

Chemical Reaction Cross Sections and Rate Constants

Studies of reaction rates and molecular structure are two main branches of chemical research, but chemists have progressed much further and more deeply in the latter than the former. Certainly, there has been some advance in recent years toward an understanding of the forces which act during a chemical reaction and their effects on the rates of reactions. Nevertheless, our knowledge of the kinetics, or rates, of most reactions remains largely empirical; we have tables of rate constants but little understanding of what happens on an atomic scale when such reactions occur. In contrast, we have learned much more about the arrangements of atoms in molecules and the energy levels of these molecules.

Experimental measurements of the rate of a chemical reaction such as that of hydrogen and iodine to form hydrogen iodide in the gas phase according to the stoichiometric equation



can be described quantitatively (1) for temperatures up to 600°K by the expression

$$\frac{dn_{\text{HI}}}{dt} = k_1(T)n_{\text{H}_2}n_{\text{I}_2} \quad (2)$$

where n_X represents the number of molecules of X per unit volume (the number density), T is the temperature at which the reaction takes place, dn_{HI}/dt is the rate of the reaction and $k_1(T)$ is the rate constant. (Although the name rate *coefficient* is more appropriate because of the dependence of k on T , we retain the name rate *constant* because of its common use.) The latter can be written in the Arrhenius form

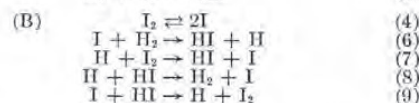
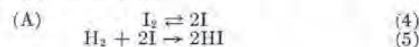
$$k_1(T) = A_1 T^{1/2} e^{-\epsilon_a/RT} \quad (3)$$

where R is the gas constant, A_1 is equal to 6.0×10^9 l mole⁻¹ sec⁻¹ deg^{1/2} = 1.00×10^{-11} cm³ sec⁻¹ deg^{1/2} per molecule, and ϵ_a , the activation energy, is equal to 40.7 kcal mole⁻¹. Eqn. (3) can also be written

$$k_1(T) = A_1 T^{1/2} e^{-E_a/\kappa T}$$

where κ is the Boltzmann constant and E_a the activation energy per molecule (rather than per mole).

Equation (2) is often called the rate law for the reaction. In this case it is a second-order rate law. In general, rate constants depend on the temperature. Furthermore, the rate of a reaction does not necessarily vary with the concentrations of the reactants raised to the powers given by the stoichiometric coefficients for the reaction. In fact, concentrations of species which do not even appear in the net reaction may influence its rate. For many years chemists have thought that eqn. (1) actually represented how the reaction of hydrogen and iodine took place on a molecular level; however, Sullivan's careful work (2) has now shown that very little if any of the HI is produced in a single step by collisions of H₂ with I₂. Instead, at least two sets of elementary steps, or mechanisms, occurring simultaneously are needed to explain all the experiments which have been done on this reaction. One possible pair of mechanisms is (A) and (B):



Perhaps further work will show these steps do not fit some new experimental observations, but for the present, at least, they do.

In this paper we are not concerned with methods for finding satisfactory mechanisms for reactions but rather with the description of one kind of elementary step, the gas phase bimolecular reaction. Eqs. (6) through (9) represent specific examples of this kind of reaction. The rate of each such reaction is measured by a rate constant. For instance, we have for reaction (6) $k_6(T) = A_6 T^{1/2} e^{-\epsilon_{a6}/RT}$ with $A_6 = 3.5 \times 10^9$ l mole⁻¹ sec⁻¹ deg^{1/2} = 5.9×10^{-12} cm³ sec⁻¹ deg^{1/2} per molecule and $\epsilon_{a6} = 32.8$ kcal mole⁻¹. For generality we do not take any particular reaction but write



and show how the rate

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$$\frac{dn_c}{dt} = k n_A n_B \quad (11)$$

may be interpreted in terms of $\sigma_R(E)$, the cross section for the reaction when A approaches B with a particular kinetic energy of relative motion E . A cross section for any specific event such as a chemical reaction or scattering (for a reaction is by no means the only way molecules can interact) is a proportionality factor which measures the likelihood of the event when A approaches B in the specified way. The cross section for chemical reactions is the quantity on the molecular scale which is most important in determining the bulk rate constant. Eliason and Hirschfelder (3) have treated in detail many of the points which we touch on only briefly here.

