

rovibronic levels. The study of collision-induced vibrational and rotational energy transfer and relaxation for an electronically excited molecule which can be followed through the emission spectroscopy<sup>30</sup> and the case involving the perturbation should be very interesting. We need further theories of radiative transitions to explain the enormous vibronic effects observed. Finally it must be emphasized that there have been a

(30) B. F. Rordorf, A. E. W. Knight, and C. S. Parmenter, Abstracts, 31st Symposium on Molecular Spectroscopy, June 14–18, 1976, Columbus, Ohio.

few surprises, as discussed above, and this fact should clearly warn us that more of the interesting and significant surprises lie ahead.

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## Temperature Dependence of Bimolecular Gas Reaction Rates

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In his classic 1889 paper<sup>1</sup> Arrhenius developed both the model and the basic equation still used today in explaining the temperature dependence of reaction rates. They might have remained merely suggested approximations were it not for the appearance a few years later of a remarkable achievement, the experiments of Max Bodenstein on  $\text{HI} + \text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ , which raised the Arrhenius model (with  $A$  and  $E_A$  as constants) to canonical status for over half a century.<sup>2-6</sup>

By the 1960s two factors could and did change the situation. First, the temperature range over which elementary gas reaction rate constants could be measured was increased an order of magnitude by the refinement of flash photolysis, discharge-flow, and shock-tube techniques. Second, the number of complementary and intercomparable studies on related reaction systems became so great that critical evaluations of the data base became capable of sorting out experimental errors and characterizing nonlinear Arrhenius graphs.<sup>7</sup> Three classes of reactions are found to exhibit such behavior. One was recognized long ago, namely H or  $\text{H}^+$  transfer reactions, where quantum-mechanical tunneling augments the classically allowed reaction rate and leads to low-temperature rates greater than a linear extrapolation of higher temperature data would suggest.<sup>8</sup> The second class is dissociation-recombination reactions. Here the temperature dependence of reaction rates is thoroughly enmeshed with the temperature dependence of energy-transfer rates, and the notion of elementary reaction becomes very blurred.<sup>9</sup> The third class is the bimolecular exchange reaction, and the discovery and interpretation of Arrhenius graph curvature for this class are our concern here.

The recognition that Arrhenius graph curvature for bimolecular exchange reactions had been characterized experimentally arose in connection with  $\text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H}$ . Since this reaction is responsible for most of the conversion of CO to  $\text{CO}_2$  in combustion, knowledge of its high-temperature rate constant is especially important. It appeared that the high-temperature and low-temperature data were simply inconcordant until Dryer, Naegeli, and Glassman<sup>10</sup> pointed out in 1970 that straightforward application of activated complex theory<sup>11</sup> reconciled both in terms of a curved Arrhenius graph (Figure 1).<sup>10,12-15</sup> For this reaction the contrast between the slight temperature dependence near room temperature and the rapid rise over 1000 K generates a dramatic pictorial effect. If the

(1) S. Arrhenius, *Z. Phys. Chem.*, **4**, 226 (1889).

(2) M. Bodenstein, *Z. Phys. Chem.*, **29**, 295 (1899).

(3) For a modern discussion of the sense in which  $\text{HI} + \text{HI} \rightarrow \text{H}_2 + \text{I}_2$  is "elementary", see L. M. Raff, D. L. Thompson, L. B. Sims, and R. N. Porter, *J. Chem. Phys.*, **56**, 5998 (1972); these authors consider their trajectory calculations to provide strong support for the proposition that the elementary  $\text{HI} + \text{HI}$  reaction is  $\text{HI} + \text{HI} \rightarrow \text{H}_2\text{I} + \text{I}$ .

(4) J. O. Sullivan, *J. Chem. Phys.*, **30**, 1292 (1959).

(5) J. O. Sullivan, *J. Chem. Phys.*, **36**, 1925 (1962).

(6) S. B. Jaffe and J. B. Anderson, *J. Chem. Phys.*, **49**, 2859 (1968); **51**, 1057 (1969).

(7) Many compilations of bimolecular gas reaction rate constants have been published; see D. L. Baulch, D. D. Drysdale, and D. G. Horne, "Evaluated Kinetic Data for High Temperature Systems", Vol. 1 and 2, Butterworths, London, 1973, for examples and references (Vol. 1, pp 7-9) to other compilations.

(8) E. F. Caldin, *Chem. Rev.*, **69**, 135 (1969); M. J. Stern and R. E. Weston, Jr., *J. Chem. Phys.*, **60**, 2803 (1974).

(9) J. H. Kiefer, H. P. G. Joosten, and W. D. Breshears, *Chem. Phys. Lett.*, **30**, 424 (1975).

(10) F. Dryer, D. Naegeli, and I. Glassman, *Combust. Flame*, **17**, 270 (1970).

