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# HISTORY OF H<sub>3</sub> KINETICS

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# **INTRODUCTION**

The gas-phase reaction of H with  $H_2$  has been of fundamental interest since London (1929) pointed out that it can be understood in terms of a potential energy surface calculated from quantum mechanics. It has also been the only gas-phase bimolecular reaction for which curvature of the Arrhenius plot could be observed at low temperature (Marshall & Purnell 1968). Thus it served as a model for theories of tunneling. Because every atom involved can be substituted by D or T, it has been an important prototype system for isotope effect considerations. Because good photochemical and nuclear recoil sources of hot (i.e. fast) H, D, or T atoms are available, it has also been studied under nonthermal high-energy conditions (Rowland 1970).

One of the reasons why the  $H + H_2$  atomic exchange reaction provides a good system for theoretical analysis is that knowledge of only one potential energy surface is required. Thus the dynamics may be treated in two stages: obtain the adiabatic surface and then solve for the reaction probabilities, cross sections, or rate coefficients using this surface to govern the internuclear motions. Of necessity, treatments of the second stage have been based on approximate surfaces. To the extent that these are realistic, the dynamical conclusions are useful. The history of attempts to calculate or approximate this surface is a long one and is reviewed elsewhere together with the present state of knowledge of the H<sub>3</sub> surface (Truhlar & Wyatt, 1977).

In shock tube and hot atom systems one must consider not only the atomic exchange reaction but also dissociation and sometimes the reverse recombination. We review experimental and theoretical studies of these three reactions in this article. Elastic scattering, nonreactive energy transfer collisions, transport in  $H:H_2$  mixtures, and  $H_3$  processes involving electronically excited H or  $H_2$  are reviewed elsewhere (Truhlar & Wyatt, 1977).

The article is divided into two parts. The first considers equilibrium and steadystate rates of reaction as studied experimentally by thermal conversion, flow tubes, and shock tubes, and theoretically using transition-state theory. The second part involves non-Boltzmann experiments (hot atom studies and molecular beam reactions) and the interpretation of these experiments as well as the equilibrium ones in terms of state-to-state cross sections. The next three paragraphs are a brief review of the ground-state potential surface of  $H_3$ .

# POTENTIAL ENERGY SURFACE

For the  $H + H_2$  atomic exchange reaction the most important quantities characterizing the potential energy surface are the saddle-point height (also called classical barrier height  $E_b$ ) and saddle-point geometry. Also of crucial importance is the vibrationally adiabatic barrier height  $E_b^{VAZC}$  (also called the transition-state-theory activation energy at 0°K) and the harmonic imaginary zero-point energy  $\frac{1}{2}hv_a$  of the transition-state reaction-coordinate normal mode. The former is given for a linear symmetric saddle point by

$$E_0^{VAZC} = E_b + E_0^{VS} + (p-1)E_0^{VB} - E_0^V, \qquad 1.$$

where p is 1 for collinear reactions, 2 for coplanar reactions, and 3 for real threephysical-dimensional (3-PD) collisions;  $E_0^{VS}$  and  $E_0^{VB}$  are the zero-point energies of the symmetric stretch and bending normal modes of the transition state; and  $E_0^{V}$  is the zero-point energy of the reactant. The most accurate available potential energy surface for H<sub>3</sub> is the ab initio one of Liu (1973 for collinear, unpublished for noncollinear), who obtained a linear symmetric saddle point with properties given in Table 1. The noncollinear surface has been fit to an analytic form and used for some calculations of cross sections (G. C. Schatz and A. Kuppermann, unpublished; Schatz 1975). All other dynamical calculations, however, have been carried out using less accurate surfaces. These have often been based on analytic formulas suggested by valence bond theory or diatomics-in-molecules theory. But the resulting surfaces are so sensitive to the input diatomic potential curves and to the various simplifications made in the theory that it is better to consider them as empirical surfaces. The four most commonly used analytic forms are the London equation (see, e.g., Hirschfelder, Eyring & Topley 1936), the Sato equation (see, e.g., Weston 1959), the Wall-Porter equation (also called the rotated Morse curve, Wall & Porter 1962), and the formula of Porter & Karplus (1964).

Early calculations (e.g. Eyring & Polanyi 1931) based on the London equation predicted that there is a local minimum for linear symmetric H<sub>3</sub> flanked by twin nonsymmetric saddle points. This predicted basin might have had interesting dynamic consequences (Eyring 1932) if real but it is now known to be an artifact of the approximation scheme. Later calculations provided more realistic surfaces, several of which are compared in Table 1. Before 1969 most surfaces had too thin a barrier, i.e., too large a value for  $|\frac{1}{2}hv_a|$  and too small a barrier height. Attempts to use such inaccurate surfaces to calculate, for example, magnitudes of rate coefficients or the quantitative extent of tunneling for comparison with experiment Annu. Rev. Phys. Chem. 1976.27:1-43. Downloaded from arjournals.annualreviews.org by University of Minnesota- Law Library on 01/09/07. For personal use only.

Table 1 Properties of potential energy surfaces

			e ≠ c	Ľ	$E_0^{VAZC}$ (hi	armonic)	$\frac{1}{2}hv_a$
Kelerence	Abbrevlation	Analync Form	K1 -	ч <sup>1</sup>		n = 3	
			$(a_0)$	(eV)	(eV)	(eV)	(eV)
Weston (1959)	M	Sato	1.76	0.358	0.216	0.324	0.118i
Porter & Karplus (1964) no. 2	PK2	Porter-Karplus	1.70	0.398	0.260	0.382	0.137i
Westenberg & deHaas (1967)	MdH	Sato	1.76	0.380	0.239	0.349	0.128i
Salomon (1969) no. 6	S6	Porter-Karplus	1.71	0.407	0.263	0.387	0.053i
Truhlar & Kuppermann (1970, 1972)	TK	Wall-Porter	1.765	0.424	0.276	q	0.091i
Saxon & Light (1971, 1972)	SĿ	c	1.765	0.424	0.269	0.382	0.091i
Diestler (1972) no. 3	D3	Wall-Porter	1.779	0.555	0.409	٩	0.081i
Jones & Rosenfeld (1973)	JR	Porter-Karplus	1.74	0.425	0.282	0.422	0.092i
Yates & Lester (1974)	٨L	Porter-Karplus	1.74	0.425	0.280	0.414	0.104i
Malcome-Lawes (1975)	Σ	extended Hückel	1.85	0.391	0.254	0.366	0.095i
Liu (1973 and unpublished)		accurate	1.757	0.425	0.279	0.391	0.094i
* Nearest-neighbor distance at linear symmetri	c saddle point.						

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\* Least-squares fit to ab initio surface of Shavitt et al (1968) times scale factor. The whole potential is scaled whereas in the TK surface the potential is scaled

along but not transverse to, the minimum-energy path.

<sup>b</sup> Not defined.

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cannot be trusted. However, the surfaces in Table 1 are realistic enough that they can and have been used to provide important insights into some other aspects of the dynamics as discussed below. Unfortunately there have been few systematic studies of how the differences among various realistic surfaces affect such results in detail.

Before Liu's (1971, 1973) calculations the most accurate ab initio surface was that of Shavitt et al (1968). Shavitt (1968) suggested that the energy profile along the reaction path of that surface should be adjusted by a uniform scale factor of 0.89 determined empirically by comparing transition-state-theory rate constants for the isotopic  $H + H_2$  reactions to experiment (Westenberg & deHaas 1967). Truhlar & Kuppermann (1970, 1972) obtained a reasonably accurate colinear surface by adjusting a Wall–Porter function according to this suggestion.

# THERMAL RATE COEFFICIENTS: EXPERIMENT

### Exchange Reactions

Thermal rate coefficients for the  $H + H_2$  reaction and three of its isotopic analogues have been measured by *thermal conversion* for temperatures T = 720-1023°K and *flow tube* techniques for T = 167-745°K. A number of reviews and compilations of results are available (see, e.g., Farkas 1935, Steacie 1954, Careri 1958, Shavitt 1959, 1968, Polanyi 1962, Johnston 1966, Schofield 1967, Lifschitz 1969, Rowland 1970, Jones, MacKnight & Teng 1973). In thermal conversion studies, repeated analyses are made of a (nonflowing) gaseous mixture. In flow-tube studies, H or D atoms are injected into a metered flow of  $H_2$  or  $D_2$ , followed by downstream analysis. Difficulties arising in the former method are temperature control and uniformity, wall reproducibility, and the assumptions that must be made to extract rate coefficients from the overall molecular conversion rates (Niki & Mains 1972). Difficulties in the latter are corrections for axial diffusion and recombination of atoms to form vibrationally excited molecules that react before relaxing. Table 2 summarizes applications to the hydrogen isotope reactions and establishes notation for the rate coefficients.

In the first studies of *para-ortho* conversion, Farkas (1930, 1930a) found pseudofirst order kinetics, which could be analyzed for  $k_1$  by using the relation  $k_{-1} \cong 3k_1$ . An Arrhenius plot of  $k_1$  was linear and yielded an Arrhenius activation energy  $E_a$  of 0.24 eV for reaction 1. Farkas & Farkas (1935) studied *ortho-para* conversion in D<sub>2</sub> and the H<sub>2</sub>+D<sub>2</sub>  $\rightarrow$  2HD reaction. For the latter they proposed a mechanism involving fast homogeneous dissociation and recombination of H<sub>2</sub>, D<sub>2</sub>, and HD and slow reactions 3 and 4 and obtained values for  $k_3 k_4/(k_3 + k_4)$ . The H+H<sub>2</sub> and H<sub>2</sub>+D<sub>2</sub> reactions were also studied by van Meersche (1951); his rate coefficients for the former reaction showed considerable scatter and are not reliable. Boato et al (1953, 1956, see also Cimino, Molinari & Volpi 1956, 1960) also studied the H<sub>2</sub>+D<sub>2</sub> reaction, and obtained results about a factor of two lower than those obtained in previous studies. Boato et al claimed that homogeneous atom production is too slow compared to the rates of reactions 3 and 4 to maintain stationary concentrations of atoms, so they postulated a wall mechanism for atom production Annu. Rev. Phys. Chem. 1976.27:1-43. Downloaded from arjournals.annualreviews.org by University of Minnesota- Law Library on 01/09/07. For personal use only.

 $9.9 \times 10^{-15^{h}}$  $1.3 \times 10^{-15}$  $1.5 \times 10^{-15}$  $1.6 \times 10^{-15}$  $1.1 \times 10^{-14}$  $3.9 \times 10^{-15}$ 425°K ł  $k(\text{cm}^3 \text{ molec}^{-1} \text{ sec}^{-1})$  $3.8 \times 10^{-16b}$  $3.5 \times 10^{-17}$  $2.7 \times 10^{-1.7}$  $2.0 \times 10^{-16}$  $3.0\times10^{-16}$  $3.0 \times 10^{-16}$ 300°K **Temperature** Range (°K) 916-1010 833-1018 850-1000 720-875 299-745 873-1023 252-745 368-468 283-373 720-875 300-444 358-468 274-468 167-346 903-981 Method<sup>a</sup> 5555 ЧЦ 2222 FT FF E LeRoy, Ridley & Quickert 1968 Ridley, Schulz & LeRoy 1966 Westenberg & deHaas 1967 Westenberg & deHaas 1967 Mitchell & LeRoy 1973 Farkas & Farkas 1935 Farkas & Farkas 1935 Schulz & LeRoy 1964 A. Farkas 1930, 1930a Schulz & LeRoy 1965 Geib & Harteck 1931 Reference Niki & Mains 1972 van Meersche 1951 van Meersche 1951 Boato et al 1956  $H + pH_2 \stackrel{k_1}{\longrightarrow} oH_2 + H$  $\mathbf{D} + o\mathbf{D}_2 \stackrel{k_1}{\stackrel{k_2}{\longleftrightarrow}} p\mathbf{D}_2 + \mathbf{D}$  $D + H_2 \stackrel{k_3}{\underset{k-3}{\leftarrow}} DH + H$  $H + D_2 \stackrel{k_4}{\leftarrow} DH + H$  $H_2 + D_2 \approx 2HD$ Reaction

 Table 2
 Thermal conversion and flow tube measurements of rate constants for hydrogen isotope reactions

 $^{a}$  TC = thermal conversion method; FT = flow tube method.  $^{b}$  Uncorrected.

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and recombination, assumed a constant [H]/[D] ratio during reaction, and derived an integrated rate law, which they used to extract  $k_3/k_4$  from the observed net conversion rate. They proposed that O<sub>2</sub> seepage through the wall of the hot quartz reaction vessels used by Farkas & Farkas led to their high reaction rates.

Niki & Mains (1972) recently studied the  $2HD \rightarrow H_2 + D_2$  reaction. Rate measurements showed an induction period, which was attributed to rapid heterogeneous production of atoms; then atomic concentrations increased by a homogeneous atomic chain mechanism. In the latter stage, varying the surface to volume ratio had a negligible effect and the assumption of constant [H]/[D] was shown to be valid. However, the rate coefficients that they obtained for four hydrogen isotope reactions were generally lower than other experimental values.

Studies of the homogeneous four-center  $H_2 + D_2$  reaction are not reviewed here. Geib & Harteck (1931) made the first flow tube studies of the hydrogen isotope reactions and reported two sets of rate coefficients computed for extreme mixing rates between the H atoms and the flowing gas stream. Their results were uncertain by a factor of as large as 3.7. LeRoy and coworkers used flow tubes with a Pt wire calorimeter to measure atomic concentrations and thermal conductivity or gas chromatography (GC) analysis of product mixtures to study four isotopic reactions (see Table 2). For  $H+D_2$  and  $D+o-D_2$  their measurements covered a narrow T range and yielded linear Arrhenius plots with  $E_a = 0.32$  and 0.33 eV, respectively. For  $H + p - H_2$  and  $D + H_2$ , the Arrhenius plots showed  $E_a = 0.33$  and 0.30 eV, respectively, at the higher T ends of the ranges studied but considerable curvature below 350° and 300°K, respectively, e.g.,  $E_a$  was 33% less below 350°K for H + p – H<sub>2</sub>. Meanwhile Westenberg & deHaas (1967, see also Westenberg 1968, 1969) employed ESR detection of atomic concentrations after variable reaction lengths in the flow tube to study  $H+D_2$  and  $D+H_2$ . For  $T \approx 450^{\circ}$ K, Arrhenius plots were linear for both reactions with respective  $E_a$  values of 0.41 and 0.33 eV; but for H+D<sub>2</sub> and  $D + H_2$ ,  $E_a$  was 35 and 42% less at 299–327 and 252–274°K than for T > 450°K. At low T their  $k_3$  disagreed with that of Ridley, Schulz & LeRoy (1966), although excellent agreement was obtained for  $T \approx 330^{\circ}$ K. Later Mitchell & LeRoy (1973) used the same ESR method and reported that the results of Ridley, Schulz & LeRoy (1966) for  $k_3$  should be corrected, particularly at low T, for back diffusion of H<sub>2</sub> (Ridley 1968). The Arrhenius plot of their new  $k_3$  showed nearly linear behavior and is in good agreement with the results of Westenberg & deHaas (1967).

Quickert & LeRoy (1970) simultaneously carried out two reactions in a flow tube and measured product molecule concentrations by GC. They found that  $k_1/k_4$  varied from 11.2 at 294°K to 3.2 at 693°K. This directly determined ratio agrees well with ratios computed from independent measurements of  $k_1$  (Schulz & LeRoy 1965) and  $k_4$  (Westenberg & deHaas 1967).

The values of the most accurate forward rate coefficients are compared at two temperatures in Table 2. At the temperatures of the thermal conversion experiments the transition-state-theory results of Shavitt (1968) for ten isotopic reactions are probably more reliable than the measurements.

