v k_v(J) \right] \quad (10)$$

Little is known in detail about the appropriate values of  $k_v(J)$ , and for the time being we may conveniently replace the term  $\sum_v k_v(J)$  by an effective value  $\bar{P}_{M,XY}$  and take it outside the  $J$  summation to give<sup>31</sup>

$$\tilde{k}_{d,M} = \frac{Z_{M,XY} \bar{P}_{M,XY}}{f_{\text{rot,vib}}} e^{-D_0/kT} \times \sum_J (2J + 1) e^{-U_{\max}(J)/kT} \quad (11)$$

We may now write the equilibrium constant for the dissociation reaction as

$$K_c = \frac{\tilde{k}_d}{\tilde{k}_r} = \frac{G_{XY}}{f_{XY}^{\text{rot,vib}}} \frac{f_{\text{el}}^X f_{\text{el}}^Y}{f_{\text{el}}^{XY}} \frac{f_{\text{trans}}^X f_{\text{trans}}^Y}{f_{\text{trans}}^{XY}} e^{-D_0/kT} \quad (12)$$

where  $\sigma_{XY}$  is the symmetry number of the diatomic molecule and the  $f$ 's are partition functions, whence the equilibrium rate constant for recombination becomes

$$\tilde{k}_r = Z_{M,XY} \bar{P}_{M,XY} \frac{f_{\text{el}}^{XY}}{f_{\text{el}}^X f_{\text{el}}^Y} \frac{f_{\text{trans}}^{XY}}{f_{\text{trans}}^X f_{\text{trans}}^Y} \times \sum_J \left( \frac{2J + 1}{\sigma_{XY}} \right) e^{-U_{\max}(J)/kT} = Z_{M,XY} \bar{P}_{M,XY} \{ Q_{\text{el}}^{XY} Q_{\text{trans}}^{XY} \}^{-1} \Phi \quad (13)$$

where the  $Q$  are the appropriate partition function ratios for the reaction, and

$$\Phi = \sum_J \left( \frac{2J + 1}{\sigma_{XY}} \right) e^{-U_{\max}(J)/kT}$$

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Table I  
The quantity  $\Phi = \sum [(2J+1)/\sigma_{XY}] e^{-U_{\max}(J)/kT}$  for Ten Different Intermolecular Potentials, in the Range  $T = 300-6000$  K