(11) W. C. Gardiner, Jr., "Rates and Mechanisms of Chemical Reactions", W. A. Benjamin, New York, N.Y., 1969, Section 4-7.

(12) D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, "High Temperature Reaction Rate Data", Report No. 1, Department of Physical Chemistry, Leeds University, 1968.

(13) I. W. M. Smith and R. Zellner, *J. Chem. Soc., Faraday Trans. 2*, **1617** (1973).

(14) D. L. Baulch and D. D. Drysdale, *Combust. Flame*, **23**, 215 (1974).

(15) W. Steinert and R. Zellner, *Proc. Eur. Symp. Combust.*, **31** (1975).

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Table I  
Some Bimolecular Gas Reactions Showing Arrhenius Graph Curvature

Reaction	Temp range, K	$E_A/R$ (low $T$ )	$E_A/R$ (high $T$ )	Ref
$H + CH_4 \rightarrow H_2 + CH_3$	400-2000	6000 (400-750)	7500 (1700-2000)	22, 23
$H + C_2H_6 \rightarrow H_2 + C_2H_5$	400-1400	4000 (400)	7500 (1400)	16
$H + HBr \rightarrow H_2 + Br$	300-2000	0 (300-600)	1500 (1000-2000)	25
$O + H_2 \rightarrow OH + H$	400-2000	5000 (400-900)	7000 (1400-1900)	26
$O + CO_2 \rightarrow CO + O_2$	1200-4500	15000 (1200-1800)	30000 (2500-4500)	27
$OH + CO \rightarrow CO_2 + H$	200-2500	0 (200-500)	4000 (1500-2000)	14, 15
$OH + H_2 \rightarrow H_2O + H$	300-1800	2000 (300-600)	3500 (1200-1800)	28
$OH + OH \rightarrow H_2O + O$	300-2000	400 (300-1000)	3500 (1500-2000)	29
$OH + CH_4 \rightarrow H_2O + CH_3$	200-2000	2000 (200-400)	5000 (800-1600)	30
$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	400-1400	6000 (400-700)	15000 (1000-1400)	16
$CO + NO_2 \rightarrow CO_2 + NO$	500-1400	15000 (500-800)	20000 (1100-1400)	31

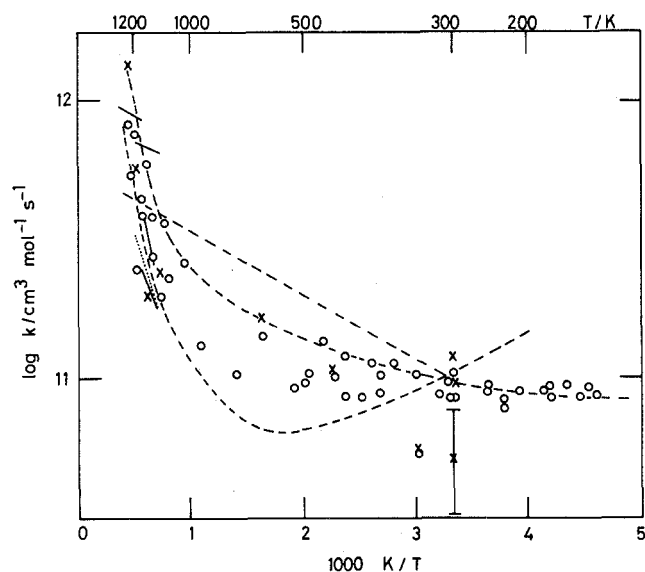


Figure 1. Data on  $OH + CO \rightarrow CO_2 + H$ .  $\times$  and  $\circ$ , pre-1968 results;  $\circ$  and  $\circ$ , post-1968 results. The straight dashed line is a 1968 compilers' linear fit.<sup>12</sup> The curved dashed lines are two activated complex theory calculations.<sup>10,13</sup> The data sources are identified in ref 14. Additional data are reported in ref 15.

low-temperature rate itself depends strongly on temperature, then a similar degree of enhancement is perceived only as a moderate curvature. This is the case, for example, for  $CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$  (Figure 2).<sup>16</sup> Experience would have and often did mislead gas kineticists to draw erroneous straight lines connecting low (say  $300 \pm 200$  K) and high (say  $>1000$  K) temperature data for both situations. After the paper of Dryer et al. it was clear, however, that experience developed within one or the other temperature ranges was not a good guide to interpreting data on Arrhenius graphs extending into both temperature ranges. It then became important to clarify further the generality of the curvature phenomenon and to see what theoretical interpretations were most reasonable.