Heidner & Kasper (1972) produced H and vibrationally excited  $H_2$  in an electrical discharge, measured their respective concentrations by isothermal calorimetry and

vacuum UV absorption spectroscopy, and determined the rate coefficient at 299°K for  $H + H_2(n = 1) \rightarrow H_2(n' = 0) + H$  where *n* and *n'* are respectively the initial and final vibrational quantum numbers and both reactive and nonreactive contributions are included. Trajectory calculations discussed below (M. Karplus and I. Wang, unpublished) indicate that the nonreactive contribution is negligible compared to the reactive one, so they interpreted their result as measuring the latter. Their value  $(3.0 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ sec}^{-1})$  is much larger than  $k_1$  for n = n' = 0 at this T (see Table 2).

An interesting aspect of H<sub>3</sub> kinetics not reviewed here is reactions of H<sub>3</sub> with other species, e.g.,  $H_3 + H \rightarrow 2H_2$  or  $\rightarrow 2H + H_2$ , which is important for the chaperone mechanism for  $k_{H_2}^a$  (Kimball 1932, Shui & Appleton 1971, Pack, Snow & Smith 1972, and Whitlock, Muckerman & Roberts 1972, 1974).

### Dissociation and Association

The  $H + H_2$  dissociation reaction and the reverse three-body recombination reaction

$$H_2 + M \frac{k_M^2}{k_M^2} H + H + M$$

where M is H, have been studied not in isolation but always in competition with at least one other third body M (H<sub>2</sub> and sometimes an inert gas). The early work on  $k_{\rm H}^{\rm a}$  was conducted at or around room temperature by passing electrolytically generated moist  $H_2$  through a discharge into a flow tube where atoms were detected by a Pt calorimeter (Smallwood 1929, Amdur & Robinson 1933, Robinson & Amdur 1933, Amdur 1935, 1938) or a Wrede gauge and  $H_{\alpha}$  emission (Steiner & Wicke 1931, Steiner 1935, see also Amdur 1933). Or the discharge products were produced in a (nonflowing) bulb where the isothermal pressure change was measured (Smallwood 1934). The various investigators obtained quite different results for  $k_{\rm H}^a/k_{\rm H}^a$ , and  $k_{\rm H}^a$ (see Amdur & Robinson 1933, Thrush 1965, Bennett & Blackmore 1968, and Stepukhovich & Umanskii 1969 for brief reviews) at least partly due to different assumptions about wall reactions. More recently Larkin (1968) pointed out that  $k_M^a$  values obtained using dry H<sub>2</sub> are smaller than those obtained with moist H<sub>2</sub>, apparently due to catalyzed recombination involving water, oxygen-containing impurities, or their discharge products. Clearly the old flow-tube work on recombination is not reliable.

H atom recombination was also studied using atoms produced by Hg photosensitization (Senftleben & Reichmeier 1930, Farkas & Sachsse 1934, Senftleben & Hein 1935, Shida 1941). Recombination was generally attributed to H<sub>2</sub> as third body but the results again varied widely.

The only recent experimental result for  $k_{\rm H}^a$  or  $k_{\rm H}^d$  at or near room temperature is Bennett & Blackmore's (1968) measurement at 300°K using ESR detection in a flow system. Their H<sub>2</sub> was dry and purified. No evidence could be found for H as third body; thus they estimated an upper bound of  $7 \times 10^{-33}$  cm<sup>6</sup> molec<sup>-2</sup> sec<sup>-1</sup> for  $k_{\rm H}^a$ . Since their value for  $k_{\rm H_2}^a$  is 2.2 times less than the more recent determination of

Trainor, Ham & Kaufman (1973) it is possible that their bound is too low by about this much or more.

Recombination has also been studied in shock tubes (Gardiner & Kistiakowsky 1961; Rink 1962, 1962a; Sutton 1962; Patch 1962; Hurle 1967, Rosenfeld 1968, Hurle, Mackey & Rosenfeld 1969; Jacobs, Giedt & Cohen 1967, 1968; Breshears & Bird 1973). In these the system reaches equilibrium or a steady state due to simultaneous occurrence of dissociation, recombination, and energy transfer processes. The effect on bulk gas properties of the net dissociation is large and these properties (density, H<sub>2</sub> concentration, temperature) have been used to monitor it. Since in general both dissociation and recombination must be considered to analyze the shock tube data it is convenient to express  $k_M^d$  in terms of the equilibrium constant and  $k_M^a$  and report only the latter. The experiments cover various ranges of temperature from 2800 to 7200°K. Some workers could not measure the temperature dependence and assumed  $k_M^a$  varies as  $T^{-1/2}$  or  $T^{-1}$  to analyze their data. If this is incorrect it affects the magnitudes of their  $k_{\rm H}^a$ . These are compared at 4000°K in Table 3. In three cases the experiments and analyses apparently did give information about the T dependence and indicate  $k_{H_2}^a$  and  $k_{Ar}^a$  vary as  $T^{-1}$  or  $T^{-2}$ . Sutton (1962) found  $k_{\rm H}^{a}$  was rising slowly (within the scatter of his data) for 2800–3100°K and decreased by about  $T^{-3/2}$  for 3100–3400°K and  $T^{-4}$  for 3400–4500°K. Hurle, Mackey & Rosenfeld (1969) found that  $k_{\rm H}^a$  varied by roughly  $T^{-5}$  or  $T^{-6}$  for  $T \approx 3500^{\circ} {\rm K}$ with a gradual reduction in slope at lower T and indications of a maximum at about  $3000^{\circ}$ K. But the method used by Hurle and coworkers to measure T has been criticized by Shui (1973). Comparison of the values in Table 3 to the upper bound of Bennett & Blackmore (1968) would also indicate a maximum at some intermediate T. Breshears & Bird (1973) found that  $k_{\rm H}^a$  varied by roughly  $T^{-3/2}$  in the range 3500-7200°K. Their results do not show the steep falloff at high temperature. Since the atomic concentration changes rapidly during the experiments  $k_{\rm H}^a$ is most sensitive to the various assumptions made in analyzing the experiments and quantitative conclusions about it should still be drawn with caution.

One may assume that thermal measurements of the rate coefficient for the  $H + H_2$  exchange reaction refer to the equilibrium rate coefficient (see, e.g., Shizgal & K arplus 1970, Shizgal 1972, and references therein) and may be calculated from equations 3

Reference	$k_{\rm H}^a$ (cm <sup>6</sup> molec <sup>-2</sup> sec <sup>-1</sup> )	$\frac{k_{\rm H}^a}{k_{\rm H_2}^a}$	$\frac{k(3\mathrm{D}\rightarrow\mathrm{D_2}+\mathrm{D})}{k_\mathrm{H}^a}$
Gardiner & Kistiakowsky (1961)	$0.8 \times 10^{-32}$	23	
Rink (1962, 1962a)	$0.7 \times 10^{-32}$	3	0.7
Sutton (1962)	$1.8 \times 10^{-32}$	10	0.6
Patch (1962)	$3.4 \times 10^{-32}$	7	_
Jacobs, Giedt & Cohen (1967, 1968)	$1.4 \times 10^{-32}$	8	1.0
Hurle, Mackey & Rosenfeld (1969)	$1.0 \times 10^{-32}$	11	_
Breshears & Bird (1973)	$1.4 \times 10^{-32}$	7	—

Table 3 Recombination rate coefficients at 4000°K

and 4 below. However, this is not necessarily true for recombination-dissociation reactions (even in a steady state) because of below-equilibrium concentrations of high-energy states of the molecule. Although the effect of this internal disequilibrium on  $k_{\rm H}^a$  has been studied (McElwain & Pritchard 1970, Kiefer 1972, Shui 1973, Kung & Anderson 1974), it is not well understood. Kiefer (1972) used model rate coefficients for energy transfer processes in H<sub>2</sub> in the presence of varying amounts of H<sub>2</sub>, Ar, and H and found the steady-state value of  $k_{\rm H}^a$  was decreased at high T as the atom concentration increased. But the experimental evidence indicates that the magnitude and temperature dependence of the rate is not a composition effect (Jones & Rosenfeld 1973, Breshears & Bird 1973).

# THERMAL RATE COEFFICIENTS: THEORY

### Exchange Reactions

The thermal rate coefficient k(T) for the H + H<sub>2</sub> exchange reaction is most sensitive to the potential energy surface near the saddle point, as was realized very early (see, e.g., Eyring & Polanyi 1931, Pelzer & Wigner 1932, Wigner 1932). Thus the most widely used method for calculating k(T) is transition-state theory (Eyring 1935, 1935a, 1938, Evans & Polanyi 1935, Wigner 1938, Glasstone, Laidler & Eyring 1941, Johnston 1966, Laidler 1969), sometimes called activated-complex theory or the theory of absolute reaction rates, but here called TST. TST assumes quasiequilibrium of reactants with activated complexes moving from reactants toward products. One generally separates out a cartesian reaction coordinate s and computes a partition function for the activated complex minus this degree of freedom. One may incorporate some quantum effects by making these partition functions quantum mechanical but quantum corrections for motion along s are harder to include. Thus one generally treats this motion classically and multiplies the result by a transmission coefficient  $\kappa(T)$ , which should account for both quantum effects on the motion along s and deviations from the quasi-equilibrium assumption. The latter are generally neglected so  $\kappa(T)$  is sometimes called the tunneling correction; however, many different definitions of tunneling are useful in different contexts (see, e.g., Hirschfelder & Wigner 1939, Karplus 1968c, Laidler 1968, Westenberg & deHaas 1967, George & Miller 1972, 1972a, Doll, George & Miller 1973, Truhlar & Kuppermann 1972, Kuppermann, Adams & Truhlar 1973, 1976).

The first collision-theory justification of TST was the "vibrational adiabatic" (VA) model in which all motions (vibrational and rotational as well as electronic) except that along *s* are adiabatic between the reactant region and the transition state region (Hirschfelder & Wigner 1939, Eyring, Walter & Kimball 1944, Eliason & Hirschfelder 1959, Noyes 1962, Hofacker 1963, Fischer, Hofacker & Seiler 1969, Marcus 1964, 1965, 1966a, 1966b, 1967, 1968, 1968a, 1968d, 1968e, 1968g, Child 1968, 1968a, Karplus 1968b, Morokuma & Karplus 1971, Wyatt 1969, Walker & Wyatt 1972a, Harms & Wyatt 1975, 1975a, Lin, Lau & Eyring 1971, Christov 1972). In this model motion along *s* for initial state  $\alpha$  is governed by a VA potential  $W_a(s)$  equal to  $V_{rp}(s) + E_a(s)$  where  $V_{rp}(s)$  is the classical potential energy along the reaction path and  $E_a(s)$  is the locally adiabatic internal rotational-vibrational energy. To the extent that

curvature may be neglected and the maximum value of  $W_{r}(s)$  occurs at the classical saddle point, the barrier height is the VAZC barrier  $E_{\alpha}^{VAZC}$  and is given by equation 1 for the ground state. If the maximum value of  $W_{\alpha}(s)$  occurs at s = 0 for all  $\alpha$ , then an equilibrium distribution of reactants plus the VA assumption generates an equilibrium distribution of activated complexes moving forward at s = 0. Otherwise it does not (Truhlar 1970), and it is necessary for such reactions, including  $H + H_2$ , to define generalized activated complexes corresponding to  $s \neq 0$  (Eliason & Hirschfelder 1959, Marcus 1964b, 1966, Truhlar 1970, Tweedale & Laidler 1970. Wong & Marcus 1971). It is difficult or impossible to formulate the equilibrium assumption for generalized activated complexes since that involves defining a freeenergy surface defined for all s, not just  $s = -\infty, 0$ , and  $+\infty$  (Szwarc 1962, Eyring 1962, Laidler & Polanyi 1965, Tweedale & Laidler 1970). Using the VA assumption, Marcus (1966c, 1967) wrote the TST rate coefficient as a product of a TST rate coefficient, for which the motion along s is classical, and an average  $\kappa(T)$ , obtained by thermally averaging the state-dependent transmission coefficient  $\kappa_{\alpha}(T)$  given by the standard expression (see, e.g., Weston 1959, 1968, Shavitt 1959, 1959a, Marcus 1968f, Truhlar & Kuppermann 1971, and references therein)

$$\kappa_{\alpha}(T) = \frac{\int_{0}^{\infty} T^{\mathrm{qu}}(E_{\mathrm{rel}}) e^{-E_{\mathrm{rel}}/kT} \mathrm{d}E_{\mathrm{rel}}}{\int_{0}^{\infty} T^{\mathrm{cl}}(E_{\mathrm{rel}}) e^{-E_{\mathrm{rel}}/kT} \mathrm{d}E_{\mathrm{rel}}}$$
2.

but where  $T_x^{qu}(E_{rel})$  and  $T_x^{cl}(E_{rel})$  are, respectively, the quantum and classical transmission probabilities at relative translational energy  $E_{rel}$  for the barrier  $W_\alpha(s)$ ; thus if we neglect reaction path curvature,  $T_\alpha^{cl}$  is unity if  $E_{rel} > E_\alpha^{VAZC}$  and zero otherwise. Several direct tests (examination of trajectories or wave functions at s = 0) of vibrational adiabaticity have been made (Karplus 1968a, 1970, Morokuma & Karplus 1971, McCullough & Wyatt 1971a, Bowman, Kuppermann, Adams & Truhlar 1973). It seems to be a good assumption in the threshold energy region for both classical and quantum mechanics but in the quantum case it fails at very low energy due to extensive shift of flux toward the concave side of the minimum-energy path and at high energies due to the opening of new vibrational channels.

Wigner (1932) approximated  $\kappa(T)$  by expressing it as a sum of coefficients times powers of  $\hbar$  and retaining only the lowest order terms. His result is valid to the extent that  $\kappa$  is close to unity and the de Broglie wavelength is small compared to the quadratic-separable region at the saddle point. Neither of these conditions is true for  $H + H_2$  at the temperatures of interest. We may estimate the size of the separable region around the saddle point using Liu's (1973) minimum-energy path and using normal coordinates  $x_1$  for the asymmetric stretch and  $x_2$  for the symmetric stretch with both coordinates scaled for a reduced mass  $\frac{2}{3}$  the mass of H. Then, on the minimum-energy path at  $x_1$  equal to 0.27 and 0.45  $a_0$ , the quadratic approximation to the energy has decreased respectively 14 and 21% too much and the symmetric stretch coordinate is respectively 0.10 and 0.29  $a_0$ . Thus these points are already out of the quadratic and separable regions. But for the same reduced mass the de Broglie wavelength at energy kT is 5.0  $a_0$  at 200°K and 2.0  $a_0$  at 1250°K so it is much greater than the distance over which the reaction coordinate is separable. But most attempts to improve on Wigner's (1932) expression involve consideration of a one-mathematical-dimensional (1-MD) barrier and assume separability of a reaction coordinate. Truhlar & Kuppermann (1971a, 1972) compared collinear TST rate coefficients  $k^{TST}(T)$  obtained using different 1-MD models of  $\kappa(T)$  to exact collinear ones  $k^{R}(T)$  for the TK surface. With  $\kappa = 1$ ,  $k^{TST}/k^{R}$  is 0.03, 0.30, and 0.70 at 200, 300, and 600°K, respectively. When  $\kappa(T)$  is computed using equation 2 with an exact calculation of  $T_{,qu}$  for the VAZC barrier,  $k^{TST}/k^{R}$  becomes 0.06, 0.29, and 0.64 at these three T. They also tested another model, not so well justified theoretically (for another opinion see Johnston 1966), in which the change in adiabatic vibration energy is neglected, i.e., the barrier  $V^{CVEZC}(s)$  is  $V_{rp}(s)$  with rp in this approximation chosen as the minimum-energy path. The ground-state VAZC barrier is broader and flatter than  $V^{\text{CVEZC}}(s)$ , so higher  $\kappa(T)$  are predicted for the latter:  $k^{\text{TST}}/k^{\text{R}}$  is 10.4, 2.4, and 1.2 at the same three T. In the only test of TST against 3-PD rate coefficients that are exact for a given surface, Schatz & Kuppermann (1976b) found that  $k^{\text{TST}}(\kappa = 1)/k^{\text{R}} = 0.04$ , 0.17, and 0.54 for the PK2 surface at the same three temperatures. Hulburt & Hirschfelder (1943) and Jepsen & Hirschfelder (1959) developed early 2-MD models for  $\kappa(T)$ ; Truhlar & Kuppermann (1971a, 1972, 1976) obtained collinear  $k^{\text{TST}}/k^{\text{R}} \cong 1$  using 2-MD calculations of  $\kappa(T)$ .