In physics, the concept and measurement of nuclear reaction cross sections has been instrumental for the understanding of nuclear structure and nuclear reactions as well as for practical applications such as the development of nuclear reactors. Chemical reaction cross sections will be quite possibly of similar importance for chemistry.

Bimolecular Collisions in a Gas and the Collision Cross Section

Molecules of Uniform Relative Speed Moving into a Collection of Dilute Target Molecules

A cross section is especially simple to discuss for the case of collisions of hard, elastic spheres in which a particle of type A, radius r_A , mass m_A , and velocity $\mathbf{v}_A$ moves toward a particle of type B of radius r_B , mass m_B , and velocity $\mathbf{v}_B$. In this case the two types of particles are taken to be noninteracting except when the distance r between their centers is $r_A + r_B$. The mutual potential energy of the two particles, which is usually called the interaction potential $V(r)$, is given by

$$\begin{aligned} V(r) &= \infty \text{ for } 0 \leq r < r_A + r_B \\ V(r) &= 0 \text{ for } r_A + r_B < r < \infty \end{aligned} \quad (12)$$

The trajectories of both particles are straight lines between collisions. The important velocity is not that of either particle alone but that of their relative motion $\mathbf{v}$ (the relative velocity). This is the velocity of A which would be recorded by an observer on B and is equal to $\mathbf{v}_A - \mathbf{v}_B$. For simplicity we begin by considering a single value of $\mathbf{v}$. In the next section we introduce the more general case in which the molecules have a distribution of relative speeds. Also the kinetic energy of relative motion, E , is not the sum of the kinetic energies of the two particles but is $\frac{1}{2}\mu v^2$. Here $\mu = (1/m_A + 1/m_B)^{-1}$ is the reduced mass of the pair of particles A, B. Figure 1 shows the paths of two colliding particles and helps to define the scattering angle θ (the angle by which $\mathbf{v}$ is deviated in this system of relative coordinates as a result of the collision) and the initial impact parameter b (the displacement of the center of particle A from a line through particle B parallel to $\mathbf{v}$). Assuming classical mechanics to be obeyed we can easily find θ in terms of b . From the small triangle in Figure 1a we have

$$\sin[\frac{1}{2}(\pi - \theta)] = \sin \phi = \frac{b}{r_A + r_B} \quad (13)$$

Thus, as b increases from zero to its maximum value $b_{max} (= r_A + r_B)$, θ decreases from π to zero. More

generally we can find (4) the relation between the deflection angle and the impact parameter for particles which interact with a potential $V(r)$ which may be different from that of eqn. (12). Here r is the distance between the particles. The result is

$$\theta(b) = \pi - 2b \int_{r_{min}}^{\infty} \frac{dr}{r^2 \left\{ 1 - \frac{2V(r)}{\mu v^2} \right\}^{1/2}} \quad (14)$$

In eqn. (14) r_{min} is the distance of closest approach during the collision; for hard spheres this is $r_{min} = r_A + r_B$.

We consider a beam of A particles with a given number crossing a unit area perpendicular to the beam per unit time and all moving with the same relative velocity $\mathbf{v}$ toward a collection of B particles having a uniform number density n_B . Its current density is $I_A = n_A \mathbf{v}$. Let the total number of A particles undergoing collisions with B particles per unit time per unit area perpendicular to the beam and in a length dl along the beam be dI_A . We assume these particles are scattered out of the original beam which is changed in current density by a negative amount dI_A , indicating a decrease. We take n_A and n_B so small that collisions involving three or more particles are negligible. A quantitative expression for dI_A , which is analogous to that describing the attenuation of a beam of light (photons) passing through an absorbing medium, is

$$dI_A = -\sigma_{AB}(v) I_A(l) n_B dl \quad (15)$$

Equation (15) defines a proportionality constant $\sigma_{AB}(v)$, the scattering cross section, which is independent of l . The larger it is, the greater is the attenuation of the beam, i.e., the more particles are scattered out of the beam, all other conditions being the same. We may integrate eqn. (15) over the range $0 \leq l \leq L$ directly to get

$$I_A(L) = I_A^0 e^{-\sigma_{AB}(v) n_B L} \quad (16)$$

where I_A^0 is the current density of A at $l = 0$. In eqn. (16) $\sigma_{AB}(v)$ is the effective area presented by a B particle to an A particle, or what is equivalent, an A particle to a B particle; it is the scattering analog of the extinction coefficient in the Beer-Lambert law for the