Once nonlinear Arrhenius graphs had become experimentally and theoretically acceptable, then curvature within and between the aforementioned temperature ranges could also be considered.<sup>17</sup> We will not enter into a discussion of such curvature except to note the following. Below 1000 K, curvature has been shown for bimolecular reactions of larger molecules and

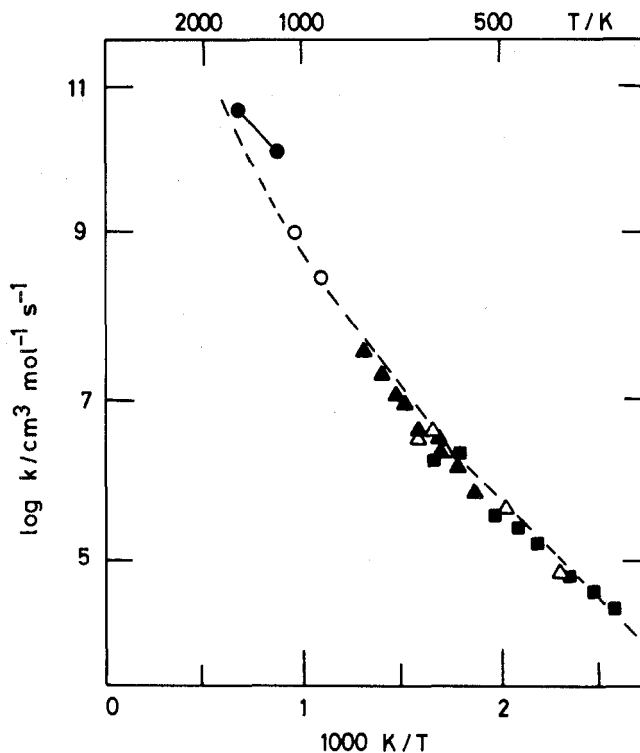


Figure 2. Arrhenius graph for  $CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$ . The dashed curve is an activated complex theory calculation presented in ref 16, where the data sources are also identified.

radicals that would be too unstable to study at much higher temperatures, for example,  $C_2H_5 + C_4H_{10}$ .<sup>18</sup> Part of this curvature is undoubtedly attributable to the internal excitation effects discussed below, while multiple transition states may also contribute. Less marked curvature below 1000 K has also been established for a few very thoroughly studied reactions of atoms.<sup>19</sup> Within the high-temperature range, it is also possible to discern the continuation of curvatures such as illustrated in Figure 2. Such curvature, as far as is known at present, is (with one exception) concave upward to a degree that is compatible with the theoretical discussions given below. The exception is  $H + O_2 \rightarrow OH + O$ , which fails to increase in rate over 1500 K as fast as an extrapolation of lower temperature data would suggest.<sup>20</sup> The explanation of this has not yet been explored in detail, but may well be connected with the special circumstance that the reverse reaction has a near-zero barrier height while the transition state is a stable radical,  $HO_2$ , excited to its continuum.<sup>21</sup>

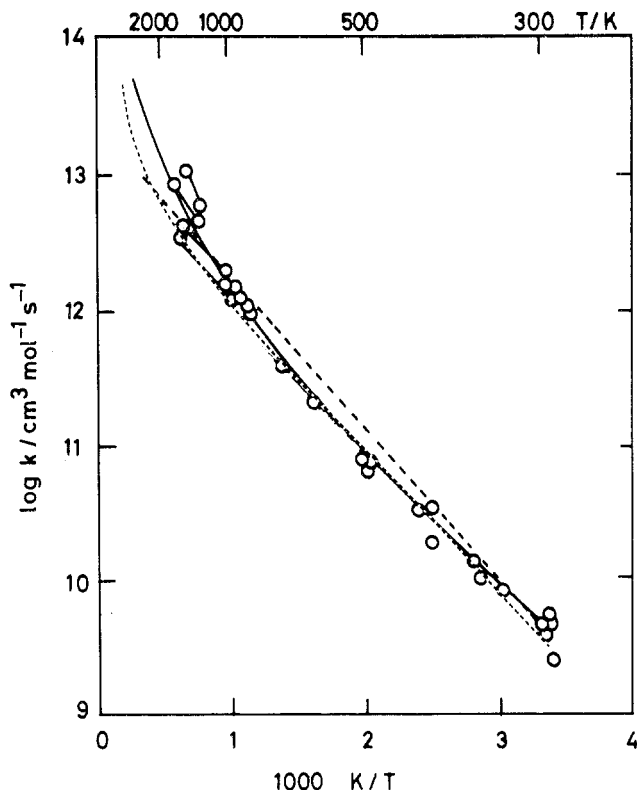
(16) T. C. Clark and J. E. Dove, *Can. J. Chem.*, **51**, 2147 (1973).

(17) A comprehensive review of Arrhenius graph curvature, also including solution reactions, has been given by B. Perlmutter-Hayman, *Progr. Inorg. Chem.*, **20**, 229 (1976); a review on temperature dependence of ion-molecule reaction rates is given by M. Meot-Ner and F. H. Field, *Origins Life*, **6**, 377 (1975).