T, K	H <sub>2</sub>	D <sub>2</sub>	HCl	O <sub>2</sub>	N <sub>2</sub>	NO	CO	Br <sub>2</sub>	I <sub>2</sub> expt	I <sub>2</sub> Morse
300	47.42	94.61	3.24 × 10 <sup>2</sup>	7.28 × 10 <sup>2</sup>	7.41 × 10 <sup>2</sup>	1.05 × 10 <sup>3</sup>	1.97 × 10 <sup>3</sup>	6.70 × 10 <sup>3</sup>	1.73 × 10 <sup>4</sup>	1.61 × 10 <sup>4</sup>
400	59.41	118.57	4.06 × 10 <sup>2</sup>	9.20 × 10 <sup>2</sup>	9.36 × 10 <sup>2</sup>	1.25 × 10 <sup>3</sup>	2.49 × 10 <sup>3</sup>	8.53 × 10 <sup>3</sup>	2.11 × 10 <sup>4</sup>	2.04 × 10 <sup>4</sup>
500	70.71	141.16	4.83 × 10 <sup>2</sup>	1.10 × 10 <sup>3</sup>	1.12 × 10 <sup>3</sup>	1.45 × 10 <sup>3</sup>	2.98 × 10 <sup>3</sup>	1.03 × 10 <sup>4</sup>	2.46 × 10 <sup>4</sup>	2.44 × 10 <sup>4</sup>
1000	120.78	241.23	8.21 × 10 <sup>2</sup>	1.92 × 10 <sup>3</sup>	1.95 × 10 <sup>3</sup>	2.38 × 10 <sup>3</sup>	5.16 × 10 <sup>3</sup>	1.82 × 10 <sup>4</sup>	3.97 × 10 <sup>4</sup>	4.25 × 10 <sup>4</sup>
2000	203.18	405.95	1.37 × 10 <sup>3</sup>	3.29 × 10 <sup>3</sup>	3.36 × 10 <sup>3</sup>	4.11 × 10 <sup>3</sup>	8.85 × 10 <sup>3</sup>	3.20 × 10 <sup>4</sup>	6.53 × 10 <sup>4</sup>	7.27 × 10 <sup>4</sup>
3000	270.98	541.80	1.82 × 10 <sup>3</sup>	4.48 × 10 <sup>3</sup>	4.58 × 10 <sup>3</sup>	5.73 × 10 <sup>3</sup>	1.20 × 10 <sup>4</sup>	4.43 × 10 <sup>4</sup>	8.81 × 10 <sup>4</sup>	9.84 × 10 <sup>4</sup>
4000	327.35	655.16	2.22 × 10 <sup>3</sup>	5.55 × 10 <sup>3</sup>	5.69 × 10 <sup>3</sup>	7.29 × 10 <sup>3</sup>	1.49 × 10 <sup>4</sup>	5.55 × 10 <sup>4</sup>	1.09 × 10 <sup>5</sup>	1.20 × 10 <sup>5</sup>
5000	374.23	749.82	2.56 × 10 <sup>3</sup>	6.54 × 10 <sup>3</sup>	6.72 × 10 <sup>3</sup>	8.78 × 10 <sup>3</sup>	1.76 × 10 <sup>4</sup>	6.58 × 10 <sup>4</sup>	1.28 × 10 <sup>5</sup>	1.39 × 10 <sup>5</sup>
6000	413.42	829.22	2.86 × 10 <sup>3</sup>	7.45 × 10 <sup>3</sup>	7.68 × 10 <sup>3</sup>	1.02 × 10 <sup>4</sup>	2.01 × 10 <sup>4</sup>	7.52 × 10 <sup>4</sup>	1.45 × 10 <sup>5</sup>	1.55 × 10 <sup>5</sup>
Φ 5000/Φ 500	5.29	5.31	5.30	5.93	5.99	6.06	5.91	6.41	5.21	5.69

The function  $\Phi$  has been calculated for a wide range of diatomic molecules from either the known exact potential curves (H<sub>2</sub>, D<sub>2</sub>)<sup>32</sup> or the experimental Rydberg-Klein-Rees potential curves (HCl,<sup>33</sup> O<sub>2</sub>,<sup>34</sup> N<sub>2</sub>,<sup>35</sup> NO,<sup>36</sup> CO,<sup>37</sup> Br<sub>2</sub>,<sup>38</sup> I<sub>2</sub>)<sup>39</sup> suitably extrapolated at large internuclear separation, and the results are shown in Table I;  $\Phi$  was also calculated for I<sub>2</sub> assuming a Morse potential<sup>40</sup> to test the sensitivity of  $\Phi$  to the assumed form of the potential. It is immediately apparent that the behavior of  $\Phi$  as a function of  $T$  is very similar for all diatomics. For example,  $\Phi_{5000}/\Phi_{500}$  lies in the range 5.2 to 6.4 for all the molecules, with most of the ratios clustering around 5.25 or 5.95. Alternatively, if the  $\Phi$  are plotted as functions of temperature, in Arrhenius form, the curves all have very similar shapes and can almost be superimposed simply by multiplying each  $\Phi$  by a constant. A third way of expressing this behavior is to plot  $\log \Phi$  vs.  $\log T$  whence (understandably) the data fall on moderate straight lines, almost parallel to each other, so that we can write

$$\Phi = aT^{0.77 \pm 0.05} \quad (14)$$

### Behavior of the Minimum Equilibrium Dissociation Rate

First let us examine eq 11 for  $\tilde{k}_d$ . Its temperature coefficient is dominated by the  $\exp[-D_0/kT]$  term, with smaller effects arising from the temperature coefficients of  $\Phi$  and  $f_{\text{rot,vib}}$  and the ZP term. Both  $\Phi$  and  $f_{\text{rot,vib}}$  increase with temperature, but  $f_{\text{rot,vib}}$  increases more quickly than  $\Phi$ . We can see this by factoring  $f_{\text{rot,vib}}$  into  $f_{\text{rot}} \times f_{\text{vib}}$ , whence  $f_{\text{rot}}$  is proportional to  $T$  and  $f_{\text{vib}}$  also increases weakly with  $T$ , whereas  $\Phi$  only varies as  $T^{0.77}$  (also, for various reasons,  $f_{\text{rot,vib}}$  increases somewhat faster with  $T$  than does the separated product  $f_{\text{rot}} \times f_{\text{vib}}$ ). Thus, eq 11, rewritten as