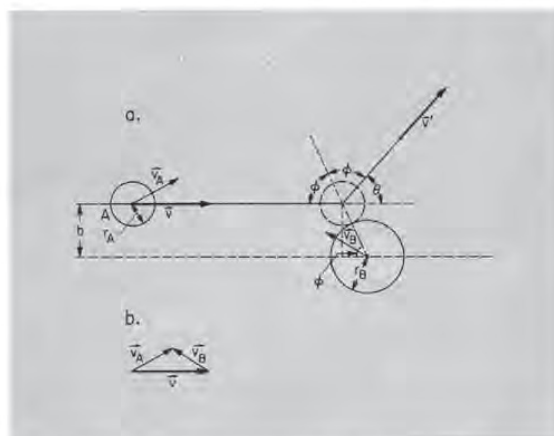


Figure 1a. Collision of two hard spheres A and B of radii r_A and r_B and with velocities $\mathbf{v}_A$ and $\mathbf{v}_B$. The relative velocity is $\mathbf{v} = \mathbf{v}_A - \mathbf{v}_B$ before the collision (see 1b) and $\mathbf{v}'$ after it. The impact parameter is b , and the scattering angle in the system of relative coordinates is θ .

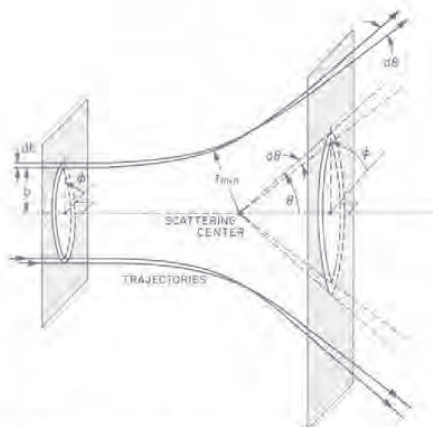


Figure 2. Deflection of particle trajectories by a scattering center. The figure illustrates the relationship between θ and b and the cylindrical symmetry of the set of trajectories of equal b around the line for $b = 0$. The closest approach of these trajectories to the scattering center is r_{min} .

absorption of light when the concentration of the light absorbing species is expressed in number of molecules per unit volume.

From eqn. (14) [or (13)] we see that to each impact parameter b there corresponds a particular scattering angle θ if μ , v , and the equation for the potential, $V(r)$, are given. For such potentials, which do not depend on the relative orientation of A and B (as is the case for spherical particles), there exists a cylindrical symmetry around the line $b = 0$ for all trajectories of equal b (see Fig. 2). Every particle having a trajectory for which θ is unequal to zero is considered to have been deflected from the beam. Because of this, and the cylindrical symmetry just mentioned, the contribution of impact parameters from b to $b + db$ to the collision cross section is

$$d\sigma_{AB}(v) = 2\pi b(\theta)db \quad (17)$$

Therefore, the total collision cross section is

$$\sigma_{AB}(v) = \int_{b_{min}}^{b_{max}} 2\pi b db \quad (18)$$

where b_{max} corresponds to $\theta = 0$ and b_{min} to $\theta = \pi$. For the $V(r)$ commonly used b_{min} is zero (head on collisions produce a 180° deflection). For this case we have the simple relation

$$\sigma_{AB}(v) = \pi b_{max}^2 \quad (19)$$

For our special case of hard spheres we have

$$b_{max} = r_A + r_B$$

and

$$\sigma_{AB} = \pi(r_A + r_B)^2 \quad (20)$$

Here σ_{AB} is independent of the relative speed v .

Let us now determine Z_B , the total number of collisions per unit time and per unit volume, made by one A particle with a collection of B particles. When the

particle radii are much smaller than the mean free paths between collisions, we obtain directly

$$Z_B = \sigma_{AB}v n_B \quad (21)$$

since $\sigma_{AB}v$ is the effective volume swept out per unit time by the A particle and Z_B is the number of B particles in this volume. When other A particles are also present in the same volume the total number of collisions Z_{AB} between A and B particles per unit time and per unit volume is³

$$Z_{AB} = n_A n_B v \sigma_{AB} \quad (22)$$

Thus the quantity $v\sigma_{AB}$ is the proportionality constant which relates Z_{AB} , the number of bimolecular collisions between A and B particles per unit time per unit volume at one relative speed v to the product $n_A n_B$, the number densities of A and B. Equation (22) is not restricted to hard spheres but applies for any $V(r)$ in a gas at pressures low enough to make interactions of three or more particles negligible.