(18) P. D. Pacey and J. H. Purnell, *Int. J. Chem. Kinet.*, **4**, 657 (1972).

(19) D. N. Mitchell and D. J. Le Roy, *J. Chem. Phys.*, **58**, 3449 (1973).

(20) G. L. Schott, *Combust. Flame*, **21**, 357 (1973).



**Figure 3.** Arrhenius graph for  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ . —, computed fit to  $k = aT^m \exp(-b/T)$ ; ---, compiler's straight-line fit; ···, activated complex theory calculation. The data sources can be identified through ref 28.

An overview of experimental results is afforded by Table I (ref 14–16, 22–31). Not all reactions are included for which extended-temperature-range curvature has been suggested, nor is the literature exhaustively cited for the reactions which are included. The amount of curvature is indicated by the negative Arrhenius graph slopes (in K) at temperatures suitable for each case. We see that the reactions span a wide variety and are led to suspect that the only bimolecular gas reactions whose Arrhenius graph curvature cannot be characterized may be those for which not enough data is available over the required temperature range. To judge whether that suspicion is justified, however, we must consider the theoretical background.

The rates of bimolecular gas reactions are traditionally described in terms of activated complex theory<sup>11</sup> or collision theory.<sup>32</sup> The latter can be set forth at several levels of elaboration, beginning with the conventional line-of-centers cross-section formula, then modifying the cross-section formula to take quan-

tum-mechanical or statistical-mechanical effects into account, and finally undertaking a master-equation approach which would describe the reacting system in terms of time-dependent populations of the quantum states of reactant and product molecules. We consider these in increasing order of complexity, using as our comparison reaction  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ , whose Arrhenius graph is shown in Figure 3.

**Activated Complex Theory.** Arrhenius' postulate of activation prior to reaction is extended here to the well-known statistical-mechanical calculation of the equilibrium concentration of activated complexes, whose decomposition rate to form products is taken as the reaction rate.<sup>11</sup> The temperature-dependent rate constant for our test reaction was evaluated over the temperature range of the data assuming a set of  $\text{H}_3\text{O}$  vibrational frequencies analogous to similar stable molecules. The resulting curve (Figure 3) behaves indeed similarly to the data.

The shortcoming of activated complex theory here, in addition to possible nonequilibrium problems discussed below, is that the spectrum of activated-complex vibrational frequencies affects the curvature very strongly. One would be able to match nearly any Arrhenius graph curvature with a variety of reasonable activated-complex parameters, none of which could be tested by experiment. Moreover, a temperature dependence of the transmission coefficient often included in the activated-complex theory formulation could also contribute.<sup>33</sup> Nonetheless, activated complex theory did lead to the recognition that Arrhenius graph curvature is important for bimolecular gas reactions, is quite capable of predicting high-temperature rate constants with reasonable activated-complex parameters (cf. Figures 1, 2, and 3 and ref 10, 13, 16, 22, 26, 34–36), and will clearly find future use in this regard.

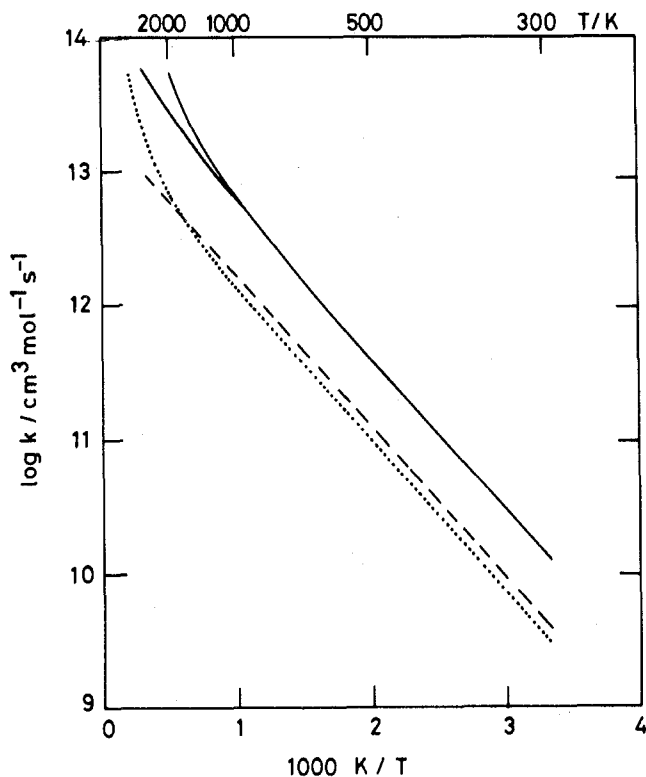
**Collision Theory.** The second traditional prescription for calculating bimolecular gas reaction rate constants is the collision theory line-of-centers formula

$$k(T) = pZ e^{-E_0/RT}$$

which gives almost no Arrhenius graph curvature below 3000 K. The traditional formula, however, is derived on the assumption that the total reactive cross section  $Q$  increases with relative kinetic energy of translation  $E$  as  $Q \sim (1 - E_0/E)$ . While this function may represent nature reasonably well for energies substantially above the threshold  $E_0$ ,<sup>37,38</sup> there is every reason to suspect that it may be a poor representation near threshold, where reaction rates are determined, as well as for very high energies.<sup>39–43</sup> Theoretical studies