All attempts to compare TST to experiment have used the CVEZC model or approximations to it [e.g., replacing  $V^{CVEZC}$  by an Eckart barrier, but this can lead to considerable error (LeRoy, Quickert & LeRoy 1970, Truhlar & Kuppermann 1971)] and most used inaccurate saddle point properties. Not much can be learned by comparing these calculations to experiment (for examples of such calculations see Farkas & Farkas 1935, Farkas & Wigner 1936, Hirschfelder, Eyring & Topley 1936, Glasstone, Laidler & Eyring 1941, van Meersche 1951, Boato et al 1956, Yasumori 1959, Weston 1959, 1967, Shavitt 1959, Johnston 1960, 1966, Schulz & LeRoy 1965, Ridley, Schulz & LeRoy 1966, LeRoy, Ridley & Quickert 1968, Laidler 1968, 1969, LeRoy 1968, Westenberg & deHaas 1967, Salomon 1969, Stern & Weston 1974, Malcome-Lawes 1975). Many of the early calculations employed the wrong symmetry number for the activated complex; the correct symmetry numbers have been discussed by Rapp & Weston (1962), Schlag (1963), Laidler & Polanyi (1965), Schlag & Haller (1965), and Bishop & Laidler (1965). In making comparison to experiment note that TST calculates the distinguishable-atom rate coefficient  $k^{R}$ which, in the classical limit, equals  $\frac{4}{5}k_1$  or  $\frac{3}{2}k_2$  (Truhlar 1976; for an alternative opinion see Britton & Hugus 1960). For  $T \approx 400^{\circ}$ K, TST calculations using  $\kappa = 1$  and reasonably accurate surfaces (Shavitt 1968, Quickert & LeRoy 1970a, Koeppl 1973, Mitchell 1973) apparently yield the correct T dependence and isotope effects but at lower T where tunneling corrections are important [but the 1-MD models which have been used for  $\kappa(T)$  are unreliable] such calculations give neither rate coefficients nor isotope effects accurately. A few investigations have attempted to improve on the CVEZC models or to test models for  $\kappa(T)$  against exact quantum collinear rate coefficients for given surfaces (Mortensen 1968, Russell & Light 1971, Truhlar & Kuppermann 1971a, 1972, Truhlar, Kuppermann & Adams 1973, Wu, Johnson &

Levine 1973; and work discussed in later paragraphs). Such comparisons indicate that the exact  $\kappa(T)$  must be greater than unity. Using  $\kappa(T) = 1$  or calculating it by the CVEZC models leads to large errors in TST that increase in the order  $H+D_2 \cong D+D_2 \ll D+H_2 < H+H_2$ .

The high T limit of TST for intramolecular isotope effects is independent of potential surface; for HT/DT in T+HD it is 1.25 and disagrees with the isotope effect for hot atom reactions discussed below (Chou & Rowland 1967).

Marcus (1966, 1966a) and Morokuma, Eu & Karplus (1969) inverted the TST expression for k(T) with  $\kappa(T) = 1$  to find an approximation for the average reaction cross section  $\bar{\sigma}(E)$  [or for collinear collisions the average reaction probability  $\bar{P}(E)$ ] for a microcanonical distribution of initial states at total energy E. These TST  $\bar{\sigma}$  and  $\bar{P}$  diverge as  $E \to \infty$ . The source of the divergence and its cure may be understood by considering maxima in  $W_{\alpha}(s)$  that do not occur at s = 0 (Truhlar 1970); it is due to activated complexes that are bound in the VA approximation. For H + H<sub>2</sub> at low E the TST  $\bar{P}(E)$  is a step function at the VA threshold. Lin & Eyring (1971), Lin, Lau & Eyring (1971), and Lau, Lin & Eyring (1973) have also obtained  $\bar{\sigma}$  from TST. Marcus (1965, 1966, 1967), Mortensen (1968), Morokuma & Karplus (1971), Diestler & Karplus (1971), Truhlar & Kuppermann (1972), Truhlar, Kuppermann & Adams (1973), Wu, Johnson & Levine (1973), and Duff & Truhlar (1974) have compared TST  $\bar{P}(E)$  curves or thresholds to collision theory results as discussed below.

Near the saddle point the reaction coordinate is curved in normal-mode coordinate space. Marcus (1964, 1964a, 1964b, 1965, 1968i; see also Hofacker 1963) avoided the assumption of a cartesian reaction coordinate by deriving TST with curvilinear coordinates that make the separability approximation more valid. Reaction path curvature leads to "centrifugal" effects that may displace the local center of vibrational motion to either side of the minimum-energy path (Marcus 1966b, 1966c), suggesting more accurate VA barriers (without the zero-curvature approximation). Marcus (1965) interpreted the error in an approximate VAZC calculation (Marcus 1964) as being due to neglect of curvature effects.

Johnston & Rapp (1961) attempted to treat tunneling in the nonseparable case by calculating the transmission through a series of barriers corresponding to  $-45^{\circ}$ sections through the potential surface in the  $(R_1, R_2)$  coordinate system  $(R_1 \text{ and } R_2$ are the two nearest-neighbor distances in H<sub>3</sub>) and averaging these thermally. This calculation ignores the motion along  $x_2$  and its associated energy requirements. Christov & Georgiev (1971) criticized the assumption that tunneling occurs only along the  $-45^{\circ}$  direction.

Pechukas & McLafferty (1973) pointed out that on many surfaces, including PK2, purely classical TST with no separation of variables yields the exact classical result for the collinear probability of reaction up to some energy cutoff  $E_{cut}$  that depends on the surface. Chapman, Hornstein & Miller (1975) determined that, for essentially exact classical results on the PK2 surface,  $E_{cut} > 0.2 \text{ eV}$ . They showed that  $E_{cut}$  is about the same for the 3-PD cross section and that classical TST yields a cross section only 10% larger than exact classical mechanics even 1 eV above threshold. These calculations demonstrate the usefulness of formulating classical

TST as exact classical mechanics plus one fundamental assumption, i.e., that all flux through a particular surface in coordinate space can be identified as reactive flux (see also Wigner 1938, Keck 1967, Miller 1974). This way of formulating TST shows that the breakdown of the equilibrium assumption and the unit  $\kappa(T)$  assumption as studied by Morokuma & Karplus (1971) are just two aspects of the same thing. But there is no unique way to formulate this assumption quantum mechanically since the projection operator corresponding to this assumption does not commute with the flux operator; thus different orderings of the operators lead to different theories (Miller 1974; McLafferty & Pechukas 1974; Y. B. Band, private communication). Miller (1974, 1975, 1975a) ordered the operators by the Weyl correspondence rule and obtained a semiclassical approximation by approximating the quantum Boltzmann operator. His theory involves a trajectory on the upside-down potential surface (compare Quickert & LeRoy 1970, Bomberger & Kostin 1973). Chapman, Garrett & Miller (1975) applied this theory to calculate reaction probabilities for collinear  $H + H_2$  on two potential surfaces and found the results were lower than but within about a factor of 2 of exact quantum results discussed below for  $E_{\rm rel} \ge 0.12 \, {\rm eV}$ . At lower energies the error was larger. They also developed another semiclassical approximation to nonseparable quantum TST, this one based on a semiclassical phase space distribution, and used it to calculate collinear rate coefficients for two surfaces. They found much better agreement with the exact quantum quantities than is obtained from separable TST.

## Association

The first reasonably accurate calculation of the recombination rate coefficient  $k_{\rm H}^a$ was made by Eyring, Gershinowitz & Sun (1935). They made TST calculations in which two degrees of freedom (rather than the usual one) were treated dynamically and estimated that the new kind of transmission coefficient ( $\theta$ ) is about 0.12. This led to  $k_{11}^a = 8.5 \times 10^{-33} \text{ cm}^6 \text{ molec}^{-2} \text{ sec}^{-1}$  at 300°K. This theory predicts that teratomic D recombination will be slower by a factor of 0.7 (Glasstone, Laidler & Eyring 1941). If  $\theta$  is temperature-independent then this theory predicts  $k_{\rm H}^a$  is an increasing function of temperature (Clarke & McChesney 1964). Jepsen & Hirschfelder (1959) calculated  $\theta$  from trajectories on idealized piecewise constant potential surfaces. They also obtained 0.12. Keck (1962, 1967), following Wigner (1937), proposed a combined-phase-space-trajectory (CPST) method for improving on the assumptions of TST, and it was applied to calculate  $k_{\rm H}^a$  by Shui (1973) and Kung & Anderson (1974). Shui used the PK2 surface and Kung & Anderson used a modified version of it. Shui's equilibrium  $k_{\rm H}^a$  include a correction of up to 22% for quantal barrier penetration effects and are  $2.3 \times 10^{-32}$  and  $1.8 \times 10^{-32}$  cm<sup>6</sup> molec<sup>-2</sup> sec<sup>-1</sup> at 300 and 4000°K, respectively, and vary as  $T^{-0.1}$  at 300–1000°K and  $T^{-0.8}$  at 5000-10,000°K. He did not obtain a maximum, and he did not obtain the controversial steep temperature dependence except for  $T > 5000^{\circ}$ K when a nonequilibrium correction is included. Comparison to the CPST calculations of Shui & Appleton (1971) yields  $k_{\rm H}^a/k_{\rm H_2}^a = 17$  at equilibrium at 4000°K. The isotope effect on  $k_{\rm H}^a$  is the same as in TST. Kung & Anderson calculated  $k_{\rm H}^a = 1.5 \times 10^{-32} \,{\rm cm}^6$ molec<sup>-2</sup> sec<sup>-1</sup> at equilibrium at 4000°K. CPST includes recombination not only

due to  $H_2(quasibound) + H$  but also due to collisions of three free atoms. Kung & Anderson found the latter contributed 31% of the equilibrium  $k_{\rm H}^a$ . They argued that the quasiclassical production rate of quasibound  $H_2$  is too small to justify the assumption that quasibound states are maintained in equilibrium so that the three-atom mechanism might even dominate the quasibound one.

# Rate Coefficients from Collision Theory Cross Sections

Later in this chapter we discuss more detailed experiments and theories that measure or predict average reaction cross sections  $\langle \sigma(E_{rel}) \rangle$  rather than the (thermal) rate coefficients k(T). For an equilibrium reacting mixture these quantities are related by (Eliason & Hirschfelder 1959, Greene & Kuppermann 1968):

$$k(T) = \int_0^\infty (2E_{\rm rel}/\mu)^{1/2} \langle \sigma(E_{\rm rel}) \rangle f(E_{\rm rel}) dE_{\rm rel}, \qquad 3.$$

where  $\mu$  is the reduced mass for relative motion of reactants,  $f(E_{rel})$  is the Maxwell-Boltzmann distribution, and the cross section averaged over internal states is

$$\langle \sigma(E_{\rm rel}) \rangle = \sum_{i} P_i^{\rm BC} \sigma_i(E_{\rm rel})$$
 4.

where  $P_i^{BC}$  is the thermal probability of finding state *i* of BC and  $\sigma_i(E_{rel})$  is the cross section for reaction of ground-state A with BC in state *i*. The temperature dependence of  $P_i^{BC}$  and  $\langle \sigma(E_{rel}) \rangle$  has been suppressed in the notation. For the H + H<sub>2</sub> exchange reactions the excited electronic and vibrational states make a negligible contribution (less than about 0.5% even at 1000°K; see Karplus, Porter & Sharma 1965) to the average in equation 4 in most experiments, so  $\langle \sigma(E_{rel}) \rangle$  becomes just the rotationally averaged cross section. While some calculations of k(T) from collision theoretical  $\langle \sigma(E_{rel}) \rangle$  have been carried out (Karplus, Porter & Sharma 1965, Lin & Light 1966, Schatz & Kuppermann 1976b), they should not be compared to experimental k(T) because they assumed inaccurate values of  $E_b$  and other surface parameters.

Menzinger & Wolfgang (1969) and LeRoy (1969) made general studies of the *T* dependence of rate coefficients and their relation to assumed analytic forms for  $\langle \sigma(E_{\rm rel}) \rangle$ . LeRoy (1969) and Malerich & Davis (1971) pointed out that the experimental results of Westenberg & deHaas (1967) at low temperature cannot be reproduced by assuming that  $\langle \sigma(E_{\rm rel}) \rangle$  is proportional to  $(E_{\rm rel})^n$  or  $(E_{\rm rel} - E_{\rm thr})^m$ , m = 1, 2, at low energy, but that an exponentially increasing function could reproduce the rate data. Lin & Eyring (1971) derived an expression for  $\langle \sigma(E_{\rm rel}) \rangle$  in terms of k(T). The resulting expression, however, need not be accurate since k(T) may be insensitive to the details of  $\langle \sigma(E_{\rm rel}) \rangle$ , even in the threshold region (Melton & Gordon 1969, LeRoy 1969). Nevertheless, Malerich & Davis applied the method of Lin & Eyring to the data of Westenberg & deHaas for  $k_3$  and  $k_4$  to obtain excitation functions that increase exponentially with an exponential parameter of about 0.025 eV in the region where  $\langle \sigma(E_{\rm rel}) \rangle$  is about 0.007–0.5  $a_0^2$ . Thermal rate coefficients are even less sensitive to  $\langle \sigma(E_{\rm rel}) \rangle$  at higher  $E_{\rm rel}$ ; thus, e.g., L. A. Melton and A. Kuppermann (unpublished, see Kuppermann 1967) concluded that if  $\langle \sigma(E_{\rm rel}) \rangle =$   $(0.3 a_0^2)[1-(0.3 \text{ eV})/E_{rel}]$ , then one must know k(T) and T to about seven significant digits each to determine the excitation function at 0.6 eV to within 10%. Hochstim & Shuler (1967) have shown that to obtain k(T) within 10% it is only necessary to have information about  $\langle \sigma(E_{rel}) \rangle$  up to an energy no more than about 10 kT above threshold. Conversely measurements of k(T) do not provide any information about high-energy processes. Next we shall consider experiments that are sensitive to reactions of high-energy reagents.

# HOT ATOM REACTIONS: EXPERIMENT

### Photosensitization

Some early experiments that were potentially sensitive to reactions of atoms with high translational energies (i.e. epithermal atoms or hot atoms) were the mercury and rare gas photosensitization experiments (Bonhoeffer & Harteck 1929, Calvert 1932, Farkas & Sachsse 1934, von Bünau & Schindler 1968, Harteck 1968, Niki, Rousseau & Mains 1965). But nothing was learned about hot atom reactions.