We can make the hard sphere model (considered above) a better representation of real molecular interactions by including an attractive force between the particles. We choose the familiar interaction potential

$$V = \infty \text{ for } 0 \leq r < r_A + r_B \\ V = -C/r \text{ for } r_A + r_B \leq r < \infty \quad (23)$$

which provides a good description of the motion of a comet in the gravitational field of a planet or of two hard sphere ions interacting according to Coulomb's law. In eqn. (23) $r_A + r_B$ is, as above, the sum of the hard sphere radii of the particles; C is the molecular analog of the gravitational constant or $-z_A z_B e^2$, the negative of the product of the net charges on the ions. In Figure 3 we show the forms of the interaction potentials for the models of this and the previous sections and also of the Lennard-Jones potential. The latter is often used as a reasonable representation of the interaction of real molecules. It is given by

$$V(r) = 4\epsilon \left[\left(\frac{r_0}{r} \right)^{12} - \left(\frac{r_0}{r} \right)^6 \right] \quad (24)$$

the parameters ϵ and r_0 are defined in Figure 3. The second model [eqn. (23)] has enough of the features of realistic potentials to be worth studying, but at the same time it keeps much of the simplicity of the hard sphere model. Calculations are more easily carried out with this equation than with eqn. (24). Figure 4 shows two types of collisions for the attractive ($z_A z_B < 0$) interaction of particles A and B according to eqn. (23). In

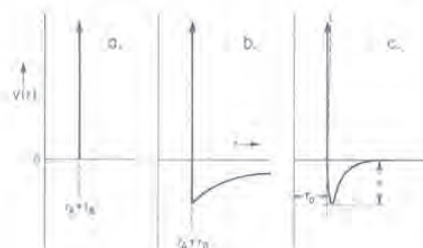


Figure 3. Three models for interaction potentials, $V(r)$. 3a, Hard spheres, eqn. (12); 3b, Hard spheres with attraction, eqn. (23); and 3c, the Lennard-Jones form, eqn. (24).

³ This formula is valid for the case in which A and B particles are of different kinds. When they are of the same kind, a factor $1/2$ must be introduced in its right-hand side since otherwise each collision is counted twice.

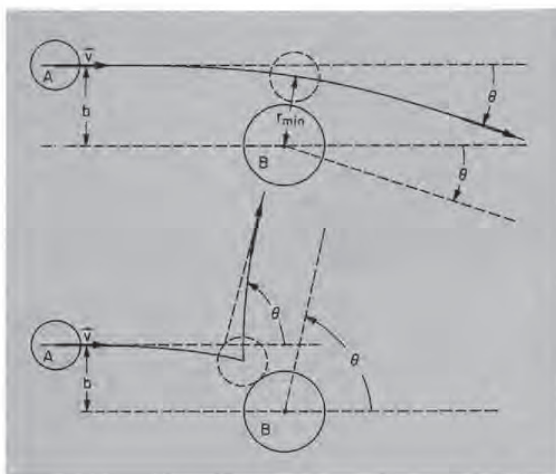


Figure 4. Two types of collisions for particles interacting with potential of eqn. (23). Upper trajectory with the larger b shows deflection by angle θ but no contact of hard cores. Lower trajectory with the smaller b shows contact of the hard cores.

one case particle A is deflected by particle B, but the hard cores do not come into contact; the trajectory, or the curve which represents the relative motion, is a hyperbola like the path followed by comets in unbound orbits which interact just once with a planet. In the second case particle A penetrates all the way to the hard center of particle B. We can distinguish two cross sections corresponding to the two types of trajectories. When the hard cores do not meet, we simply use $V(r) = -C/r$ or $z_A z_B e^2/r$ in eqn. (14) to get

$$b(\theta) = \frac{z_A z_B e^2}{2E \sin^2 \frac{\theta}{2}} \quad (25)$$

where E is $\frac{1}{2}\mu v^2$. From eqn. (19) we have

$$\sigma_{AB}(b_{\max}) = \sigma_{AB}(\theta_{\min}) = \frac{\pi(z_A z_B e^2)^2}{4E^2 \sin^2 \frac{\theta_{\min}}{2}} \quad (26)$$