$$\tilde{k}_d = Z_{M,XY} \bar{P}_{M,XY} \frac{\Phi}{f_{\text{rot,vib}}} e^{-D_0/kT} \quad (11a)$$

falls more and more below the traditional collision-theory expression

$$\tilde{k}_d = Z_{M,XY} P_{M,XY} e^{-D_0/kT} \quad (11b)$$

as the temperature increases, and therefore, plotted in Arrhenius form, gives an Arrhenius temperature coefficient which is less than  $D_0$ , as observed in all shock-tube experiments.<sup>4</sup> The *physical reason* for this behavior is fairly simple: we have insisted that a molecule in state  $J$  must have an energy [ $D_0 + U_{\max}(J)$ ] before it can dissociate, and in writing eq 11 we have also insisted that we have a Boltzmann distribution of rotational states; thus, as we raise the

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temperature, more molecules find themselves in high  $J$  states, and therefore require more energy to dissociate—which means that the rate of dissociation does not increase with  $T$  as rapidly as it would if the critical energy had remained constant at  $D_0$ . The critical energy is not constant, but is a function of temperature  $E^*(T) = [D_0 + f(T)]$ , and it is a matter of simple differentiation to show that if  $k = \text{const} \times \exp[-E^*(T)/kT]$ , the Arrhenius temperature coefficient, eq 3, will be numerically less than  $D_0$  if  $f(T)$  increases with  $T$ . Looking at it in a slightly different way, eq 11a tells us that of those collisions in which  $M$  and  $XY$  have between them more energy than  $D_0$ , only the fraction  $\Phi/f_{\text{rot,vib}}$  has enough energy to surmount the necessary rotational barriers, and the fraction decreases as  $T$  goes up.

### Behavior of the Minimum Equilibrium Recombination Rate

We now turn to eq 13 for  $\tilde{k}_r$ . Assuming for the moment that the electronic partition function ratio  $Q^{\text{XY}}_{\text{el}}$  is independent of temperature and  $\bar{P}_{M,XY} = 1$  then, term by term, the temperature dependence is given by

$$\tilde{k}_r \sim T^{1/2} \{T^{-3/2}\} T^{+0.77 \pm 0.05} \quad (15)$$

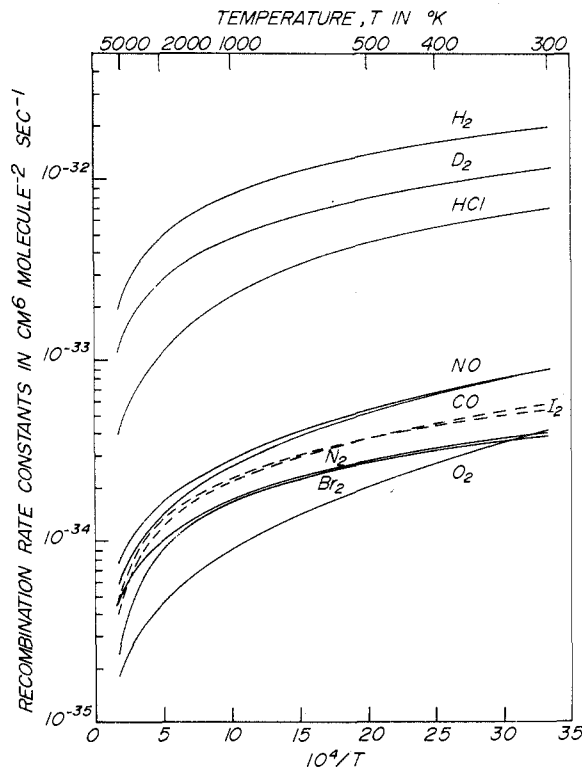
which is a *decreasing* function of  $T$ . We can put eq 13 in another interesting form: as we have noted,  $\Phi$  behaves similarly for all diatomics as a function of temperature, having an Arrhenius temperature coefficient of about +500 cal/mol near room temperature and about +5000 cal/mol in the 2000–6000 K region; hence, in the high-temperature range, eq 15 could be written

$$\tilde{k}_r \sim T^{1/2} \{T^{-3/2}\} e^{-5000/RT} \quad (16)$$

which is remarkably like a recombination rate equation given recently by Wagner and Zabel.<sup>41</sup>