### Photodissociation

Another source of hot hydrogen atoms is photodissociation of hydrides. The steadystate distribution of atomic velocities in a hot atom system satisfies the Boltzmann integral equation, whose kernel depends on the cross sections for reactive and nonreactive processes. Solution of this equation for representative cases using an approximate form of the kernel shows that the steady-state relative velocity distribution of hot atoms in photolytic systems should show a peak at the nascent energy (Kuppermann 1967, Kuppermann, Stevenson & O'Keefe 1968), although there is likely to be a larger thermal peak. The velocity distributions for H atoms introduced into mixtures of  $D_2$ , Ar, and  $I_2$  have also been obtained using other models (Chapin & Kostin 1968, Keizer 1973), but all the treatments assume that inelastic collisions may be neglected in the slowing down of hot D by  $H_2$ .

Carter, Hamill & Williams (1955) photolyzed DI in the presence of  $H_2$  using 2537 Å radiation. Because of the large mass ratio of I to D, most of the photon energy in excess of the bond energy and of any electronic excitation of I appears as translational energy of D. In this case about 90% of the I atoms are produced in the ground state yielding 1.8 eV D atoms and 10% are produced in the first excited state yielding 0.9 eV D atoms (Vermeil 1970). Carter et al measured the product ratio D<sub>2</sub>/HD using a mass spectrometer and found it was a linear function of the reactant ratio DI/H<sub>2</sub> independent of T in the range 298–373°K and with a positive intercept of 1.40. Adding He (with the He:H<sub>2</sub>:DI ratio of 1.7:1.0:1.0) increased D<sub>2</sub>/HD by about 45%. The D atoms reacted much more readily with H<sub>2</sub> than do thermal D atoms. Although the D atoms were produced hot they may be thermalized by only a few collisions and the thermal atoms react much more rapidly with a hydrogen halide than with a hydrogen molecule. Thus the thermal atoms were essentially all converted to D<sub>2</sub> and the increase of D<sub>2</sub> with addition of He substantiates the interpretation that hot reactions were occurring.

t

Martin & Willard (1964) photolyzed HBr:  $D_2$  and DBr:  $H_2$  mixtures using 1849 Å radiation. Interpretation of the spectra of HBr indicates that at least 98% of the photodissociation events produce ground state Br (Mulliken 1940) yielding H atoms with initial laboratory energies  $E_{lab} = 2.9 \text{ eV}$ . If this interpretation is correct, up to 2% of the H atoms are produced with only 2.4 eV. Again the atoms will react hot or be thermalized. Thermal D (or H) atoms will react essentially entirely with DBr to form  $D_2$  (or HBr to form  $H_2$ ), since those reactions have much lower energies of activation than reaction with hydrogen molecules. H<sub>2</sub>/HD (and D<sub>2</sub>/HD) ratios were determined by mass spectrometry. Martin & Willard found these ratios were linear functions of  $HBr/D_2$  (and  $DBr/H_2$ ) in the two mixtures. The intercepts were again positive and were interpreted as the ratios of the fraction of H (or D) atoms that are moderated to thermal energies to the fraction that reacts hot in pure  $D_2$  (or  $H_2$ ). By using this interpretation and comparing their results to those of Carter et al it is possible to get some idea of the energy dependence of the reaction  $D+H_2$ . Carter et al found that 42% of the D atoms produced at 0.9-1.8 eV react hot with H<sub>2</sub> while Martin & Willard (1964) found 62% of the D atoms produced at 2.9 eV react hot. By treating the moderating collisions as hard-sphere collisions Martin & Willard estimated that  $5.1 \text{ H} + D_2$  collisions or  $2.2 \text{ D} + H_2$  collisions were needed to reduce the hot atoms to the point where the center-of-mass translational energy for the next collision was 0.325 eV. Combining this estimate with the fraction of atoms reacting hot (i.e. the integral reaction probability IRP) in unmoderated systems yields an average probability of reaction per hot collision of 0.17 for  $H + D_2$  and 0.35 for  $D + H_2$ . They noted that the ratio of these numbers is within 21% of the ratio of experimental high-temperature rate coefficients. A similar treatment of the cooler D atoms in the experiments of Carter et al yields a probability of reaction per hot collision of about 0.32 for  $D+H_2$ . There are experimental indications that moderation of D by H<sub>2</sub> proceeds by soft elastic collisions (Gann & Dubrin 1972, Fass & Wong 1973) so this treatment overestimates the reaction probabilities.

Kuppermann & White (1966) photolyzed mixtures of DI and H<sub>2</sub> with monochromatic radiation of various wavelengths in the range 3660-3030 Å. At these wavelengths only ground state I is produced and the D atoms initially have  $E_{lab} = 0.28-0.96 \text{ eV}$ . Plots of  $D_2/HD$  vs  $DI/H_2$  were again linear with positive intercept and were independent of temperature in the range 196-298°K. By plotting  $HD/D_2$  (corrected for HD formed from reaction of D with HI impurities) vs nascent D atom energy they obtained a threshold of  $E_{lab} = 0.66 \,\text{eV}$  that corresponds to  $E_{\rm rel} = 0.33 \, {\rm eV}$ . This threshold energy is a phenomenological quantity that does not have a precise meaning since the real  $\langle \sigma(E_{rel}) \rangle$  probably does not show a welldefined threshold but decreases roughly exponentially as  $E_{rel}$  decreases (see, e.g., Lin & Eyring 1971, Malerich & Davis 1971, Truhlar & Kuppermann 1972, Schatz & Kuppermann 1976b). Further photolysis experiments (Kuppermann 1967; J. M. White, D. R. Davis, J. A. Betts, A. Kuppermann, unpublished; see Kuppermann 1969) led to a phenomenological threshold of  $E_{lab} = 0.50 \text{ eV}$ . Due to the large spread in  $E_{rel}$  caused by thermal motion of  $H_2$ , the actual phenomenological threshold for  $\langle \sigma(E_{rel}) \rangle$  must be somewhat larger than  $E_{rel} = 0.25 \,\text{eV}$  (Kuppermann 1967). Using

the elastic scattering calculations of Tang & Karplus (1968) and numerically solving the steady-state Boltzmann equation the results were inverted to obtain  $\langle \sigma(E_{rel}) \rangle$ in the range 0.35–1.1 eV (Kuppermann 1969). The cross section obtained at  $E_{rel} = 0.7 \text{ eV}$  is 4.6  $a_0^2$  and at 1.1 eV it is 8.0  $a_0^2$ . Melton & Gordon (1969), neglecting the difference between the steady-state and nascent relative velocity distributions, showed that these experiments can be used to place upper and lower bounds on the cumulative integral of  $\langle \sigma(E_{rel}) \rangle$  for D + H<sub>2</sub> that differ by about a factor of 3 at a relative collision energy of 0.5 eV and a factor of 2 at 1.0 eV. Since the quantum calculations discussed below show  $\langle \sigma(E_{rel}) \rangle$  is monotonically increasing up to 0.6 eV, the uncertainty at this energy and lower can probably by made smaller.

Chou & Rowland (1967) used 1849 Å radiation to photolyze TBr in the presence of  $H_2: D_2: Br_2$  and  $HD: Br_2$ , to which they also added  $O_2$ . The HT/DT ratios were measured by radio GC. They found  $(HT/H_2)/(DT/D_2) \cong 0.97$  in the first mixtures and HT/DT  $\cong 0.71$  in the second ones.

White (1969) photolyzed HBr:HD and HBr:HD:Ne mixtures with 1849 Å radiation. He found  $D_2/HD$  ratios as large as  $2.7 \times 10^{-2}$ , which could only be explained if the products of  $H(hot) + HD \rightarrow H_2 + D$  are themselves at least sometimes hot. By modeling the reaction system he estimated that the D atom was produced with  $E_{lab} \cong 1 \text{ eV}$ . Since previous work did not take this effect into account, some of it, especially at high  $E_{lab}$ , should be re-interpreted.

Additional photolysis experiments have been performed on  $HCl:D_2$ ,  $HBr:D_2$ ,  $H_2S:D_2$ ,  $DCl:H_2$ , and  $DBr:H_2$  (deVries & Klein 1964);  $H_2S:D_2$ ,  $CH_3SH:D_2$ , and  $HBr:D_2$  (Sturm & White 1969);  $H_2O:D_2$  and  $D_2O:H_2$  (Masenet & Vermeil 1969);  $CH_4:D_2$  and  $CD_4:H_2$  (Hellner, see Vermeil 1970); and  $HBr:D_2$  and  $HI:D_2$  (A. Persky and A. Kuppermann, unpublished).

## Nuclear Recoil

Another (quite different) source of hot H atoms is recoil from nuclear reactions. Thus one may cause the nuclear reaction  ${}^{3}\text{He}(n, p){}^{3}\text{H}$  by bombarding a vessel containing a small amount of  ${}^{3}\text{He}$  (and for the present purposes also some molecular H<sub>2</sub>, a scavenger, and possibly an inert moderator) with slow neutrons. This creates T ions with energy 192 keV. These ions are slowed down and neutralized and eventually enter the chemical energy range (below about  $10^{2} \text{ eV}$ ), where stable product formation is possible almost entirely as neutral T atoms (Wolfgang 1965). Upon subsequent collisions, these hot T atoms can then react or be further slowed down. Those that are slowed down below the effective threshold for reaction with hydrogen react with the scavenger (thus the scavenger should have a low activation energy for reaction with T). The tritiated products are then separated and measured by radio GC.

Lee, Musgrave & Rowland (1960) performed nuclear recoil T experiments in  $H_2:D_2$  mixtures with no inert moderator and found a preference for reaction with  $H_2$  by a factor of 1.55. If NO or  $O_2$  was added as scavenger, this ratio was increased to 2.6 or 2.8. Root & Rowland (1963, 1967) produced nuclear recoil T atoms in  $D_2:CH_4$  mixtures containing a 3%  $O_2$  scavenger and measured the absolute yields of DT. Extrapolating their results to 97%  $D_2$  and 3%  $O_2$  shows the

IRP is about 88%. This is higher than photochemical IRP because the T atoms enter the chemical energy region at higher energies and therefore suffer more collisions to become thermalized. This study was later extended to  $H_2$ : CD<sub>4</sub> mixtures (Root & Rowland 1970, Wolfgang 1970, Rowland 1970a).

Seewald, Gersh & Wolfgang (1966) produced recoil T atoms in H<sub>2</sub> and D<sub>2</sub> and in H<sub>2</sub>: D<sub>2</sub> mixtures, in each case in a 3-to-15-fold excess of Ar as inert moderator with 1.5% I<sub>2</sub> present as scavenger. They obtained IRP = 0.92 for D<sub>2</sub>. They noted that they were unable to reproduce the results of the scavenged runs of Lee et al although they did not attempt to reproduce them under the original conditions. They also concluded that O<sub>2</sub> is an unacceptable scavenger. Hawke & Wolfgang (1970) repeated these measurements using ICl and IBr as scavengers and obtained results in agreement with the I<sub>2</sub>-scavenged runs. Seewald et al interpreted their results on H<sub>2</sub> and D<sub>2</sub> samples using the kinetic theory of hot atom reactions developed earlier by Wolfgang (1963). If the hot T atoms are slowed down by classical hard-sphere scattering in a target medium at rest then the average logarithmic energy loss per collision  $\langle \alpha \rangle$  is independent of energy and the probability of a collision at laboratory energy  $E_{\rm lab}$  is proportional to  $1/E_{\rm lab}$  multiplied by the probability that the atom has escaped combination in cascading through the energy range down to  $E_{\rm lab}$ . If we define the reactivity and reaction integrals, respectively, as

$$I = \int_{E_1}^{E_2} (1/E_{lab}) p(E_{lab}) dE_{lab} \text{ and } R = \int_{E_1}^{E_2} \langle \sigma(E_{lab}) \rangle (1/E_{lab}) dE_{lab},$$

where  $E_1$  and  $E_2$  are the lower and upper laboratory energies where hot-atom reaction can occur and  $p(E_{lab})$  is the probability of reaction, then their kinetic theory treatment yields IRP =  $1 - \exp[-I/\langle \alpha \rangle]$  in a system containing only T atoms in pure reactive substrate. But the kinetic theory treatment is expected to be most applicable for systems moderated by a large excess of rare gas both because the assumption of an energy-independent average logarithmic energy loss should be better and also because the theory assumes that the reaction probability is small (see, e.g., Wolfgang 1963, Estrup 1964, Rowland & Coulter 1964, Felder & Kostin 1965, and Porter & Kunt 1970). Thus Seewald et al extrapolated their hot yields to infinite fraction of Ar moderator. The kinetic theory treatment of the  $H_2$  and  $D_2$ runs then yielded  $I_{\text{H}_2} = 6.0 \langle \alpha \rangle_{\text{Ar}} S_{\text{T}-\text{Ar}} / S_{\text{T}-\text{H}_2}, I_{\text{D}_2} = 5.9 \langle \alpha \rangle_{\text{Ar}} S_{\text{T}-\text{Ar}} / S_{\text{T}-\text{D}_2}$  where the subscript on  $\langle \alpha \rangle$  reminds us that it is the average logarithmic energy loss in collisions of hot T with Ar and  $S_{T-X}$  is a total collision cross section. The isotope effect was obtained with greater precision from  $H_2: D_2$  mixtures, for which HT/DT approaches  $I_{\rm H_2}/I_{\rm D_2}$  as the fraction of Ar becomes unity. This yielded  $I_{\rm H_2}/I_{\rm D_2} = 1.15$ . This is lower than the value (1.55) of Lee et al for unmoderated mixtures. Seewald et al also found that HT/DT was decreased by dilution of  $H_2$ :  $D_2$  mixtures by inert gas. This is an "energy shadowing effect" (Estrup & Wolfgang 1960, Wolfgang 1963) and indicates  $D_2$  reacts at a lower mean  $E_{lab}$  than  $H_2$ . This is reasonable since at a given  $E_{lab}$ ,  $E_{rel}$  is less for H<sub>2</sub> than for D<sub>2</sub>. Seewald et al assumed  $S_{\Gamma-H_2}$  is constant over the hot atom reaction range [and thus  $R_{H_2} = S_{\Gamma-H_2} I_{H_2}$ ] and used Estrup's (1964) theoretical estimate of  $S_{T-\Lambda_T} \langle \alpha \rangle_{\Lambda_T}$  to obtain  $R_{H_2} = 27 a_0^2$  and similarly  $R_{D_2} = 26 a_0^2$ . While better values are now available for hydrogen atom total collision

cross sections for scattering by Ar and  $H_2$ , it is probably best to compare theory and experiment for the measured IRP than for the derived I and R integrals (see, e.g., Porter & Kunt 1970, discussed below).

Seewald & Wolfgang (1967) performed similar experiments producing recoil T atoms in systems containing HD. The kinetic theory treatment yielded  $I_{\text{HD}}/I_{\text{DH}} \equiv I_{\text{T}+\text{HD}} \rightarrow \text{TH}+\text{D}/I_{\text{T}+\text{DH}} \rightarrow \text{TD}+\text{H}} = 0.62$ , which compares reasonably well with the isotope effect found at lower energy by Chou & Rowland (1967; see above). Seewald and Wolfgang also found  $I_{\text{T}+\text{HD}} \rightarrow \text{all products} = 6.6 \langle \alpha \rangle_{\text{Ar}} S_{\text{T}-\text{Ar}}/S_{\text{T}-\text{HD}}$ .

Malcome-Lawes (1975 and references therein) has pointed out that collisional dissociation of translationally excited products may significantly modify the interpretation of some of the nuclear recoil experiments.