which yields

$$\lim_{\theta_{\min} \rightarrow 0} \sigma_{AB} = \infty \quad (27)$$

Eqn. (26) is equivalent to Rutherford's expression for Coulomb scattering. Thus all collisions, even those with very large impact parameters, lead to some deflection ($\theta \neq 0$) because the potential does not vanish until r becomes infinite. The scattering cross section is infinite because even infinitesimal deflections scatter A particles out of the beam. On the other hand, the cross section for the second case, in which the hard cores come into contact, remains finite except at the limit $E \rightarrow 0$. Given values of v and $r_A + r_B$ we can find $(b_{\max})_{\text{core}}$, the largest b for which the cores touch. This trajectory is tangent to a circle of radius $r_A + r_B$ centered on particle B. We find $r_{\min}$ from eqn. (14) by noting that at this value of r dr/dt is zero or, what can be shown to be equivalent (4), the denominator of the integrand goes to zero. This gives

$$r_{\min} = \frac{b}{\left[1 - \frac{V(r_{\min})}{E}\right]^{1/2}} = r_A + r_B \quad (28)$$

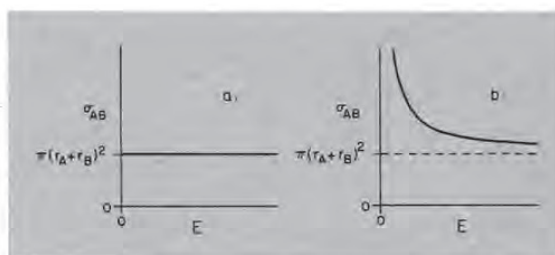


Figure 5. The energy dependence of the cross section for the contact of the hard cores, for two models. 5a, Hard spheres, eqn. (20); 5b, Hard spheres with attraction, eqn. (30). The special case $z_B = -z_A = 1$ and r_A and $r_B = 3.3 \text{ \AA}$ in 5b gives $\sigma_{AB, \text{core}} = 2\pi(r_A + r_B)^2$ for $E = 4.3 \text{ eV}$ ($100 \text{ kcal mole}^{-1}$).

and

$$(b_{\max})_{\text{core}} = (r_A + r_B) \left[1 - \frac{V(r_A + r_B)}{E}\right]^{1/2} \quad (29)$$

The corresponding expression for the cross section for contact of the hard cores is

$$\sigma_{AB, \text{core}}(E) = \pi(b_{\max})_{\text{core}}^2 = \pi(r_A + r_B)^2 \left[1 - \frac{V(r_A + r_B)}{E}\right] \quad (30)$$

The important difference between eqns. (30) and (20) is the inclusion of the energy dependent factor in the former. This energy dependence of $\sigma_{AB, \text{core}}$ is shown in Figure 5. Note that the attractive force between particles A and B increases the chance of contact between the hard cores for the model of eqn. (23) over that for the model of eqn. (12) but that as v gets larger the former approaches the latter. The number of collisions between particles A and B for which the hard cores come into contact is given by the expression, exactly analogous to eqn. (22),

$$Z_{AB, \text{core}} = n_A n_B v \sigma_{AB, \text{core}}(v) \quad (31)$$

In this paper we use the word collision in a general sense to indicate that two particles come close enough together to interact, i.e. they approach to a distance at which the forces between them are different from zero. Thus contact between the hard cores is not a necessary condition for a collision of A with B if the interaction is given by eqn. (23), but it is if the interaction is described by eqn. (12).

Potentials with hard cores like those of Figures 3a and b do not represent real molecules as well as does the Lennard-Jones potential (Fig. 3c). The classical scattering cross sections for molecules interacting according to this potential is infinite because the potential, although it falls off much more rapidly with interparticle distance than does the Coulomb potential, still does not become zero except for infinite separation of the two particles. However, for large impact parameters the deflection angle θ , expected according to eqn. (14), becomes so small ($\theta < \theta^\dagger$) that a measurement of it, simultaneously with a determination of the relative velocity of the incoming particle, would be inconsistent with the limitations imposed by the uncertainty principle which requires $\theta > \theta^\dagger$ with $\theta^\dagger \simeq (\hbar/\mu v r_{\min})$ in order that classical mechanics be applicable. Here $r_{\min}$ is the minimum separation of A and B along the trajectory, and $\theta^\dagger \mu v$ is the corresponding momentum in a direction perpendicular to the trajectory. For $\theta < \theta^\dagger$ quantum

mechanics must be used, and calculations using it in conjunction with Lennard-Jones potentials as well as experiments show that the cross sections are finite⁴ at $\theta = 0$.