Whichever equation we use, (13), (15), or (16), the negative temperature coefficient for recombination can be rationalized by arguing that except for head-on collisions, which are rather rare events, all collisions between two atoms contain angular momentum; as the temperature increases, the atomic approach velocities increase, and so the average angular momentum of the collisions between atoms increases—but this carries with it the requirement that, for the two atoms to approach each other sufficiently closely that they can form a molecule, they need on average more kinetic energy to surmount the rotational barrier, and the net effect is that the rate of recombination actually falls. In effect, this is only a slight extension of the argument that the reaction cross section for a reaction with no threshold decreases with increasing relative translational energy of the reactants.<sup>12b</sup>

It may be tempting to look at eq 13 and try to interpret the “meaning” of each term: hence, one would try to ascribe the dominant behavior to the  $T^{-3/2}$  term, which could then be interpreted as a difference in Helmholtz free energy between reactants and products. However, we should be very careful of trying to read too much meaning into apparent ther-



**Figure 4.** Arrhenius plots of  $\{Z_{M,XY}\bar{P}_{M,XY}\} \{Q^{\text{XY}}_{\text{el}} Q^{\text{XY}}_{\text{trans}}\}^{-1} \Phi$ , eq 13, where the terms in the first bracket are held constant at the value of  $Z_{M,XY}^{300\text{K}}$ . This is therefore not exactly the recombination rate constant of eq 13, but is plotted in this way because the quantity  $\{Q^{\text{XY}}_{\text{el}} Q^{\text{XY}}_{\text{trans}}\}^{-1} \Phi$  can be calculated unambiguously from the known spectroscopic data, whereas  $\{Z_{M,XY}\bar{P}_{M,XY}\}$  is a rather ill-defined quantity; moreover, we really require the quantity  $\{Q^{\text{XY}}_{\text{el}} Q^{\text{XY}}_{\text{trans}}\}^{-1} \Psi$ , which behaves in a similar fashion; cf. eq 17, Table III, and the relevant discussion. For clarity, the recombination curves for the two trial internuclear potentials of  $I_2$  are shown dotted. Note that the scale of this diagram is the same as for Figure 1.

modynamic components of reaction rate expressions:<sup>42</sup> our term  $\Phi$  (and  $\Psi$  below in eq 17) also is in the nature of a partition function, and so these individual terms should not be separated out of eq 13 except as a computational convenience. Figure 4 shows plots of this partition function ratio for all the molecules listed in Table I, and it is seen not only that its variation with temperature is very similar for each molecule but also that the curves have some resemblances to the generally observed behavior, Figure 1.

For the moment, let us confine our remarks to the *shapes* of the curves depicted in Figure 4. Firstly, the shapes are very insensitive to the form of the assumed internuclear potential, as evidenced by the very close correspondence of the two  $I_2$  curves (shown dotted), and the similarity in shape of the curves for  $H_2$  and  $D_2$ . Thus, any decline in rate constant arising from this mechanism must be common to all diatomics. The second point is illustrated by the bottom three curves for  $O_2$ ,  $N_2$ , and  $Br_2$ . In the absence of electronic partition functions, all three curves would have been almost identical, following very closely the  $N_2$  line. The  $O_2$  line falls much more steeply at low temperatures, because of the variation of the state-sum for the three components of the ground state of the O atom, and it is only at the higher temperatures that  $f^0_{\text{el}}$  can be considered constant. On the other

(41) H. G. Wagner and F. Zabel, *Ber. Bunsenges. Phys. Chem.*, **78**, 705 (1974).