# **REACTIONS IN CROSSED BEAMS: EXPERIMENT**

Crossed molecular beam experiments on the atomic exchange reactions yield rotationally averaged cross sections and product energies as well as differential cross sections (DCS) per steradian of scattering angle. In the first three applications to the present reactions a modulated atomic beam at high temperature (2800°K–3000°K) intersected a low-temperature (77°K–100°K) molecular beam at 90° and products, and sometimes reagents, were detected by an in-plane phasesensitive mass spectrometer. In two cases the time lag of product molecules behind an unscattered beam indicated the final laboratory velocities. Datz & Taylor (1963) studied the D + H<sub>2</sub> reaction using this method. They measured angular distributions for laboratory scattering angles of  $-20^{\circ}$  to  $-14^{\circ}$  and  $+13^{\circ}$  to  $+26^{\circ}$  (all scattering angles are measured with respect to the atomic reactant beam). Using the measured velocity distribution they interpreted their laboratory DCS as consistent with backscattering in the center-of-mass (com) system. This asymmetry implied a collision complex which is short-lived compared to a rotational period. They conjectured that the backwards scattering indicated collinear geometries at the onset of reaction.

Fite & Brackman (1964, 1965) measured the nonreactive DCS for  $H-D_2$  and normalized their results to Harrison's (1962)  $S_{H-H_2}$ . They also measured the ratio H/HD of scattered particles at selected laboratory angles corresponding to angles near backwards in the com system. For these angles they found a fairly constant reactive DCS which they interpreted as about  $0.8 a_0^2 \text{ sr}^{-1}$  into the backward-most steradian in the com system.

The third experiment employing mass spectrometric detection was a study of  $D+H_2$  by Geddes, Krause & Fite (1970, 1972). They used an improved mass spectrometric detector and more elaborate pumping to reduce interfering background at the detector. They detected product HD at laboratory angles  $-35^{\circ}$  to  $-15^{\circ}$  and  $+15^{\circ}$  to  $+48^{\circ}$  and found no significant signal for wider angles in either direction. They measured HD velocities which were consistent with an average translational exoergicity of zero. Assuming a threshold  $E_{thr}$  of 0.33 eV, a dependence of the DCS on energy proportional to  $[1 - (E_{thr}/E_{rel})]$ , and the separability of the distributions of velocity and scattering angle, Geddes et al found the best fit to their results was a com DCS for molecular product proportional to  $\cos^2[1.35(180^{\circ} - \theta)]$ 

for  $\theta > 113^{\circ}$  and zero otherwise. Their laboratory angular distributions disagreed considerably with those of Datz & Taylor (1963) and they and Datz (private communication mentioned in Geddes, Krause & Fite 1972) attributed this to improper detector collimation in the earlier experiment. To put their results on an absolute scale, Geddes et al also measured the angular distribution of nonreactively scattered D, normalized this to Harrison's  $S_{H-H_2}$  (196 $a_0^2$ ), measured the ratio HD/D of scattering particles, and thus put the HD scattering on an absolute basis. This yielded  $(d/d\Omega)\langle\sigma(E_{rel})\rangle = (3.2 a_0^2 \text{ sr}^{-1})(1 - E_{thr}/E_{rel}) \cos^2 [1.35(180^{\circ} - \theta)]$  for  $\theta > 113^{\circ}$  and  $E_{rel} > E_{thr}$  and zero otherwise.

Kwei, Lo & Entemann (1973) crossed a 2120°K H beam with a 300°K T<sub>2</sub> beam, collected the reactive product T atoms on MoO<sub>3</sub>-coated detector "buttons" in the beam plane at laboratory angles  $-170^{\circ}$  to  $+170^{\circ}$ , and measured the radioactivity of the coatings. In this system the transformation from laboratory to com scattering angles is single-valued and the laboratory angular distribution immediately implied that the HT product was backscattered in the com system. Making reasonable assumptions about the energy dependence of the cross sections and the product velocity distributions and also assuming separability of the velocity and angular distributions they obtained a com DCS that was backward peaked and had its half-height value at about 85° molecular scattering angle. Thus their distribution is considerably broader than that deduced by Geddes et al for D + H<sub>2</sub>. They attributed the differences to the separability assumptions they and Geddes et al used, to the difficulty of transforming from laboratory to com frames in the experiments of Geddes et al, or to real differences caused by the different averages over  $E_{rel}$  in the two experiments.

Gengenbach, Hahn & Toennies (1975) renormalized the experiment of Geddes, Krause & Fite (1972) using their new  $S_{H-H_2}$ . Their recalibration requires the previous results be multiplied by 0.73. In addition they showed their  $\langle \sigma(E_{rel}) \rangle$ for the average  $E_{rel}$  (0.48 eV) decreases by a factor of 2 if  $E_{thr}$  is decreased from 0.33 eV to 0.22 eV. They suggested using  $E_{thr}$  equal to 0.26 eV, which yields  $\langle \sigma(E_{rel}) \rangle = 1.25 a_{el}^{2} [1 - (0.26 eV)/E_{rel}].$ 

# **REACTION CROSS SECTIONS: THEORY**

### Exchange Reaction: Classical Mechanics

TRAJECTORIES Classical trajectory studies of reaction dynamics began with an unfinished trajectory calculated by Hirschfelder, Eyring & Topley (1936). This was the first attempt to use more than just the saddle-point region in a study of reactivity that was not based upon equilibrium statistical mechanics. Further use of the trajectory method (Porter 1974) had to wait until Wall, Hiller & Mazur (1958) applied computers to the problem. They numerically integrated Hamilton's equations of motion for collinear trajectories on a London-equation surface with a basin. They began trajectories with initial H<sub>2</sub> vibrational energy level) and found relative translational thresholds of 0.51, 0.46, and 0.38 eV. Thus only  $\frac{1}{6}$  of the initial vibrational energy was available for overcoming the barrier. They also found that the initial and final vibrational energies tended to be nearly the same. Marcus (1965) pointed

out that this result can be understood as a manifestation of vibrational adiabaticity. As a function of  $E_{rel}$ ,  $P_0^{R}$  (the probability of reaction of ground-state reactants) rose to  $\frac{1}{2}$  within 0.004 eV of threshold, then fell to about  $\frac{1}{4}$ . They observed that the amount of time trajectories spend in the "reaction shell" is a banded irregular function of total energy and initial vibrational phase (this was re-observed by Duff & Truhlar 1974 and Wright and coworkers, 1975, 1976). Wall & Porter (1963) later showed threshold energies for collinear reactions on Wall-Porter surfaces with symmetric barriers were not strongly sensitive to alteration of barrier location but product vibrational energy was. They examined several reactive trajectories and found that they all were short-lived and crossed the saddle-point region on the convex side of the minimum-energy reaction path in the  $(R_1, R_2)$  coordinate system. They made the analogy to a bobsled. Later Marcus (1966b, 1966c, 1968h) obtained such centrifugal and bobsled effects for colinear and coplanar reactions using analytical mechanics. Wall & Porter found that the reaction threshold increased as the mass of the outer atoms increased and that the upper energy limit for reactive collisions, i.e., the antithreshold, was 1.8 eV to greater than 2.4 eV.

Wall, Hiller & Mazur (1961) also performed 3-PD calculations using their London equation surface but not many conclusions could be drawn since only 6 collisions were reactive. A few years later Karplus, Porter & Sharma (1965) made the first trajectory calculations in which the initial collision variables were properly sampled so reaction cross sections and rate coefficients could be calculated. They used the realistic PK2 potential surface. The calculations were quasiclassical in that the initial molecular vibration-rotation energies were forced to be the appropriate quantum values. [Quantizing initial orbital angular momentum of relative motion  $(\ell)$  does not make much difference (Karplus 1968).] Having selected the initial vibrational and rotational quantum numbers n and j and the initial  $E_{rel}$ , other collision variables were selected randomly from the relevant classical distribution functions. The observed threshold energy for n = j = 0 was  $E_{rel} = 0.25 \text{ eV}$  (total energy  $E = 0.52 \,\text{eV}$ , compared to the 0.40 eV barrier height); for i = 5 reactant molecules (containing an additional 0.22 eV of rotational energy), the observed threshold energy increased to 0.31 eV. The reaction cross section for i = 0 increases very slowly for the first 0.05 eV until the effective threshold (defined as where the cross section is  $0.01 a_0^2$ ) of 0.30 eV, then roughly linearly until it reaches what was believed to be a plateau of about  $4.5 a_0^2$  at  $E_{rel} = 1.1 \text{ eV}$ . The curves become steeper and the plateau increases to  $5.5 a_0^2$  as j increases from 0 to 5. The impactparameter dependence of the reaction probability for n = j = 0 was well fit by  $P_0^{\mathsf{R}}(b) = A \cos(\pi b/2b_{\max})$  for  $b < b_{\max}$  and 0 otherwise with  $A \leq 0.6$  and  $b_{\text{max}} \cong 1.0-2.5 a_0$ . The parameters A and  $b_{\text{max}}$  increased with  $E_{\text{rel}}$ . The energy dependence of A and a study of bond angles at the onset of reaction were interpreted as evidence of a "steric factor," which limits reactive collisions to a small range of near-linear orientations in the reaction zone. Collisions were typically simple. The Arrhenius plot was linear for  $T = 300-1000^{\circ}$ K with  $E_{act} = 0.32 \text{ eV}$ . Rate coefficients for fixed *j* showed a large dependence on *j*. For the same potential surface, TST rate coefficients are smaller than collision theory ones by ratios of 0.16 and 0.84 at 300 and 1000°K, respectively, and TST predicts  $E_{act} = 0.38 \text{ eV}$ .

Karplus, Porter & Sharma (1964, 1966), Karplus & Porter (1968), Suzukawa et al (1973), and M. Karplus, L. Pederson, R. N. Porter, and D. L. Thompson (unpublished, quoted in Adams & Porter 1973) extended the calculations to higher  $E_{rel}$  and other isotopes. At  $E_{rel} = 1.1 \text{ eV}$  they found  $\langle \sigma(E_{rel}) \rangle$  for D+H<sub>2</sub> is 5.8  $a_0^2$  as compared to the hot-atom experimental result (Kuppermann 1969) of 8.0 $a_0^2$ . For D+H<sub>2</sub> and H+D<sub>2</sub> the Arrhenius plots showed slight (smaller than experimental) positive curvature at low *T*. For n = j = 0, the cross section for H+H<sub>2</sub> peaks at 6.5  $a_0^2$  at  $E_{rel} = 3.0 \text{ eV}$  and decreases to 3.0 and 0.4  $a_0^2$  at 8.4 and 18.9 eV, respectively. Dissociation begins when the energy is increased to its energetic threshold and at the two higher energies the dissociation cross section is 0.7 and 2.4  $a_0^2$ , respectively. Similar high-energy results were obtained for T+H<sub>2</sub> and D<sub>2</sub> with antithresholds (where the cross section is 0.01  $a_0^2$ ) at  $E_{rel}$  equals 30.4 and 30.9 eV, respectively. The calculated ratio of reaction integrals  $R_{H_2}/R_{D_2}$  is 1.37, in qualitative agreement with the experimental value of about 1.15 (see above). For T+HD, production of TH is favored for  $E_{rel} < 8.5 \text{ eV}$  and vice-versa at higher  $E_{rel}$ .

Yates & Lester (1974) calculated trajectories on a more accurate surface with a higher barrier (see Table 1). At  $E_{rel} = 0.35 \text{ eV}$ , the cross section was smaller than for the PK2 surface but at 0.52 eV it is larger, indicating that more than the saddle-point region must be considered even within 0.3 eV of threshold.

Malcome-Lawes (1975) studied the reactions  $H + H_2$  and  $T_2$ ,  $D + D_2$ , and  $T + H_2$ , D<sub>2</sub>, and HD on the M surface for  $E_{rel}$  generally in the range 0.31–10.4 eV. He obtained  $R_{H_2}/R_{D_2} = 1.18$  and  $R_{HD}/R_{DH} = 0.7$  for comparison with nuclear recoil experiments and HT/DT  $\simeq 0.95$  and 0.6 for  $H_2 : D_2$  and HD photochemical experiments. All four ratios are in good agreement with experiments discussed above.

Karplus (1970a) and Malcome-Lawes (1975) discussed the change in mechanism with increasing energy. At low energy, abstraction dominates, wherein the incoming atom reacts with the atom of the molecule that is closest during the significant "strong-interaction" part of the trajectory; the newly formed molecule "rebounds" backwards in the direction from which the reactant atom arrived (see, e.g., the angular distributions published in these references and by Tang & Karplus 1971 and Wolken & Karplus 1974). At higher  $E_{rel}$ , displacement becomes dominant, where the incoming atom knocks out the closest atom of the molecule, and then "reacts" with the remaining one. At still higher  $E_{rel}$ , spectator stripping and rebound stripping, wherein the incoming atom (at relatively high b) strips off the closest atom in the molecule, become the dominant mechanisms (low b collisions at these energies tend to dissociate the molecule). The peak in the DCS shifts forward as  $E_{rel}$  increases (see also Karplus & Tang 1968 and Polanyi 1968); for  $T + H_2$  on the PK2 surface it moves into the forward hemisphere at  $E_{rel} = 0.7 \text{ eV}$ . Brumer & Karplus (1971) computed a scattering-angle-product-velocity contour map for this surface by averaging the DCS for  $D+H_2$  over appropriate initial beam temperatures and collision geometries. The angle-dependence of the in-plane result is in good agreement with the experiment of Geddes, Krause & Fite (1972) except the peaks are narrower. The comparison may be sensitive to the averaging procedure (K wei, Lo & Entemann 1973). Malcome-Lawes (1975) also presented scattering-angle-productvelocity contour maps. He showed that in the reaction T+HD, the HT product shifts forward at a lower energy than DT.

Karplus & Wang (unpublished, quoted by Heidner & Kasper 1972) extended the calculations on the PK2 surface to  $H+H_2$   $(n = 1, j = 0) \rightarrow H_2 + H$ . Product molecules  $H_2(n' = 0)$  and  $H_2(n' = 1)$  were produced in nearly equal amounts, and the contribution from nonreactive vibrational relaxation  $n = 1 \rightarrow n' = 0$  was negligible. Smith & Wood (1973) used a Sato equation surface and calculated quasiclassical cross sections for deexcitation of  $H_2$  (n = 1 and 2) for several different *j*. They concluded that some of the vibrational excitation energy can be used to lower the translational energy threshold for reaction. Jones & Rosenfeld (1973) studied reactions of quasibound  $H_2$  and found no translational threshold.

Saxon & Light (1972b) computed the reaction cross section, the DCS (back-scattering), and the final rotational state distribution (peaked about j' = 0) for coplanar H + H<sub>2</sub> (n = 0, j = 0).

The mechanics of reactions has also been investigated through analytic approximate trajectories. Marcus (1966c, 1968a, 1968c, 1968h) formulated the equations of motion in natural collision coordinates (Marcus 1966b, 1968g), which for collinear geometries are curvilinear translation-vibration coordinates that evolve smoothly from those suited for reactants into those suited for products; in the transition state region, they describe motions along  $x_1$  and  $x_2$ . For nonlinear geometries, smoothly evolving rotation-bend coordinates are added. He applied the "adiabatic-separable" approximation in which the classical vibrational action (the classical analogue of a quantum number) was conserved, and the action associated with rotation or bending was conserved except where the motion changes abruptly from unidirectional (rotation) to bidirectional (bending). In the coplanar case, the adiabatic model predicts that two j' correlate with each j. Wu & Marcus (1970, 1972) presented computational results, including nonadiabatic corrections, for colinear and coplanar  $H+H_2$  and compared them to numerical trajectory calculations for the PK2 surface. At low energy, for both dimensionalities, vibrational "statistical adiabaticity" was observed: the final vibrational action was well preserved on the average. In the coplanar case, the distribution of signed j'was bimodal, with the peaks rather well predicted by the adiabatic model. However, for  $E_{\rm rel} > 0.6 \, {\rm eV}$ , the distribution lost its bimodal character.