In this paper we emphasize the model of hard spheres with attraction, eqn. (23), because it gives a scattering cross section $\sigma_{AB,core}$ which (1) varies with energy and (2) is finite (for $E > 0$) and only part of the total scattering cross section (see Fig. 4). These are just the features which make the model useful in illustrating the interpretation of reaction cross sections.

Molecules with a Distribution of Speeds Colliding with a Gas of Moving Target Molecules

Under ordinary conditions the molecules of a gas have speeds which are not uniform but distributed over a range. In general, both kinds of molecules A and B move at laboratory speeds which are distributed as required by Maxwell's law

$$f_T(v_i)dv_i = \left(\frac{2}{\pi}\right)^{1/2} \left(\frac{m_i}{\kappa T}\right)^{3/2} v_i^2 e^{-m_i v_i^2 / 2\kappa T} dv_i, \quad i = A, B \quad (32)$$

where $f_T(v_i)dv_i$ is the fraction of molecules of type i which have speeds in the range v_i to $v_i + dv_i$; m_i and T are the mass and temperature of these molecules; and κ is the Boltzmann constant (δ). In considering collisions between molecules of types A and B we are interested in the number of pairs of molecules per unit volume as a function of their relative speeds. Each pair may be described either by the positions ($\mathbf{r}_A$, $\mathbf{r}_B$) and laboratory velocities ($\mathbf{v}_A$, $\mathbf{v}_B$) of the two particles, or by the position ($\mathbf{r}_0$) and laboratory velocity ($\mathbf{v}_0$) of the center of mass of the two particles together with the position ($\mathbf{r}$) and speed (v) of one of the particles (A for example) relative to the other. The fraction of the number of A,B pairs whose relative speed is in the range v to $v + dv$ is given (6) by

$$f_T(v)dv = 4\pi \left(\frac{\mu}{2\pi\kappa T}\right)^{3/2} e^{-\mu v^2 / 2\kappa T} v^2 dv \quad (33)$$

when each of the particles obey's Maxwell's law. The only changes from eqn. (32) are (1) the use of the relative speed v for v_i ; (2) the use of the reduced mass μ for m_i ; and (3) $f(v)dv$ now represents a fraction of A,B particle pairs rather than of individual particles. Now we find the total number of collisions Z_{AB} for all relative speeds directly, just as we did in eqns. (22) and (31),

$$\begin{aligned} Z_{AB} &= \int_0^\infty n_A n_B v \sigma_{AB}(v) f(v) dv \\ &= n_A n_B 4\pi \left(\frac{\mu}{2\pi\kappa T}\right)^{3/2} \int_0^\infty \sigma_{AB}(v) v^3 e^{-\mu v^2 / 2\kappa T} dv \end{aligned} \quad (34)$$

Eqn. (34) corresponds to the statement: the total number of collisions between molecules of type A with those of type B is the sum over the contributions of collisions occurring at all relative speeds. The number of collisions occurring in the relative speed range v to $v + dv$ is the product of the number density of the particles, the relative speed, the cross section, and the fraction of molecule pairs whose relative speed is in that range.

⁴ The Coulomb potential approaches zero so slowly that the quantum mechanical total cross section also diverges; the results are the same in this particular case as for classical mechanics.

Reaction Rates and Cross Sections for Chemical Reactions

Definition of Reaction Cross Section

For the reaction represented by eqn. (10) the number of reactive collisions per unit time and per unit volume between molecules of type A and those of type B (both in given internal quantum states) which are moving towards each other with relative speed v may be written,

$$\left(\frac{dn_c}{dt}\right)_v = - \left(\frac{dn_A}{dt}\right)_v = \sigma_{AB,R}(v) n_A n_B \quad (35)$$

Eqn. (35) can serve as the definition of a reaction cross section $\sigma_{AB,R}(v)$. It is a proportionality constant with dimensions of an area per molecule which measures the effective size of the molecules for reaction to occur, that is, the likelihood that a collision between a pair of molecules will lead to reaction. It depends on the forces which are involved during a chemical reaction.

Rate of Reaction for Molecule Pairs Which All Have the Same Relative Speed

By comparing eqns. (11) and (35) we see that the rate constant k_r for a reaction in which all the interactions occur at the same relative speed v is

$$k_r = v \sigma_{AB,R}(v) \quad (36)$$

The rate constant is related to the cross section in the same way the current density of a beam of particles is related to the number density of particles in the beam.