(42) E. A. Guggenheim and J. Weiss, *Trans. Faraday Soc.*, **34**, 57 (1938), and discussion thereof by M. G. Evans, M. Polanyi, and E. Wigner, pp 70 and 81.

Table II  
Contributions to the Rate Constants for Recombination at 300 K, Assuming  $\bar{P} = 1^a$

Molecule	Z	$\Phi$	$Q^{XY}_{el}$	$Q^{XY}_{trans}$	$\tilde{k}_r$
H <sub>2</sub>	$5.70 \times 10^{-10}$	47.42	4	$3.49 \times 10^{23}$	$1.9 \times 10^{-32}$
D <sub>2</sub>	$4.65 \times 10^{-10}$	94.61	4	$9.88 \times 10^{23}$	$1.1 \times 10^{-32}$
HCl	$1.62 \times 10^{-10}$	323.8	8.12	$9.47 \times 10^{23}$	$6.8 \times 10^{-33}$
O <sub>2</sub>	$1.60 \times 10^{-10}$	727.9	13.02	$2.21 \times 10^{25}$	$4.0 \times 10^{-34}$
N <sub>2</sub>	$1.53 \times 10^{-10}$	740.7	16	$1.81 \times 10^{25}$	$3.9 \times 10^{-34}$
NO	$1.57 \times 10^{-10}$	1047	7.22	$1.99 \times 10^{25}$	$8.8 \times 10^{-34}$
CO	$1.57 \times 10^{-10}$	1968	19.74	$1.75 \times 10^{25}$	$8.9 \times 10^{-34}$
Br <sub>2</sub>	$2.23 \times 10^{-10}$	6699	16	$2.47 \times 10^{26}$	$3.8 \times 10^{-34}$
I <sub>2</sub> <sup>expt</sup>	$2.58 \times 10^{-10}$	17350	16	$4.94 \times 10^{26}$	$5.7 \times 10^{-34}$
I <sub>2</sub> <sup>Morse</sup>	$2.58 \times 10^{-10}$	16144	16	$4.94 \times 10^{26}$	$5.3 \times 10^{-34}$

<sup>a</sup> All rate quantities are in centimeter, molecule, and second units.

hand, the temperature dependence of  $f_{Br_{el}}^{Br_2}$  (due to thermal population of  $Br^2P_{1/2}$  as well as  $Br^2P_{3/2}$ ) causes a marked fall-off beginning at about 1500 K. Notice also that a rather similar feature shows up in the experimental data for  $Br_2$  where the fall in rate is rather smooth between room temperature and 1500 K, and then falls away very sharply indeed; it would seem therefore that this marked change in the shape of the observed recombination curve is associated with the opening of a second thermal channel via  $^2P_{1/2}$ .

### An Easier Alternative Channel

Now let us examine the actual rates of recombination predicted by this theory and compare them with experimental values. It appears that, with argon as a third body, rate constants for the recombination of H<sub>2</sub>, Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub> at 300 K all lie within the range<sup>3,8,43,44</sup>  $1.2\text{--}2.0 \times 10^{-32}$  cm<sup>6</sup> molecule<sup>-2</sup> sec<sup>-1</sup>. The values calculated according to eq 13 are shown in Table II for 300 K, and it is obvious that, while the rate constant for H<sub>2</sub> recombination is reasonably acceptable, that for I<sub>2</sub> recombination is a lot too low. The reason for this is very simple. We have insisted that, to dissociate, a molecule must *climb over* the rotational barrier—but in fact it does not need to do this, even if we do not invoke tunneling. A molecule trapped in a quasi-bound state may easily dissociate if it suffers a collision which *removes* some angular momentum—then the barrier it needs to surmount is less. However, a simple collision which removes only rotational energy will always leave the quasi-bound molecule either in another quasi-bound state, or perhaps in a bound state; what is needed is a collision which does not take away energy, but which simultaneously reduces the rotational energy and increases the vibrational energy, so that the total energy remains *about* the same—such a collision simply leaves the molecule dissociated. It has been argued before on intuitive grounds that such collisions must be important,<sup>5,45–47</sup> and recent trajectory calculations on iodine dissociation have confirmed that such processes are in fact very frequent.<sup>23b</sup>

An upper limit to the rate of dissociation by this mechanism would then be obtained if we assumed

(43) J. E. Bennett and D. R. Blackmore, Thirteenth Symposium (International) on Combustion, The Combustion Institute, Pittsburgh, Pa., 1971, p. 51.