STATISTICAL-DYNAMICAL THEORIES A statistical-dynamical theory of reaction cross sections and reaction probabilities has been derived by Marcus (1966, 1966a, 1967, 1968, 1968b). The quasi-equilibrium assumption and two dynamical assumptions were introduced to compute cross sections for 3-PD H + H<sub>2</sub>. When compared with the trajectory result (Karplus, Porter & Sharma 1965) for n = 0, j = 3, good agreement was obtained with no adjustable parameters for  $E_{rel} < 0.8$  eV, but the predicted cross section exceeds the trajectory value at higher  $E_{rel}$ . A different statisticaldynamical model for reaction cross sections is the statistical phase space theory for bimolecular reactions with an activation barrier (Lin & Light 1966); it has been applied to the nonobservable intramolecular isotope effects on the rate coefficients for H and D + HD. Bunker & Chang (1969) developed a model in which the degree of statistical or vibrationally adiabatic character could be varied.

HARD-SPHERE MODELS Hard-sphere models have been developed especially for the treatment of high-energy collisions. Suplinskas (1968) applied such a model to

calculate rate coefficients and/or high-energy cross sections for  $H + H_2$  and eleven isotopic variations. The general shape and characteristics of the cross section curves were in good agreement with those of Karplus, Porter & Sharma (1966), showing the important role of simple kinematic considerations for these curves. At high energy, the main criterion for reaction is the ability of the incoming atom to lose enough energy to a third particle to "stick." Dissociation cross sections also agreed well with the trajectory results. But for T + HD, production of TH is favored at all energies, in disagreement with the trajectory results. Baer & Amiel (1969, 1969a, 1971), Grice (1970), Malcome-Lawes & Urch (1972a) and Kendall (1973) developed improved hard-sphere models. All four hard-sphere calculations yield a ratio of reaction integrals  $R_{H_2}/R_{D_2} = 1.15-1.20$ , in good agreement with the hot atom experiment. Suplinskas obtained  $R_{HD}/R_{DH} = 1.6$  but Baer & Amiel, Malcome-Lawes & Urch and Kendall obtained 0.89, 1, and 1.2, respectively, in better agreement with experiment (0.62). The magnitudes obtained for  $R_{H_2}$  were 23  $a_0^2$  (Karplus, Porter & Sharma 1966) and 20  $a_0^2$  (Baer & Amiel 1969a).

MODELS OF HOT ATOM SYSTEMS There have been several attempts to develop good physical models of energy loss processes in hot atom systems, to obtain the steadystate distribution of collision energies, and to obtain more detailed information about the reaction cross sections from the experiments. We have already mentioned the kinetic theory of nuclear-recoil hot-atom systems and the numerical solution of the Boltzmann equation. Further work has involved approximate analytic solutions of the Boltzmann equation (Kostin 1965, 1966, 1966a, Felder & Kostin 1965, 1967, Chapin & Kostin 1968, Baer & Amiel 1967, 1970, Baer 1968, 1969, Keizer 1973, Malerich & Spicer 1973, 1973a); stochastic computer models of the energy cascade process (Rowland & Coulter 1964, Chapin & Kostin 1967, 1968, Wotzak & Kostin 1968, Rebick & Dubrin 1970, Gann, Ollison & Dubrin 1971, Malcome-Lawes 1972, 1972a, Malcome-Lawes & Urch 1972, 1972a); and an integral equation for the integral reaction probability (Porter 1966, 1968, Porter & Kunt 1970, Adams & Porter 1973, Baer 1971a). These theories have been applied to analyze further the T+H<sub>2</sub> and D<sub>2</sub> (Porter & Kunt 1970, Malcome-Lawes 1972, 1972a, 1975, Wotzak 1973, Malerich & Spicer 1973, 1973a); T + H<sub>2</sub>: D<sub>2</sub> (Malcome-Lawes & Urch 1972a, Malcome-Lawes 1975); and T+HD (Malcome-Lawes 1972, 1972a) systems. In each case a set of reaction cross sections was assumed and the theory was applied to predict collision densities, yields, or isotope effects. The yields and isotope effects can be compared with experiment. Porter & Kunt (1970), Wotzak (1973), Malcome-Lawes & Urch (1972a), and Malerich & Spicer (1973) computed hot-reaction yields from the trajectories of Karplus, Porter & Sharma (1966) and obtained good agreement (within 10%) with experiment.

CLASSICAL-QUANTAL COMPARISONS Detailed comparisons between collinear reaction probabilities  $P_n^{\mathsf{R}}(E_{rel})$  (for initial vibrational state *n*) computed from quasiclassical trajectories and accurate quantum probabilities discussed below have been made for several surfaces. In all cases the quasiclassical reaction probability grows rapidly for energies just above threshold. For n = 0 it often reaches unity before decreasing but for n > 0 the increase is more gradual and the peak generally lower due to

recrossing, i.e., passing two or more times through geometries with  $R_1 = R_2$  (Smith & Wood 1973). Mortensen (1968a) and Careless & Hyatt (1972) compared  $P_0^{\mathsf{R}}$  for the W surface for  $H+H_2$ ,  $D+D_2$ ,  $D+H_2$ , and  $H+D_2$ . The classical thresholds were from  $0.065 \text{ eV} (H + D_2)$  to  $0.11 \text{ eV} (D + H_2)$  above the quantum "effective threshold" where the reaction probability is 0.01. Diestler & Karplus (1971) studied the PK2 surface and found the quantum  $P_0^{R}$  was 0.1 and 0.5 at energies about 0.04 and 0.014 eV, respectively, lower than the quasiclassical one. At higher energies the curves agreed well on the average but the quasiclassical one did not show the resonance at  $E_{rel} = 0.60 \text{ eV}$ . Bowman & Kuppermann (1971, 1973, 1973a, Bowman, Kuppermann & Schatz 1973, see also Bowman, Schatz & Kuppermann 1974) studied the TK surface. For  $P_0^R$  and  $P_1^R$  the effective (0.01) quantum thresholds were 0.07 and 0.09 eV, respectively, below the respective classical values. In addition, the quasiclassical  $P_1^{R}$  exhibited several sharp oscillations just above threshold. At higher energies, the quantum  $P_0^{R}$  and  $P_1^{R}$  oscillated about the gradually declining quasiclassical values. The ratio of the quasiclassical to the quantum k(T) is 0.04, 0.32, and 0.83 at 200, 300, and 1000°K, respectively. Another important difference between quasiclassical and quantum calculations is that microscopic reversibility is not obeyed by the former. The calculated probability  $P_{01}^{R}$  for the reactive process  $n = 0 \rightarrow n' = 1$  differed significantly from its time-reverse  $P_{10}^{\mathbf{R}}$  and from the exact quantum value  $P_{01}^{R} = P_{10}^{R}$ . Just above threshold,  $P_{10}^{R}$  agreed better with the oscillatory structure of the accurate result. Fong & Diestler (1972, see also Duff & Truhlar 1974) studied  $P_0^{R}$ ,  $P_1^{R}$ , and product vibrational energy on several parameterized Wall-Porter type surfaces so that  $E_b$ ,  $\frac{1}{2}hv_a$ , and reaction path curvature could be altered. They agreed with the previous comparative studies in that the quantum effective thresholds were always lower than the quasiclassical ones (both thresholds increased when either  $E_b$  or  $\frac{1}{2}hv_a$  increased); specific quantum effects are not produced by classical mechanics, but the quasiclassical results agree "on the average" with the quantum ones.

McCullough & Wyatt (1971, 1971a) studied the time-dependent evolution of quantum mechanical wave packets and classical phase point ensembles on the collinear PK2 surface. Comparisons between classical and quantum dynamics were made for various times during the reaction. At early times (when the high-energy components of the wave packet or ensemble enter the interaction region), classical mechanics accurately described the flux across the saddle point region and the probability of being there. However, at late times during the reaction (when only low-energy components of the wave packet or ensemble are present in the interaction region), classical mechanics underestimated both the probability of being near the barrier and the probability of crossing from reactants to products. Thus the classical reaction "shut down" before the quantum reaction. J. M. Bowman and A. Kuppermann (unpublished, Bowman 1974) calculated probability current densities and their associated streamlines and profiles from batches of quasiclassical trajectories on the TK surface for comparison with quantum results discussed below. The quantum and trajectory results are most similar above the vibrational excitation threshold. Below this the trajectory results are much more "turbulent" than the quantum ones.

Schatz & Kuppermann (1976) compared the 3-PD quasiclassical trajectory results

for n = 0 on the PK2 surface against accurate quantum calculations discussed below for  $E \leq 0.7$  eV. For  $E \geq 0.6$  eV, the cross sections for j = 0 and 1 are in excellent agreement. At E = 0.65 eV, the quantum cross section for j = 2 is about four times larger than the quasiclassical one. The quantum k(T) for distinguishable-atoms is larger at all temperatures (by factors of 200, 18, and 1.1 at 200, 300, and 600°K).

#### Association

The simplest collision-theory approach to recombination is to calculate the rate coefficient Z<sub>triple</sub> for triple collisions (Rabinowitch 1937, Bunker 1960, Clarke & McChesney 1964, Stepukhovich & Umanskii 1969) and to multiply by an efficiency factor. This was applied to H recombination by Steiner (1932), Benson & Fueno (1962), and Levine (1967), who estimated  $Z_{triple}$  as the equilibrium constant  $K_{ab}$  for quasibound H<sub>2</sub> times the collision rate coefficient of this intermediate with M. Levine obtained a  $T^{-1}$  temperature dependence.  $K_{ab}$  for H<sub>2</sub> has been estimated more recently by Hurle, Mackey & Rosenfeld (1968), Roberts, Curtiss & Bernstein (1969), and Jones & Rosenfeld (1973). To apply this method accurately, Jones & Rosenfeld (1973) and Whitlock, Muckerman & Roberts (1974) used the quasiclassical trajectory method to calculate the  $\sigma_{ii}$  for deactivation of each state of quasibound H<sub>2</sub> by collisions with H. Jones & Rosenfeld found that the energy transfer stabilization cross section was small  $(3-79 a_0^2, \text{typically } 20 a_0^2)$  and insensitive to  $E_{rel}$  in the range 0.035-35.7 eV, but the exchange stabilization was large  $(170-270 a_0^2)$  at the lowest  $E_{rel}$  where it was insensitive to internal energy but decreased roughly as  $E_{rel}^{-1/3}$  below 2eV and as  $E_{rel}^{-2/3}$  at the highest energy. In contrast to an earlier mechanism proposed by Hurle, Mackey & Rosenfeld (1968, see also Rosenfeld 1968) they found no translational threshold for the exchange reaction initiating in quasibound states. They calculated that exchange stabilization accounted for 71-83 of  $k_{\rm H}^{a}$  in the range 500-6000°K, that  $k_{\rm H}^{a} = 5.2 \times 10^{-33} \,{\rm cm}^{6}$ molec<sup>-2</sup> sec<sup>-2</sup> at 4000°K, and that it has roughly a  $T^{-0.4}$  temperature dependence. Whitlock, Muckerman & Roberts used Sato-type potential surfaces and found energy transfer stabilization cross sections of 5–55  $a_0^2$  that were generally insensitive to  $E_{\rm rel}$  in the range 0.004–0.026 eV and exchange stabilization cross sections 47–258  $a_0^2$ (typically 180  $a_0^2$ ) that decreased with increasing  $E_{rel}$ . This large contribution of exchange stabilization was judged to be the reason  $k_{\rm H}^a$  exceeds  $k_{\rm H}^a$ , by so much. They calculated that  $k_{\rm H}^a$  equals  $2.6 \times 10^{-32}$  cm<sup>6</sup> molec<sup>-2</sup> sec<sup>-1</sup> at 300°K and at lower temperatures varies roughly as  $T^{-0.2}$ .

### Exchange Reaction: Semiclassical Mechanics

In the quasiclassical trajectory method energy-quantization of some degrees of freedom is enforced at the beginning (or end) of the classical trajectory. Another approach using classical trajectories is the multidimensional WKB method (which is called classical *S* matrix theory when it is applied to calculate probability amplitudes for inelastic or reactive collisions; Miller 1975b). This theory involves trajectories satisfying double-ended quantized boundary conditions for the internal degrees of freedom and complex-valued transition amplitudes calculated from such trajectories and their associated action integrals. For classically allowed processes,

i.e., for initial and final states connected by trajectories with real values of the positions, momenta, and time, the amplitudes interfere, and including these interference effects can provide a more accurate approximation to state-to-state reaction probabilities above the classically allowed threshold. At lower energies the reaction is called classically forbidden and the reaction probability may be approximated using classical *S* matrix theory and one or more trajectories involving complex-valued positions, momenta, and time.

The first application of classical S matrix theory to  $H + H_2$  was the calculation that collinear  $P_0^R$  at  $E_{rel}$  equals 0.02–0.22 eV by George & Miller (1972, 1972a) using the PK2 surface. In this case the quasiclassical relative translational threshold is 0.233 eV. Using a single complex-valued trajectory at each energy, they found reaction probabilities in the range  $10^{-8}$ -0.5, which are in agreement with the exact quantum results (Duff & Truhlar 1973; G. C. Schatz and A. Kuppermann, quoted by Bowman & Kuppermann 1973a and Hornstein & Miller 1974) to within a factor of 0.87–0.65 but always too low. Hornstein & Miller (1974) later pointed out that the results are raised about a factor of two and are in better agreement with the exact ones if the theory is renormalized so that the probability is unity in the classical limit (but the same kind of renormalization would lead to worse results for other scattering problems). George & Miller also developed a steepest descent approximation to the integral, which relates the collinear k(T) to  $P_0^{\mathsf{R}}$  when the unrenormalized classical S matrix theory is used for the latter. They obtained  $k(T) = 7.1 \text{ cm molec}^{-1} \text{ sec}^{-1}$  at 300°K, which may be compared to either of two quantum results: 24 and 30 cm molec<sup>-1</sup> sec<sup>-1</sup> (Wu, Johnson & Levine 1973, and G. C. Schatz, J. M. Bowman and A. Kuppermann, unpublished, respectively). Bowman & Kuppermann (1973a), however, calculated k(T) from these same semiclassical probabilities using the collinear analog of equation 3 and found it was 0.73–0.64 times the latter quantum one for  $T = 100-300^{\circ}$ K. Doll, George & Miller (1973) used the same surface and calculated the reaction probability for 3-PD collisions with total angular momentum J = 0 for  $E_{rel} = 0.20-0.25 \text{ eV}$ . Their results for  $j = 0 \rightarrow j = 1$ , obtained with four complex-valued trajectories at each energy, are six to ten times larger than the exact quantum results (Schatz & Kuppermann 1976b), which are  $1.3 \times 10^{-4} - 3.2 \times 10^{-3}$  in this energy range. Doll, George & Miller also did a few calculations at higher J and used these to compute a relative DCS at 0.20 eV which is in excellent agreement with the shape of the exact result.