Rate of Reaction for Collisions Which Occur with a Distribution of Relative Speeds

For the collisions which take place in real mixtures of chemically reactive gases there is not a single relative speed but a distribution of speeds. Thus, we should compare eqn. (11) not with eqn. (35) directly but only with the result of averaging it over the appropriate distribution of speeds $f(v)$ as we did in eqn. (34) for the total number of collisions. This gives the general reaction rate constant,

$$k_f = \int_0^\infty f(v) v \sigma_{AB,R}(v) dv \quad (37)$$

This expression is true for any distribution function of relative speeds, whether it is Maxwellian or not. Photochemical, hot-atom, and radiation-chemical reactions are examples for which reactions can occur under non-Maxwellian distributions of relative speeds. However, in gaseous mixtures under ordinary thermal conditions the nonreactive collisions are sufficiently frequent to maintain a speed distribution which is essentially Maxwellian. Under these conditions we can use eqn. (33) for $f(v)$ to get an expression for the thermal rate constant $k(T)$. If we wish we may replace the variable v by the relative kinetic energy, $E = \frac{1}{2}\mu v^2$, to get

$$k(T) = \left(\frac{1}{\pi\mu}\right)^{1/2} \left(\frac{2}{\kappa T}\right)^{1/2} \int_0^\infty \sigma_{AB,R}(E) E e^{-E/\kappa T} dE \quad (38)$$

In this equation the factor $E^{1/2} e^{-E/\kappa T}$ in the integrand arises only from the Maxwellian collision statistics; all the information about the reaction rate, on the molecular scale, is contained in the cross section $\sigma_{AB,R}(E)$ times $E^{1/2}$.

If we now consider distributions of internal energy

states for the reactants in addition to the distribution of relative speeds, or kinetic energies, we can write one k_{ij} for each pair of reacting molecules for which the particular internal states of molecules A and B are indicated by the subscripts i and j , respectively, and the corresponding cross section by $\sigma_{A,B,i,R}(E)$. Now the overall rate constant is given by

$$k_{f,FA,FB} = \frac{1}{n_A n_B} \sum_{i,j} \langle k_{ij} \rangle n_{A,i} n_{B,j} \quad (39)$$

with

$$n_{A,i} = F_A(i) n_A$$

and

$$n_{B,j} = F_B(j) n_B$$

where the F 's are the distribution functions for the internal quantum states. Once more, they need not be equilibrium, Boltzmann distributions. Two examples of nonequilibrium distributions commonly observed are those of vibrational states of molecules just behind shock fronts and of electronically excited states in photochemical reactions. However, under ordinary thermal conditions the F 's (as well as f) can be approximated closely enough by using equilibrium distributions

$$F_{Xl} = \frac{n_{Xl}}{n_X} = \frac{\exp(-\epsilon_{Xl}/kT)}{q_X(T)} \quad (40)$$

where ϵ_{Xl} ($X = A, B$) is the energy of state l of molecule X and q_X is the partition function defined by

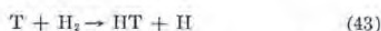
$$q_X(T) = \sum_l \exp(-\epsilon_{Xl}/kT) \quad (41)$$

Using eqns. (40) and (41) in conjunction with (39), we obtain the following very general expression for the overall rate constant of a bimolecular reaction occurring under thermal conditions:

$$k(T) = \frac{1}{q_A(T)q_B(T)} \sum_{i,j} \exp[-(\epsilon_{A,i} + \epsilon_{B,j})/kT] k_{ij}(T) \quad (42)$$

Here, $k_{ij}(T)$ is the thermal rate constant for molecules A and B in individual internal quantum states i and j , respectively, obtained from eqn. (38) by replacing $\sigma_{A,B,R}$ by $\sigma_{A,B,i,R}$.

Some qualitative features of a representative reaction cross section can be seen immediately in Figure 6a which shows $\sigma_R(E)$ for the reaction



as calculated by Karplus, Porter, and Sharma (7) by the method described below. These features are: (1) the existence of a threshold energy E_0 such that $\sigma_R(E)$ is zero for E less than E_0 ; (2) a rise of σ_R with increasing E above the threshold to a maximum value σ_{Rmax} ; and (3) a fall of $\sigma_R(E)$ at still higher E . From (7) we get the values $E_0 = 0.25$ eV (5.8 kcal mole⁻¹) and $\sigma_{Rmax} = 2.4 \text{ \AA}^2$ at $E \simeq 4$ eV (90 kcal mole⁻¹).