- (21) S. C. Kurzius and M. Boudart, *Combust. Flame*, **12**, 477 (1968).  
 (22) P. Roth and Th. Just, *Ber. Bunsenges. Phys. Chem.*, **14**, 682 (1975).  
 (23) M. J. Kurylo and R. B. Timmons, *J. Chem. Phys.*, **50**, 5076 (1969).  
 (24) A. A. Westenberg and N. de Haas, *J. Chem. Phys.*, **48**, 4405 (1968).  
 (25) Trajectory calculations of J. M. White and D. L. Thompson, *J. Chem. Phys.*, **61**, 719 (1974).  
 (26) G. L. Schott, R. W. Getzinger, and W. A. Seitz, *Int. J. Chem. Kinet.*, **6**, 921 (1974).  
 (27) W. C. Gardiner, Jr., M. McFarland, K. Morinaga, T. Takeyama, and B. F. Walker, *J. Phys. Chem.*, **75**, 1504 (1971).  
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 (34) S. W. Mayer, L. Schieler, and H. S. Johnston, "Eleventh Symposium (International) on Combustion", The Combustion Institute, Pittsburgh, Pa., 1967, p 837; *J. Chem. Phys.*, **45**, 385 (1966).  
 (35) S. W. Mayer, *J. Phys. Chem.*, **71**, 4159 (1967).  
 (36) G. W. Koeppel, *J. Chem. Phys.*, **59**, 3425 (1973).  
 (37) R. G. Gann, W. M. Ollison, and J. Dubrin, *J. Chem. Phys.*, **54**, 2304 (1969).  
 (38) J. G. Pruett, F. R. Grabner, and P. R. Brooks, *J. Chem. Phys.*, **63**, 1173 (1975).  
 (39) A. B. Elkowitz and R. E. Wyatt, *J. Chem. Phys.*, **62**, 2504 (1975); G. C. Schatz and A. Kupperman, *ibid.*, **65**, 4642, 4668 (1976).  
 (40) A. Kuppermann and J. M. White, *J. Chem. Phys.*, **44**, 4352 (1966).  
 (41) M. Menzinger and R. L. Wolfgang, *Angew. Chem., Int. Ed. Engl.*, **8**, 438 (1969).  
 (42) R. L. Le Roy, *J. Phys. Chem.*, **73**, 4338 (1969).



**Figure 4.** Comparison of activated-complex and collision theory calculations for  $\text{OH} + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$ . The compiler's straight line (---) and activated complex theory (—) curves are as in Figure 3. The two collision theory curves (---) differ in that the upper one assumed a cross section for  $\text{H}_2$  or  $\text{OH}$  in the  $v = 1$  state ten times greater than for  $v = 0$ ; both cross sections were taken to be larger than necessary in order to separate the collision theory curves from the others.

suggest that the near-threshold behavior is concave upward, e.g., like  $Q \sim (E - E_0)^n$ ,  $n = 2$  or  $3$ , which would have a very strong effect upon Arrhenius graphs.<sup>41,43</sup> For example, if  $n = 2$  and  $E_0 = 40$  kJ (10 kcal), then  $E_A$  would be 44 kJ at 300 K, 56 kJ at 1000 K, and 74 kJ at 2000 K.<sup>42</sup> So curvature of the  $Q(E)$  function is capable of accounting for Arrhenius graph curvature also.<sup>44</sup>

The weaknesses of this collision theory approach are that there are as yet no sufficiently accurate theoretical methods for obtaining  $Q(E)$  except for  $\text{H} + \text{H}_2$  and its isotopic analogues<sup>39</sup> and perhaps  $\text{H}_2^+ + \text{He}$ , that the  $Q(E)$  function also depends upon temperature, and that molecular beam<sup>38</sup> or related<sup>40</sup> methods are inaccurate in determining  $Q(E)$  in the critical near-threshold region. Writing  $Q(E)$  rather than  $Q(E, T)$  is equivalent to focussing too much attention on the coordinate of reactant approach, for, as we see in a moment, other degrees of freedom are also important in determining cross sections. Nonetheless, near-threshold  $Q(E)$  curvature deserves just as much attention as activated-complex vibrations as a way of thinking about Arrhenius graph curvature.

**Collision Theory with Internally Excited Reactants.** As temperature increases, significant

(43) C. J. Malerich and D. R. Davis, *J. Chem. Phys.*, **55**, 4141 (1971).