There have been calculations of the collinear  $P_n^R$  above the classically allowed threshold on the TK (Bowman & Kuppermann 1973, 1973a, Stine & Marcus 1974), PK2 (Wu & Levine 1973, Duff & Truhlar 1976), and D3 (Duff & Truhlar 1974, 1976) surfaces. These calculations often lead to reaction probabilities greater than unity and generally they do not agree as well with the exact quantum results as the results of the quasiclassical trajectory method. For many processes involving more than one trajectory, accurate results can be obtained only from a uniform asymptotic expression that yields a smooth probability as a process changes from classically not allowed to classically allowed or as contributing trajectories change from complex-valued to real-valued. At some energies for  $H + H_2$ , "there may actually

be no uniform asymptotic expression which is possible" (Miller 1973). One notable exception is the successful treatment (Stine & Marcus 1974) of a resonance (described below), but extension of this result to another potential surface apparently requires interference of real and complex-valued trajectories (Duff & Truhlar 1976) which has never been treated for a chemical reaction. Tyson, Saxon & Light (1973) applied classical S matrix theory to the coplanar reaction with j = j' = 0 on the SL surface at  $E_{rel} = 0.373 \text{ eV}$ , where reaction is classically allowed. For J = 0-3 the transition probabilities agree with approximate quantum ones (Altenberger-Siczek & Light 1974) within 16 to 26%, while for J = 6 the semiclassical result is a factor of 9 higher.

There is another category of semiclassical theory in which the translational motion is treated classically and the internal motion is treated quantum mechanically. Ritchie (1974) applied this kind of theory to  $H+H_2$  using a simplified two-state approximation and a crude potential surface.

# Exchange Reactions: Quantum Mechanics

COLLINEAR REACTIONS We have considered using classical trajectories to calculate approximate cross sections and reaction probabilities for the  $H+H_2$  exchange reaction. Quantum mechanical collision theory is capable of yielding the exact cross sections and reaction probabilities for a given potential energy surface and by substituting these into equations 1 and 2 or their lower dimensional analogues the exact equilibrium rate coefficients for the given surface may be obtained. Quantum methods for calculating reactive probabilities and cross sections have been reviewed recently by George & Ross (1973), Kouri (1973, 1973a) and Micha (1975). Exact calculations have been more difficult to perform than trajectory calculations and until very recently they have been carried out only for collinear collisions. So we consider first the calculation of exact collinear reaction probabilities and rate coefficients and quantal approximations to them.

The first attempts to calculate the exact collinear reaction probabilities for a given surface were made by Mortensen & Pitzer (1962). The collinear reaction involves two independent coordinates (2 mathematical dimensions, i.e., 2-MD) after separation of the center-of-mass motion. Mortensen & Pitzer solved the 2-MD time-independent Schroedinger equation for the W surface by a finite difference method and found  $P_0^{\mathbf{R}}$  was 0.140 at  $E_{rel} = 0.165 \,\mathrm{eV}$ , increased to 0.999 at 0.339 eV, and decreased to 0.910 at 0.599 eV. They also found  $P_1^{R}$  equals 0.511 at  $E_{rel} = 0.086$ eV. Later work (Mortensen & Gucwa 1969) uncovered errors in the results of up to 9% so they may be considered essentially exact (various workers have considered errors of about 2-5% as reasonable for numerically "exact" solutions to reactive scattering problems). Mortensen & Pitzer (1962, Mortensen 1968) also calculated reaction probabilities for the collinear reaction which included a hindered rotor energy term as a correction for nonseparability of the rotational and bending degrees of freedom; these are approximations to 3-PD reaction probabilities and are considered below. Mortensen & Gucwa (1969) performed additional calculations for total energies E = 0.412 - 0.759 eV for the strictly collinear reaction on the same surface using the Kohn variational method and the minimum variance variational method. At the lowest E,  $P_0^{\mathsf{R}}$  was 0.035.

What was learned from these calculations? Collinear calculations should not and cannot be compared directly to experiment. They do provide a testing ground for the development of more efficient computational schemes for solving 3-PD scattering problems. Also they may be used as one step in approximate treatments of 3-PD reactions. But their best use is to test rigorously qualitative concepts and approximate theories. Thus Mortensen & Pitzer compared their reaction probabilities to those computed using an approximate 1-MD barrier of the same height and curvature at the top. At  $E_{rel} = 0.165 \text{ eV}$  they found that the barrier transmission coefficients are lower than the 2-MD results by a factor of 34; further, the 2-MD reaction probability reaches 0.5 at a value of  $E_{rel}$  0.14 eV lower (or a total energy 0.13 eV higher) than the barrier transmission probability does. The significance of this result was first pointed out by Marcus (1964), who did 1-MD calculations using a barrier with the VAZC height [but for convenience the curvature at the top was computed from  $V_{rp}(s)$  rather than  $W_{\alpha}(s)$  and obtained a result within 70% of the 2-MD reaction probability. Thus the reaction must be at least roughly vibrationally adiabatic and about 0.14 eV (zero-point energy of H<sub>2</sub>, equal to 0.27 eV, minus  $\frac{1}{2}hv_s$ ) is released for overcoming the barrier. Mortensen & Pitzer (1962) plotted the density of their wave function at  $E_{rel} = 0.165 \text{ eV}$  and found a negative centrifugal effect of about  $0.13 a_0$  which indicates the need to consider reaction-path curvature at such low energies. But the centrifugal effect is opposite in direction to the one Marcus (1966) considered.

McCullough & Wyatt (1969, 1971, 1971a) used the finite-difference method to solve numerically the time-dependent Schroedinger equation for the scattering of a wave packet on the PK2 surface. The rms spread of  $E_{rel}$  for their wave packets was 0.06 eV and for most calculations the average value of  $E_{rel}$  was 0.38 eV. They followed the time evolution of the wave packet and noticed ripples in the direction of the reaction coordinate, flux circulating around a probability hole on the concave side of the reaction path, the early formation of an almost stationary maximum on its convex side (positive centrifugal effect), and the later shifting of the maximum probability and reactive flux to the concave side (negative centrifugal effect or "corner cutting"). Only the positive effect was observed in their batch of classical trajectorics. The circulating flux on the concave side of the reaction path was named the "quantum whirlpool effect" [although they and later J. M. Bowman and A. Kuppermann (unpublished, Bowman 1974) observed such vortex-like phenomena in classical calculations] and is associated with multiple crossing of the symmetric geometry (another feature that showed up in later trajectory calculations).

Several different features of the dynamics have been studied on the TK surface. Truhlar & Kuppermann (1970, 1972, see also Diestler, Truhlar & Kuppermann 1972) used the finite difference boundary value method to compute  $P_0^R$  for  $E_{rel} = 0.005-1.227 \text{ eV}$ . At the higher total energies (E = 0.79-1.50 eV) they also computed  $P_1^R$  and  $P_2^R$ . At low energy  $P_0^R$  increases rapidly with  $E_{rel}$ , becoming 0.5 at  $E_{rel} = 0.266 \text{ eV}$ , 0.010 eV less than  $E_0^{VAZC}$ . Yet the classical barrier is 0.424 eV. Thus the energy released by vibration for overcoming the barrier is only about 7% greater than predicted by the VAZC model. They also calculated the reaction probability by assuming that the VAZC model for the vibrational degree of freedom

is exact and by solving the resulting 1-MD problem for motion along the reaction coordinate exactly. They found this led to too small a reaction probability at low energy; the error was a factor of  $5\frac{1}{2}$  at  $E_{rel} = 0.005 \text{ eV}$  where the exact  $P_0^{R}$  is  $1.85 \times 10^{-7}$ , but only a factor of 1.8 at 0.198 eV where  $P_0^{\rm R}$  is  $1.49 \times 10^{-2}$ . Thus the approximations which separate out a reaction coordinate do not appear to be valid at very low energy. This is consistent with conclusions drawn from the late part of McCullough & Wyatt's (1971, 1971a) wave packet.  $P_1^{R}$  becomes 0.25 at  $E_{rel} = 0.08 \text{ eV}$ and in the first 0.08 eV above the vibrational threshold at E = 0.79 eV ground-state reactants react much more readily than vibrationally excited ones with the same total energy. Truhlar & Kuppermann (1970) discovered that just above this energy the state-to-state transition probabilities associated with reactive and nonreactive processes begin to oscillate with half-oscillation periods of a few tenths of an eV. The total probability of reaction for the ground vibrational state also shows resonance oscillations at total energies E of about 0.9 and 1.3 eV. Truhlar & Kuppermann (1972) interpreted the resonance features they found as interference of different quasiclassical trajectories and predicted that they could be explained by classical S matrix theory. Schatz & Kuppermann (1973) studied these resonances further using exact quantum calculations (close-coupling method). They found resonance widths of 0.05 and 0.008 eV and time delays of  $3 \times 10^{-14}$  and  $1.6 \times 10^{-13}$  sec for the 0.90 and 1.28 eV resonances, respectively. They also found a resonance of intermediate width at 1.67 eV. Argand plots of the S matrix elements demonstrated conclusively that the oscillations in the reaction probability are due to interference of direct and compound states processes. Then Stine & Marcus (1974) showed that the 0.90 eV resonance could be interpreted by classical S matrix theory as interference of direct and long-lived quasiclassical trajectories. Truhlar & Kuppermann (1970, 1972) found that for E greater than the first resonance energy the reaction probabilities agreed on the average with those computed from the statistical phase space theory; at these energies they found roughly equal probability for all energetically allowed processes and no evidence for vibrational adiabaticity.

A more detailed test of the VAZC model was performed by Bowman et al (1973, Bowman 1974). They used the scattering wave functions of the above calculations to calculate the distribution of vibrational state populations as a function of reaction coordinate and energy. At total energies 0.51-0.72 eV a projection of the scattering wave function on the vibrational eigenfunctions of the symmetric stretch normal mode shows that the contribution of the ground state accounts for 90% of the total, close to the 100% predicted by the VAZC model. At lower energies the VAZC model does not work as well, which is consistent with the failure of the VAZC barrier calculation to explain the tunneling. At higher energies the VAZC model also fails, which is consistent with the change to statistical dynamics above the first vibrational threshold. The VAZC analysis explains the 0.87 eV resonance as a virtual excitation of the first excited state of the activated complex symmetric stretching mode; this state has greater than 90% population at the resonance energy but less than 45% population at energies more than 0.06 eV away from it. Schatz & Kuppermann (unpublished, see Schatz 1975) showed that the resonance at E = 1.286 eV is due to virtual excitation of both the n = 2 and n = 3 states of the symmetric stretch in this representation. At nonresonance energies some of the nonadiabaticity present in the VAZC calculations for n = 0 can be accounted for by the inclusion of curvature but such inclusion is difficult (J. M. Bowman and A. Kuppermann, unpublished, see Bowman 1974).

The exact wave functions have also been examined in terms of probability current densities and their associated streamlines and profiles (Kuppermann, Adams & Truhlar 1973, 1976). At low energy this reactive flux cuts the corner and flows directly to products. At higher energies it resembles that found in time-dependent calculations by McCullough & Wyatt (1971, 1971a) and is characterized as "turbulent" flow around vortices and involves "sloshing" from the convex to the concave side of the reaction path and back. At  $E_{rel} = 0.20$  and 0.25 eV, 75 and 50% respectively of the reactive flux is associated with streamlines that pass through a classically forbidden region.

The PK2 surface has also been well studied using exact quantum calculations (Diestler 1971; Johnson 1972; Wu, Johnson & Levine 1973; Duff & Truhlar 1973; Schatz & Kuppermann 1975, see also Hornstein & Miller 1974) but the results have not been as extensively analyzed for this surface. The reaction probability vs. energy is similar to that for the scaled TK surface. Wu & Levine (1971) made calculations involving a harmonic approximation (Madden 1975) to the local vibrational potential; their  $P_0^{R}$  curves are shifted to higher  $E_{rel}$  as compared to the calculations without this approximation. The VAZC barrier height on the PK2 surface is 0.258 eV and  $P_0^{R}$  becomes 0.5 at  $E_{rel} = 0.220 \text{ eV}$ . Thus the VAZC model works a little less well on this surface than on the TK surface. Levine & Wu (1971) performed approximate quantum calculations on the PK2 surface, found the phases of the S matrix elements increased by about  $\pi$  at  $E = 1.24 \,\text{eV}$ , and predicted a resonance feature in the reaction probability at this energy. Further, at this energy they found quasiclassical trajectories involving transfer of energy into the symmetric stretch vibration of the activated complex with extensive "healing" as the products separate so the net translation-vibration energy transfer is small [illustrations of such trajectories for the D3 potential surface are given by Duff & Truhlar (1974); this healing is also observed classically and quantally at nonresonance energies [Marcus 1966c, 1968a; Karplus 1968a, Morokuma & Karplus 1971; Bowman et al 1973]. The resonance was found by Johnson (1972) and Wu, Johnson & Levine (1973) at 1.3 eV. Diestler (1971), Johnson (1972), Wu, Johnson & Levine (1973), and Schatz & Kuppermann (1975) found a resonance at 0.87 eV, analogous to the 0.90 eV resonance on the TK surface.

The distorted wave approximation (DWBA) has been applied to collinear  $H + H_2$ on the PK2 surface by Walker & Wyatt (1972) and Gilbert & George (1973). The distortion potential in the former calculations is a set of perturbed Morse-like potentials the curve of whose minima leaves the minimum-energy path before the saddle point at a point determined by an adjustable parameter. Comparison to the exact quantum results (Duff & Truhlar 1973) shows it is possible to choose this parameter so the approximate and exact  $P_0^{R}$ 's are in good agreement in the threshold

region. The calculations of Gilbert & George were similar but did not involve an adjustable parameter and their probability curve is displaced 0.04–0.022 eV to higher energies from the exact one.

Diestler (1972) studied the exact reaction probabilities at energies above the tunneling region on seven different realistic surfaces. He found that variations in the surfaces affect the probability of vibrational excitation of the products differently near and far from threshold.

Exact reaction probabilities and collinear rate coefficients (computed from the collinear analogues of equations 3 and 4) have been reported for  $H + H_2$  (Truhlar & Kuppermann 1971a, 1972) and for H+D2, D+H2, and D2 (Truhlar, Kuppermann & Adams 1973) for the TK surface and for six isotopic reactions for the PK2 surface (Wu, Johnson & Levine 1973; G. C. Schatz, J. M. Bowman, A. Kuppermann, D. G. Truhlar, and J. Dwyer, unpublished). The VAZC model correlated the energies where  $P_0^{R}$  reaches 0.5 within about 0.01 eV. Quantum scattering by a 1-MD VAZC barrier was compared to  $P_0^{\rm R}$  for the isotopic reactions with about the same success and lack of it as for  $H + H_2$ ; it does explain the observed result that  $P_0^{R}(E_{rel})$  rises more steeply for  $D + D_2$  than  $H + H_2$ . The isotopic reactions also showed a low probability of reaction from (or into) vibrationally excited states just above threshold. The rate coefficients for the TK surface were fit to the Arrhenius form at 200-750°K and 750–1250°K. The Arrhenius activation energies  $E_a$  at low temperature were 0.036– 0.049 eV lower than at high temperature. This illustrates how cautious one must be about equating Arrhenius activation energies to barriers or thresholds, although  $E_a^{\text{high T}} - E_0^{\text{VAZC}} = 0.02 - 0.03 \text{ eV}$  and  $E_0^{\text{VAZC}} - E_a^{\text{low T}} = 0.01 - 0.03 \text{ eV}$  in all cases.

The accurate reaction probabilities for the various surfaces discussed above have also been used to test new methods for solving the scattering problem (Crawford 1971, 1971a, Middleton & Wyatt 1972, Adams, Smith & Hayes 1974, Der, Gebhardt & Haberlandt 1974, Zvijac & Light 1976).

Some exact quantum results have also been calculated for the  $H+H_2$  mass combination using highly idealized or oversimplified surfaces (Mazur & Rubin 1957, Diestler & McKoy 1968, Tang, Kleinman & Karplus 1969, Kleinman & Tang 1969, Baer 1971, Tang & Liebelt 1972, and one of the surfaces in Diestler 1972; see also Middleton & Wyatt 1973). There is some correspondence to results obtained with more realistic surfaces but the quantum effects may be much more dramatic.