(44) M. A. A. Clyne and D. H. Stedman, *Trans. Faraday Soc.*, **64**, 2698 (1968).

(45) S. H. Bauer and S. C. Tsang, *Phys. Fluids*, **6**, 182 (1963).

(46) V. H. Shui and J. P. Appleton, *J. Chem. Phys.*, **55**, 3126 (1971).

(47) A. Gelb, R. Kapral and G. Burns, *J. Chem. Phys.*, **59**, 2980 (1973); H. W. Chang and G. Burns, *ibid.*, **62**, 2426 (1975).

that a substantial fraction  $P'$  of collisions between quasi-bound molecules and third bodies M leads to this kind of dissociation. The number of molecules, at equilibrium, in quasi-bound states is

$$\frac{N_{XY}}{f_{rot,vib}} e^{-D_0/kT} \sum_{\substack{\text{all } v, J \\ E_v(J) \geq 0}} (2J + 1) e^{-E_v(J)/kT}$$

whence by the same arguments as above

$$\tilde{k}_r = Z_{M,XY} P'_{M,XY} \{Q^{XY}_{el} Q^{XY}_{trans}\}^{-1} \Psi \quad (17)$$

where

$$\Psi = \sum_{\substack{\text{all } v, J \\ E_v(J) \geq 0}} \left( \frac{2J + 1}{\sigma_{XY}} \right) e^{-E_v(J)/kT}$$

This quantity  $\Psi$  is much more difficult to calculate than the  $\Phi$  of eq 13 because it requires a knowledge of all the quasi-bound levels in the molecules;<sup>48</sup> there are, from the work of LeRoy,<sup>29</sup> 48 such levels in H<sub>2</sub> and 131 in D<sub>2</sub>, and our own calculations show that there are about 11 000 quasi-bound levels in I<sub>2</sub>. Surprisingly, there is an almost constant ratio between  $\Phi$  and  $\Psi$ , as can be seen from the data for H<sub>2</sub>, D<sub>2</sub>, and I<sub>2</sub> in Table III, so that the temperature dependence of the ratio  $\Psi/f_{rot,vib}$  is the same as that of  $\Phi/f_{rot,vib}$ ; hence this approach gives virtually the same temperature coefficients as the simpler argument given above (i.e., eq 13 and Figure 4) but allows a maximum increase in the upper bound for the rates of a factor of about 2 for H<sub>2</sub>, 4 for D<sub>2</sub>, and 30 for I<sub>2</sub>, which is much more realistic. The fundamental physical reasons for reduced Arrhenius temperature coefficients for dissociation, or the complementary negative temperature coefficients for recombination, remain unchanged, but there is another channel which we did not consider before. Thus, when we said that a rotating pair of atoms had to be *knocked down* into a quasi-bound state on collision with M, we now accept a more efficient route whereby the collision with M traps the pair in a quasi-bound state without altering the total energy very much. All it does is to impart to the pair a little more angular momentum, at the same time removing a little of the relative energy of the pair along their line of centers so that, when the two atoms begin to recede from each other, they find they cannot escape, and the pair is trapped, apparently a relatively frequent occurrence.<sup>23b</sup> Consequently,

(48) Technically also, for hydrogen-containing molecules, some of these levels are quite wide and we should really use an integral rather than a summation in forming  $\Psi$ —see, e.g., R. Kosloff, R. D. Levine, and R. B. Bernstein, *Mol. Phys.*, **27**, 981 (1974).