(44) Quantum-mechanical tunneling requires the "true"  $E_0 = 0$  for exoergic reactions. Tunneling contributions to cross section and rate constant, however, are found to be small compared to the other effects discussed in this section.<sup>5</sup> The effect of  $Q(E)$  curvature upon Arrhenius graph curvature for  $\text{HI} + \text{HI}$  was investigated by L. S. Kassel, *Proc. Natl. Acad. Sci. U.S.A.*, **16**, 358 (1930), who assumed  $Q(E) \sim (1 - E_0/E)(E - E_0)^{n-1}$ .

**Table II**  
Acceleration of Some Bimolecular Reactions by  
Vibrational Excitation

Reaction	$f_{mn} = k(v=m)/k(v=n)$	Ref
$\text{H} + \text{HF}^\dagger \rightarrow \text{H}_2 + \text{F}$	$f_{10} = 5 \times 10^8$ ; $f_{32} = 3 \times 10^6$	47, 48
$\text{O} + \text{HCl}^\dagger \rightarrow \text{OH} + \text{Cl}$	$f_{10} = 250$	49
$\text{F} + \text{HCl}^\dagger \rightarrow \text{HF} + \text{Cl}$	$f_{10} = 3.5$	50
$\text{Br} + \text{HCl}^\dagger \rightarrow \text{HBr} + \text{Cl}$	$f_{20} = 10^{11}$ ; $f_{32} = 3.6$ ; $f_{43} = 1.5$	51, 52
$\text{S} + \text{CO}^\dagger \rightarrow \text{O} + \text{CS}$	$f_{v+1, v} = 10^4$ ; $6 < v < 14$	47, 53
$\text{OH}^\dagger + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3$	$f_{10} \leq 3.5$	54
$\text{OH}^\dagger + \text{H}_2 \rightarrow \text{H}_2\text{O} + \text{H}$	$f_{10} \leq 1.5$	54
$\text{OH}^\dagger + \text{HBr} \rightarrow \text{H}_2\text{O} + \text{Br}$	$f_{10} = 9$	55
$\text{CN}^\dagger + \text{O} \rightarrow \text{CO} + \text{N}$	$f_{v+1, v} = 1$ ; $0 < v < 6$	56
$\text{CN}^\dagger + \text{O}_2 \rightarrow \text{products}$	$f_{v+1, v} = 0.82$ ; $0 < v < 7$	56
$\text{O}_3^\dagger + \text{NO} \rightarrow \text{NO}_2 + \text{O}_2$	$f_{10}'' = 10$	57
$\text{NO}^\dagger + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$	$f_{10} = 5.7$	57

populations of excited internal states may become important contributors to the net reaction rate through all states. The effect will then be upward curvature of the Arrhenius graph if higher specific reaction rates from excited states can overcome the necessarily unfavorable Boltzmann factors.

This viewpoint is illustrated by the pair of collision-theory Arrhenius graphs shown in Figure 4. In one, only the  $T^{1/2}$  factor of  $Z$  contributes to curvature. In the other, reaction was considered separately for  $v = 0$  and  $v = 1$  quantum states, with the cross section tenfold greater if either reactant is in the  $v = 1$  state. It can be seen that the larger reactive cross sections for  $v = 1$  then do overcome the Boltzmann disadvantage in such a way that the curvature resembles the experimental results quite well. Participation of reagent internal excitation in the reaction process is therefore an additional possibility for understanding Arrhenius graph curvature.

A collision theory explanation in terms of increased cross sections for excited internal states has the attractive feature that its principal ingredients, the specific rate constants, have become accessible to direct and indirect experimental measurements. If only fragmentary experimental results are available, then methods for extending them over the whole range of internal quantum states also exist.<sup>45,46</sup> The direct experiments require creation of nonthermal populations of reactant states, either by generating them in highly exoergic chemical or photochemical reactions or by laser excitation of internal modes. The amount of rate enhancement can then be determined by the same methods used to measure thermal rates. The indirect experiments involve measuring the nascent populations of product states in exoergic reactions and invoking the principle of microscopic reversibility.<sup>45</sup> A selection of some cases where vibrational enhancement has recently been measured is given in Table II (ref 47–57).

(45) A. Ben-Shaul, R. Levine, and R. B. Bernstein, *J. Chem. Phys.*, **57**, 5427 (1972); R. D. Levine and J. Manz, *J. Chem. Phys.*, **63**, 4280 (1975).

(46) M. Quack and J. Troe, *Ber. Bunsenges. Phys. Chem.*, **80**, 1140 (1976).

(47) H. Kaplan, R. D. Levine, and J. Manz, *J. Chem. Phys.*, **12**, 447 (1976).

(48) M. J. Berry, *J. Chem. Phys.*, **59**, 6229 (1973).