PARTICLE INDISTINGUISHABILITY In quasiclassical trajectory studies the three atoms are distinguishable but in classical S matrix theory or quantum mechanics one can consider the effects of particle indistinguishability. In studies of collinear collisions it is customary to consider the atoms to be distinguishable and one may calculate distinguishable-atom cross sections and rate coefficients in higher dimensionality also (Truhlar 1976). But to treat the 3-PDH + H<sub>2</sub> reaction for comparison with experiment requires a quantum treatment equivalent to using wave functions that are antisymmetric with respect to interchange of the protons (Micha 1965a, Tang 1965, Miller 1969, Tang & Karplus 1971, Saxon & Light 1972a, Doll, George & Miller 1973, Micha 1974, Schatz & Kuppermann 1976, 1976a). We denote reactive

transitions calculated for distinguishable atoms by R. Transitions with  $(-1)^j = (-1)^{j'}$ and n = n' = 0 are dominated by nonreactive collisions with small contributions from reactive ones. These contributions interfere and cause oscillations in the rotational excitation cross sections (Saxon & Light 1972a, Wolken & Karplus 1974, Schatz & Kuppermann 1976, 1976b). Ortho-para transitions are due entirely to reactive collisions of distinguishable particles.

NONCOLLINEAR REACTIONS The first quantum mechanical calculations for the noncollinear reaction were performed by Mortensen & Pitzer (1962, Mortensen 1968). Micha (1965, 1965a, 1965b, 1968), and Karplus & Tang (1968, Karplus 1970a, Tang & Karplus 1971, Tang 1972; see also Fite 1972). Mortensen & Pitzer made essentially exact calculations for collinear collisions of  $H + H_2$  and  $D_2$  and  $D + H_2$  and  $D_2$  with an effective potential added to the potential energy surface to account approximately for nonlinearity and for the neglected rotational and bending motions. For  $H+H_2$ they found the accurate  $P_0^{\rm R}$  became 0.5 at an  $E_{\rm rel}$  0.04 eV less than  $E_0^{\rm VAZC}$ , a larger discrepancy than has been found in pure collinear calculations. Micha (1965, 1965a, 1965b) and Karplus & Tang (1968) used the DWBA for  $H + H_2$ . Micha also considered  $H+D_2$  and  $D+H_2$ ; he used a free-molecule vibration-rotation basis and excluded rotational transitions by his "almost linear" approximations. His reaction cross section had several artifactual oscillations. Karplus & Tang used the PK2 surface, made less approximations than Micha, and examined both unperturbed and adiabatic bases; the latter led to much larger cross sections. Most of their calculations were performed with delta functions inserted to enforce linear geometry and simplify the calculations; they were normalized to the full adiabatic results at one energy. The most-favored j' for j = 0,  $E_{rel} = 0.5 \text{ eV}$  is 1; the dependencies of reaction probability on / and of scattering angle on  $E_{\rm rel}$  are similar to the quasiclassical trajectory results. As compared to exact calculations discussed below, the threshold energy region was about 0.1 eV too high and the reaction cross section rises too steeply above this. Choi & Tang (1974, 1974a, 1975a, Tang & Choi 1975, 1975a, Tang, private communication) made adiabatic DWBA calculations for  $H + H_2$  and  $D + H_2$ on the same surface without the linear approximation. For low energy  $H + H_2$ , their  $0 \rightarrow 1$  cross section is 1.5-2.5 times lower than, but their DCS is in good agreement with, accurate results (discussed below) for this surface. The relative DCS becomes less backwards-peaked as  $E_{rel}$  or j' increases. At  $E_{rel} = 0.48 \text{ eV}$ , they found a preference for  $j' \leq 6$  and  $J \leq 12$ . They also performed calculations for  $D + H_2$  on the YL surface that yielded an effective threshold (0.01  $a_0^2$ ) about 0.15 eV higher than the other surface (although the difference in barriers is much smaller, see Table 1). At  $E_{rel} = 0.48 \text{ eV}$  they found that there was a preference for  $j' \leq 3$ and that the DCS is back-peaked with a half-maximum of about 145° (vs about 110° for the PK2 surface). Brodsky & Levich (1973) have also commented on the application of DWBA theory to the hydrogen isotope exchange reactions and Bauer (1951, 1952) calculated very approximate dissociation cross sections using a renormalized Born theory. Walker & Wyatt (1974, 1974a) applied two adiabatic DWBA models to coplanar  $H + H_2$  on the PK2 surface. At low energy their results

bracket the accurate ones (discussed below) but the DCS for j = 0, j' = 1 does not agree very well with the accurate ones. They converted their results to 3-PD cross sections by an approximate method.

McGuire & Mueller (1971, 1971a) proposed a different kind of approximation to the reactive scattering problem in which coupling between different arrangement channels is due to off-diagonal matrix elements between valence bond configurations for the initial and final arrangements. Their results are too large (McGuire & Micha 1973, Tang & Choi 1975). This approximation and some others (Micha 1972, Micha & McGuire 1972, McGuire & Micha 1973; see also Gilbert & George 1973) have the disadvantage of not allowing the use of an accurate Born-Oppenheimer adiabatic surface but may yield useful trends. For example, Micha & McGuire (1972) calculated that in the spectator-stripping limit the most probable n' for the T + H<sub>2</sub> reaction increases from 6 at  $E_{rel} = 4 \text{ eV}$  to 16 at 9 eV.

Wolken & Karplus (1974) made close coupling calculations for the 3-PD reaction using Miller's (1969) integrodifferential equation method and the PK2 surface. For J = 0, 3, ..., 12 they included 4-7 free rotational states but only one unperturbed vibrational function (this is the one vibration approximation or OVA) in the expansion of the wave function. For other J they interpolated. Their calculations are inaccurate, at least in part because of the OVA (Elkowitz & Wyatt 1975, Choi & Tang 1975, Schatz & Kuppermann 1975, 1976b).

Other close coupling calculations described below have used a propagationmatching technique in which configuration space is divided into three arrangement zones. In each zone the wave function is expanded in a vibration-rotation basis and a set of close coupling equations is solved for the translational wavefunctions. At small atom-molecule separations the arrangement zones meet on matching surfaces and the separate arrangement solutions are combined so the wave function and its normal derivatives are continuous on the matching surfaces and asymptotically satisfy scattering boundary conditions. Exact (converged) resulte may be obtained if the basis is large enough. Some of these methods were stimulated by the earlier development of natural collision coordinates and their use in model studies (Marcus 1966b, 1968g, Wyatt 1969, Light 1971, 1971a).

Saxon & Light (1971, 1972, 1972a) and Altenberger-Siczek & Light (1974) made close coupling calculations on coplanar  $H + H_2$  for a fit to the SL surface. At each J their basis consisted of up to 19 free rotor functions but only one adiabatic vibrational function. The DCS was strongly back-peaked (half-maximum at about 160° for  $E_{rel} = 0.46 \text{ eV}$ ) and reaction was due primarily to  $\ell \leq 7$ . The effective threshold (0.01  $a_0$ ) is about  $E_{rel} = 0.24 \text{ eV}$ .

Wyatt's group developed an asymmetric-top hindered-rotor procedure using natural-collision-coordinates for the propagation-matching calculations (Wyatt 1972, Harms & Wyatt 1972, 1975, 1975a, Walker & Wyatt 1972a, Elkowitz & Wyatt 1975, 1975a, 1975b, 1976, Walker & Wyatt 1972a, Harms, Elkowitz & Wyatt 1976, Redmon & Wyatt 1975). Elkowitz & Wyatt (1975a) used this method to study  $H + H_2$  for J = 0 for the PK2 surface and they (Elkowitz & Wyatt 1975) calculated cross sections for model analytic fits in natural coordinates to both the PK2 and YL surfaces. As many as 3 or 5 vibrational basis functions were used for calculations on these two

surfaces, respectively, with up to 50 local asymmetric top-Morse-oscillator basis functions for a given J. On the PK2 surface the effective threshold  $(0.01 a_0^2)$  is  $E_{\rm rel} = 0.26 \, {\rm eV}$ , about 0.04 eV below the quasiclassical effective threshold. The effective translational thresholds for collinear (0.14 eV), coplanar (0.20 eV from the calculations of Schatz & Kuppermann discussed below) and 3-PD reactions on the PK2 surface increase by about 0.06 eV for each dimension just as predicted by the VACZ model (see Table 1) or the statistical-dynamical theory of Marcus (1967). Wyatt (1975) used an information-theory approach to show that the j' distribution is very cold compared to a statistical distribution; rotational surprisals are linear in  $E'_{\rm rot}$  at several energies. Elkowitz & Wyatt (1976) showed that a  $j_z$ -conserving approximation based upon the natural coordinate-asymmetric top formulation gives reasonable reaction cross sections for i = 0. An error has been discovered in the cross sections plotted by Elkowitz & Wyatt (1975), its correction leads to better agreement with the results of Schatz & Kuppermann (1976b) discussed below, although there are still differences in the degree of product rotational excitation (Wyatt and Elkowitz's result for j = 0, j' = 3 is  $2\frac{1}{2}$  times larger than Schatz & Kuppermann's although the j = 0, j' = 1 results agree well).

Kuppermann, Schatz & Baer (1976, Kuppermann 1971, 1975, 1975a, Schatz & Kuppermann 1976) formulated a propagation-matching technique that uses a novel system of internal coordinates. Schatz & Kuppermann (1975, 1975a, 1976, 1976b, and also Kuppermann, Schatz & Baer 1974) applied it to coplanar and 3-PD H+H<sub>2</sub> using the PK2 surface. They used free rotational functions and 4–6 adiabatic vibrational basis functions, leading to 32–100 rotational-vibrational channels for each J. Convergence tests indicated cross sections are accurate to about 5%.

For the coplanar reaction, the "cross sections" showed approximately exponential growth up to  $E_{\rm rel} = 0.25 \, {\rm eV}$ , followed by linear growth up to  $0.40 \, {\rm eV}$ . For  $E_{\rm rel} < 0.09 \, {\rm eV}$ , the OVA overestimated the cross section by 3 orders of magnitude but for  $E_{\rm rel} > 0.26 \, {\rm eV}$  (where the cross section is  $0.1 \, a_0$ ) it underestimates it. The large errors in the OVA imply the DWBA should not be trusted at low  $E_{\rm rel}$  either. The relative DCS is back-peaked for  $E_{\rm rel} = 0.03$ – $0.38 \, {\rm eV}$  and is predictable by the OVA; it is wider than that calculated by Altenberger-Siczek & Light (1974) using the OVA for the SL surface. Schatz & Kuppermann (1976b) calculated exact rate coefficients and found  $E_a = 0.23 \, {\rm eV}$  and its width increased to  $0.045 \, {\rm eV}$ . Nonnegligible reaction probabilities were found for  $J \leq 17$ , and the resonance occurred with no significant change in position or width for all  $J \leq 7$ . Thus it is not averaged out by the sum over J.

For the 3-PD reaction, Schatz & Kuppermann (1975, 1976b) found the energy dependence of the J = 0 reaction probability (in the range  $10^{-13}$  and 0.2) and the position of the lowest-energy resonance is very similar to the coplanar J = 0 and the collinear results except for the shift (about 0.05 eV) per added dimension to higher  $E_{\text{rel}}$ . The resonance width is 0.035 eV. Examination of cross sections for  $njK \rightarrow n'j'K'$  transitions (where K is the angular momentum component along the rotating atom-diatom separation vector) showed that, because near-collinear reactions are favored, there is a propensity rule that (a) K = K' = 0 dominates,

(b)  $K = 0, K' \neq 0$  and  $K \neq 0, K' = 0$  processes which have zero probability in those  $j_z$ -conserving schemes which neglect remixing on the arrangement channel matching surfaces, are of secondary importance, and (c)  $K \neq 0, K' \neq 0$  processes, some of which obey  $j_z$ -conservation, are less important. For example, for  $E_{rel} = 0.33 \text{ eV}$ , the cross sections for n = j = K = n' = 0, j' = 1 are 0.072 and 0.032  $a_0^2$  for K' = 0 and  $\pm 1$ , respectively, and for n = n' = 0, j = K = j' = 1 are 0.0060, 0.00055, and 0.00084 for K' = 0, 1, and -1, respectively. Product rotational polarization has also been noticed by Wolken & Karplus (1974), Walker & Wyatt (1974), and Choi & Tang (1974). The j = 0, j' = 1 distinguishable-atom reactive relative DCS is smooth and back-peaked with half-maximum values at 133°, 148°, and 129° at E = 0.03, 0.13, and 0.43 eV, respectively. At low T the Arrhenius plot for  $k_1(T)$  is significantly curved and at 500°K  $E_a$  is about 0.28 eV (compared to 0.33 eV for TST and 0.38 eV for quasiclassical trajectory calculations).

G. C. Schatz and A. Kuppermann (unpublished, Schatz 1975) also performed some exact 3-PD cross section calculations for an accurate fit to the Liu surface. The general features are unchanged. The threshold region is shifted up about 0.05 eV but at lower energies the Liu cross sections are larger. The rotational distributions are broader and the DCS is narrower.

# CONCLUSIONS

Seven years ago Kaufman (1969) summarized progress in H<sub>3</sub> kinetics as follows:

Of all the elementary chemical processes, the  $H+H_2$  exchange reaction and its isotopic equivalents continue to be the critical test of theory and experiment...I would stress that the reaction well deserves the wide attention which it is receiving, that more kinetic data would be welcome, especially at the low end of the temperature range, that crossed molecular beam experiments would be particularly valuable..., that rigorous computer calculations are still needed for comparison with quasiequilibrium theories, but the calculations of transition state theory including tunneling corrections are based on too many questionable assumptions to represent a fruitful approach.

Since then accurate rate data have become available at T as low as  $167^{\circ}$ K, molecular beam studies have been reported for H+T<sub>2</sub> and D+H<sub>2</sub>, classical, semiclassical, approximate quantum, and TST calculations have been compared to exact quantum calculations for given potential surfaces, especially at energies up to about  $\frac{1}{2}$  eV above threshold, the breakdown of TST including one-dimensional tunneling corrections at low T has been well studied and explained in terms of the separability assumption, and semiclassical theories that offer new hope for overcoming this assumption have been developed. The sensitivity of reaction attributes to the whole potential surface is also becoming more clear and we still look forward to extensive use for dynamical studies of a surface accurate enough to allow meaningful testing of theory against experiment. But there has been no progress so far in the rigorous quantum treatment of dissociation and recombination, and nuclear recoil hot atom experiments have still not been interpreted using an accurate treatment of the nonreactive energy-moderation processes. As always, further experimental work would still be desirable in many areas, e.g., measurements of rate coefficients for intramolecular isotope effects and for recombination or beam studies with velocityselected reactants. It appears that  $H_3$  kinetics will continue to be a fruitful area of research for a long time.

#### ACKNOWLEDGMENTS

The authors are grateful to Y. B. Band, J. M. Bowman, W. D. Breshears, W. C. Gardiner, T. F. George, J. H. Kiefer, A. Kuppermann, D. Kouri, D. J. LeRoy, J. C. Light, G. J. Mains, D. A. Micha, W. H. Miller, R. E. Roberts, G. C. Schatz, K. T. Tang, A. A. Westenberg, and J. M. White for providing unpublished material or comments on drafts of parts of this article or both. One of the authors (DGT) is grateful for an Alfred P. Sloan Research Fellowship, for research support by the National Science Foundation, and to H. Eyring for an invitation to write this article. The other author is grateful to the Robert A. Welch Foundation and to the Alfred P. Sloan Foundation for financial support.

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