Table III  
The Quantity  $\Psi = \sum_{\substack{\text{all } v, J \\ E_v(J) \geq 0}} [(2J+1)/\sigma_{XY}] e^{-E_v(J)/kT}$  for  $H_2$ ,  $D_2$ , and  $I_2$

T, K	$H_2$		$D_2$		$I_2$	
	$\Psi$	$\Psi/\Phi$	$\Psi$	$\Psi/\Phi$	$\Psi$	$\Psi/\Phi$
300	62.0	1.31	319	3.37	$4.71 \times 10^5$	29.3
400	88.0	1.48	433	3.63	$6.05 \times 10^5$	29.7
500	113	1.60	544	3.85	$7.33 \times 10^5$	30.0
1000	224	1.85	1037	4.30	$1.29 \times 10^6$	30.6
2000	396	1.95	1787	4.40	$2.15 \times 10^6$	29.6
3000	524	1.93	2309	4.26	$2.79 \times 10^6$	28.4
4000	619	1.89	2685	4.10	$3.28 \times 10^6$	27.3
5000	693	1.85	2966	3.95	$3.66 \times 10^6$	26.3
6000	752	1.82	3181	3.80	$3.97 \times 10^6$	25.5

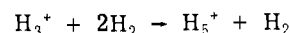
whereas at one time, vibrational relaxation was thought of as the key to understanding the relative efficiencies of third bodies in catalyzing these reactions,<sup>49</sup> what is in fact more important is the ability of M to change the angular momentum of the energetic molecules—and more than that, its efficacy in a very special kind of collision, one which causes an interchange of rotational and vibrational energy *within* the quasi-bound molecule, and only affecting the total internal energy sufficiently to allow the total angular momentum of the collision to be conserved; little is known about such transitions.

### Conclusions

As mentioned earlier, there is no single or simple explanation of the negative temperature coefficients observed in diatomic recombination reactions. However, if we can assume that the term  $\{Z_{M,XY}P'_{M,XY}\}$  varies only weakly with temperature and that flux coefficients<sup>30</sup> and rate constants have similar temperature coefficients, then eq 17 presents a very attractive way of accounting for them in a rough and ready fashion. Of course, eq 17 is far from describing the complete picture: its variation with temperature is too weak, even in the form plotted in Figure 4 where the  $ZP'$  term is omitted; moreover, it is already well known that both nonequilibrium and chaperon effects play important roles in these processes. But the ideas embodied in eq 17 are already well entrenched in the language of molecular dynamics, and it seems likely, therefore, that they are also central in this problem. Thus if the recombining atoms and the third body are all light, and the temperature is high, the basic description of the recombination process will be this angular-momentum-restricted mechanism with a strong nonequilibrium component, but with chaperon effects subsidiary; on the other hand, if the atoms and the third body are heavy, or the temperature is low, we will need the angular-momentum-restricted mechanism with a strong chaperon component, but with nonequilibrium ef-

fects rather subsidiary. The highly successful numerical theories we have already mentioned obviously select the appropriate weightings of these three components in a realistic manner, but do not lend themselves easily to a pictorial analysis of the kind presented here.

Centrifugal potential energy barriers and quasi-bound states are responsible for many experimental observations on a microscopic level,<sup>50,51</sup> e.g., phase shifts in collisions between atoms or ions in beams, or certain kinds of predissociation in diatomic spectroscopy, but it might be fair to say that this is the first time their existence has been known to lead to a gross macroscopic effect, namely the decline in the rate of recombination as the temperature increases. Perhaps, also, these ideas could be extended to other reactions which have negative temperature coefficients, e.g.



which are at the moment being described in Hinshelwood-Lindemann terms.<sup>52</sup>

Finally, one must add that there is not very much new in this formulation: eq 11 is rather like those given by Rice a few years ago<sup>53</sup> and is almost identical with one given by Glasstone, Laidler, and Eyring in 1941 in discussing the rotational contribution to the dissociation of hydrogen;<sup>54</sup> it is simply that the useful properties of these equations were not recognized previously.

An early version of this account was presented at the Charles Coulson Memorial Symposium on Theoretical Chemistry in Ottawa, June 27, 1974; the detailed numerical results presented here for the first time were calculated by Andrew Yau, and were made possible by a grant from the National Research Council of Canada.

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(54) S. Glasstone, K. J. Laidler, and H. Eyring, "The Theory of Rate Processes", McGraw-Hill, New York, N.Y., 1941, p 141.

(49) E. Rabinowitch, *Trans. Faraday Soc.*, **33**, 283 (1937).