(49) Z. Karny, B. Katz, and A. Szöke, *Chem. Phys. Lett.*, **35**, 100 (1975).

(50) L. J. Kirsch and J. C. Polanyi, *J. Chem. Phys.*, **57**, 4498 (1972); A. M. Ding, L. J. Kirsch, D. S. Perry, J. C. Polanyi, and J. L. Schreiber, *Faraday Discuss. Chem. Soc.*, **55**, 252 (1973).

So far only fragmentary information is available on the temperature dependence of vibrationally enhanced reaction rates. In the language of the Arrhenius equation, then, it is unclear whether an enhancement should be assigned to an increase in  $A$  or to a decrease in  $E_A$ ,<sup>57</sup> in the language of collision theory, whether the cross section or the effective threshold energy is primarily affected. This distinction is crucial as far as Arrhenius graph curvature is concerned. If only the effective barrier height is affected, then an Arrhenius graph for the thermal rate will show no curvature at all due to increased populations of excited vibrational states at higher temperatures. In this case, the  $hc\omega_0$  appearing in Boltzmann factors of vibrational distribution functions will exactly make up for reduced values of  $E_0$ . Upward curvature can only arise if a substantial part of the enhancement appears in  $A$ .

It can be seen that increasing the vibrational energy of reactants can have large, negligible, or even negative effects upon reaction rate, depending upon the particular reaction. Since vibrationally excited states with  $n$  quanta will always be lower in population than ground states by  $\exp(-nhc\omega_0/kT)$ , only those reactions for which large vibrational enhancements of cross section are found can be accelerated in thermal systems beyond the ordinary collision-theory rates. Thus it would appear that the Arrhenius graph curvature for  $\text{OH} + \text{H}_2$  or  $\text{CO}$  cannot be due to increased populations of  $\text{OH}(v = 1)$ <sup>54</sup> (assuming that the fractional enhancement itself is not strongly temperature dependent). Such negative results, if confirmed for all internal degrees of freedom in a reaction, would imply that the reactive cross section  $Q(E)$  is essentially temperature independent, in which case any experimentally observed Arrhenius graph curvature would have to be interpreted as near-threshold  $Q(E)$  curvature alone.

**Classical Trajectories.** The course of a reactive collision can be studied by numerical integration of the classical equations of motion for a phase point moving on a  $(3N - 3)$ -dimensional potential-energy surface. Thermal averages of the resulting trajectories then provide thermal-average reaction probabilities and thence rate constants, thus bypassing the  $Q(E, T)$  function of collision theory or the transmission coefficient and structural assumptions of activated complex theory, and directly translate interatomic forces into rate constants.

So far only a single trajectory study of Arrhenius graph curvature has been reported, on  $\text{H} + \text{HBr}$ , which we have included as experimental data in Table I. It is to be expected, however, that many more will come. Trajectory studies can clarify the contributions of in-

ternal and translational energy to reactivity and thus Arrhenius graph curvature, identify the features of potential-energy surfaces which are responsible, and assist in deciding what type of potential-energy surface describes a reaction.<sup>58</sup> Since the shape of the surface also determines the structural parameters required for activated complex theory, comparing trajectory results with activated complex theory predictions would also permit one to decide how much a temperature-dependent transmission coefficient contributes to Arrhenius graph curvature.

Trajectory studies share with the other approaches the shortcoming that the key molecular information—here the surface parameters—is not well known. In addition, trajectory studies require extensive computation, both to obtain the surface and to integrate the trajectories, and are questionable for H-atom transfers, which comprise the bulk of the best data so far obtained. They will nevertheless play important roles in developing an understanding of Arrhenius graph curvature.

**Master Equations.** We have assumed so far that reacting atoms and molecules are characterized by thermal distributions of translational and internal energy. Theoretical studies lead to the general conclusion that only unusually rapid reactions are capable of perturbing the translational distribution perceptibly.<sup>59</sup> Much the same is likely to be true for rotational distributions, but vibrational disequilibrium is another matter. The relatively low probabilities for transfer of vibrational energy, coupled with the possibility that excited vibrational states may react much faster than ground states, mean that rate constants measured experimentally may pertain to nonequilibrium vibrational distributions and thus reflect a combined rate of reaction and energy transfer.

In principle this circumstance does not impede our understanding, for energy-transfer rates can be measured independently of reaction rates. In practice, however, one is then faced with the necessity of describing a reacting system in terms of molecules in specific vibrational states. The system of kinetic equations then becomes a "master equation", and one's procedure of data interpretation becomes a sequence of numerical integrations of many simultaneous, coupled, complicated ordinary differential equations.

To illustrate this, we consider what must be done with a reaction mechanism for the  $\text{H}_2\text{-O}_2$  explosion including the reaction  $\text{H} + \text{O}_2 \rightarrow \text{OH} + \text{O}$  if its rate constant depends upon the vibrational state of  $\text{O}_2$ . (A complete description would of course also include the dependence of the reverse rate constant upon the vibrational state of  $\text{OH}$ .) The differential equations governing the time dependence of each  $\text{O}_2(v)$  concentration must contain terms describing the translation-vibration and vibration-vibration energy transfer rates with all species present,<sup>60</sup> as well as each specific reaction rate. The entire system of differential equations, which for most conditions is very likely to be a stiff system,<sup>61</sup> has to be integrated numerically

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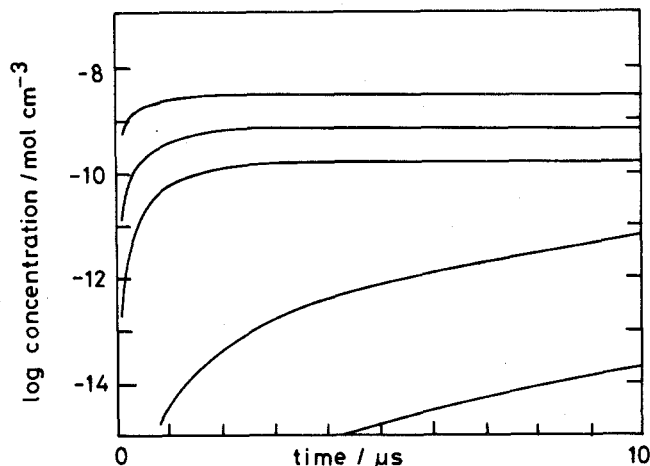
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**Figure 5.** Example of a master-equation solution for a chemical reaction in which internal excitation of  $O_2$  to  $v = 3$  is required prior to its reaction with H to form OH and O. The reaction conditions are  $T = 1500$  K and initial concentrations of  $H_2$  and  $O_2$  of  $1.87 \times 10^{-7}$  and  $1.87 \times 10^{-8}$  mol  $cm^{-3}$ , respectively. The upper three curves show the rapid relaxation of the  $v = 1, 2,$  and  $3$  states of  $O_2$ , the lower two curves the growth of H- and O-atom concentrations leading to explosion. The slopes of the latter curves are experimental measures of the rate of the  $H + O_2$  reaction for these conditions.<sup>20</sup>

from whatever starting conditions pertain through the observed reaction time. An example of the resulting profiles from a system containing altogether 14 differential equations (11 species and 24 reactions) is shown in Figure 5. The fairly clear separation between vibrational relaxation and chemical reaction for these conditions permits an assignment of reactive flux to well-defined steady state, if not equilibrium,  $O_2(v)$  concentrations.

Such master-equation solutions are well known in the gas laser field, and their application to studies of Arrhenius graph curvature does not introduce new difficulties. What is involved is primarily a substantial complication in data interpretation. If it turns out to be generally true that vibrationally excited states carry large fractions of the reactive flux at high temperatures, then the general effect of vibrational disequilibrium will be to suppress the reaction rate below its equilibrium value and counteract an upward Arrhenius graph curvature.

**Still-Wider Temperature Ranges.** Bodenstein's extension of rate measurements to over 200 K, and modern technology's further extension to over 2000 K, are really only small samples of the span of energies with which potentially reactive molecules can be made to encounter one another. While the modern tem-

perature range does encompass the whole range in which molecules exist and react, we may still investigate what can happen in "nonthermal" energy ranges in the expectation that insights so gained may be valuable in the thermal range also.

Very high collisional energies can be achieved for ion-molecule reactions. Recent advances in the theory of drift tubes, in particular, show that ion-molecule rate constants measured in drift tubes can be assigned to well-defined translational energies, which may reach equivalent translational temperatures of  $10^5$  K while internal temperatures are still near 300 K. Remarkable (compared to a chemist's normal experience) dependences of rate upon temperature can be found.<sup>62-65</sup>

The low-temperature limit of translational energy is of course zero, achieved when matter solidifies; even at  $T = 0$ , however, a zero-point phonon energy and zero-point molecular vibrational energies exist. Near this limit, only quantum-mechanical tunneling can lead to reaction. While numerous experimental difficulties cloud the interpretation of solid-phase reaction rates, tunneling-limit rates may have been observed in some cases.<sup>66</sup>

## Conclusions

It has been established experimentally that Arrhenius graphs for bimolecular gas reactions over extended temperature ranges are curved. The curvature, which was anticipated on various theoretical bases long in advance of experiment, reflects in as yet unclear ways the participation of internal degrees of freedom in the reaction as well as the dependence of reactive cross section upon relative translational energy. Since all theoretical considerations indicate that the effects of activated-complex vibrations, reactive flux through vibrationally excited states, or  $Q(E)$  curvature are capable of explaining far more Arrhenius graph curvature than is actually observed, we may soon have to come to grips with the converse question: why do most Arrhenius graphs look so straight?

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