Chemical reaction cross sections $\sigma_R(E)$ are generally of the order of molecular sizes, when the energy is in the range near which the cross section is a maximum. Typically we have $10^{-1} \text{ \AA}^2 \lesssim \sigma_{Rmax} \lesssim 10^2 \text{ \AA}^2$ except for the special cases such as ionic reactions where the reaction cross sections are still larger because long-range forces are involved. Similarly, nuclear reaction cross

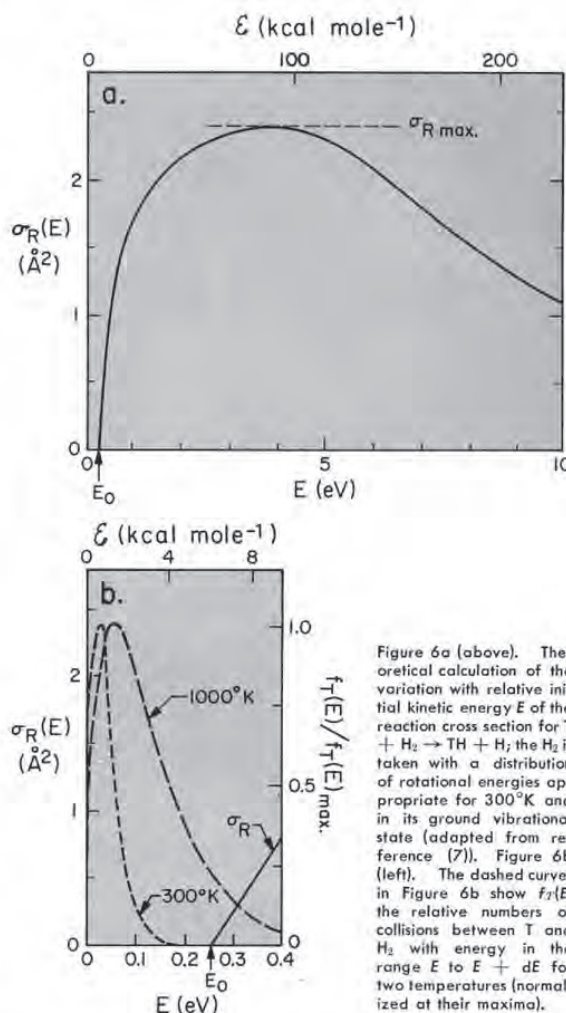


Figure 6a (above). Theoretical calculation of the variation with relative initial kinetic energy E of the reaction cross section for $T + H_2 \rightarrow TH + H$; the H_2 is taken with a distribution of rotational energies appropriate for 300°K and in its ground vibrational state (adapted from reference (7)). Figure 6b (left). The dashed curves in Figure 6b show $f_T(E)$ the relative numbers of collisions between T and H_2 with energy in the range E to $E + dE$ for two temperatures (normalized at their maxima).

sections are of the order of nuclear sizes and are usually measured in barns, a unit equal to 10^{-24} cm^2 or $10^{-8} \text{ \AA}^2$. Thus, they are smaller than their chemical counterparts by a factor of about 10^5 .

For thermal reactions which are slow enough to occur at one atmosphere without leading to explosions, only a small fraction of all the collisions is reactive. This means that if we plot a typical distribution of relative translational energies $f_T(E)$ on the same abscissa as σ_R (see the dashed lines in Fig. 6b) the two curves overlap (have values of their ordinates differing from zero by an appreciable fraction of their maximum values) for only a small range of E just greater than E_0 . The exponential drop of $f_T(E)$ at high energies effectively cuts off the distribution just above E_0 . In other words, for those reactions which are not as fast as explosions, the Maxwell distribution only samples the reaction cross section near its threshold. An increase of temperature increases the fraction of collisions for which E is greater than E_0 , but still a negligible fraction of the collisions have energies substantially greater than E_0 . In principle, sufficiently detailed knowledge of $k(T)$ would permit a determination of $\sigma_R(E)$; in practice the experimental accuracy required is beyond anything likely to be obtainable for many years.

Calculations of Reaction Cross Sections

Simple Reactions—Problems in Molecular Mechanics and Molecular Trajectories

On the molecular scale a chemical reaction becomes a problem in mechanics, once the forces between the various atoms are known. For instance, we consider the reaction



in which A is an atom and BC a diatomic molecule. Let r_{AB} , r_{BC} , and r_{AC} be the internuclear distances for the pairs AB, BC, and AC, respectively. These distances change with time. Before the reactants have

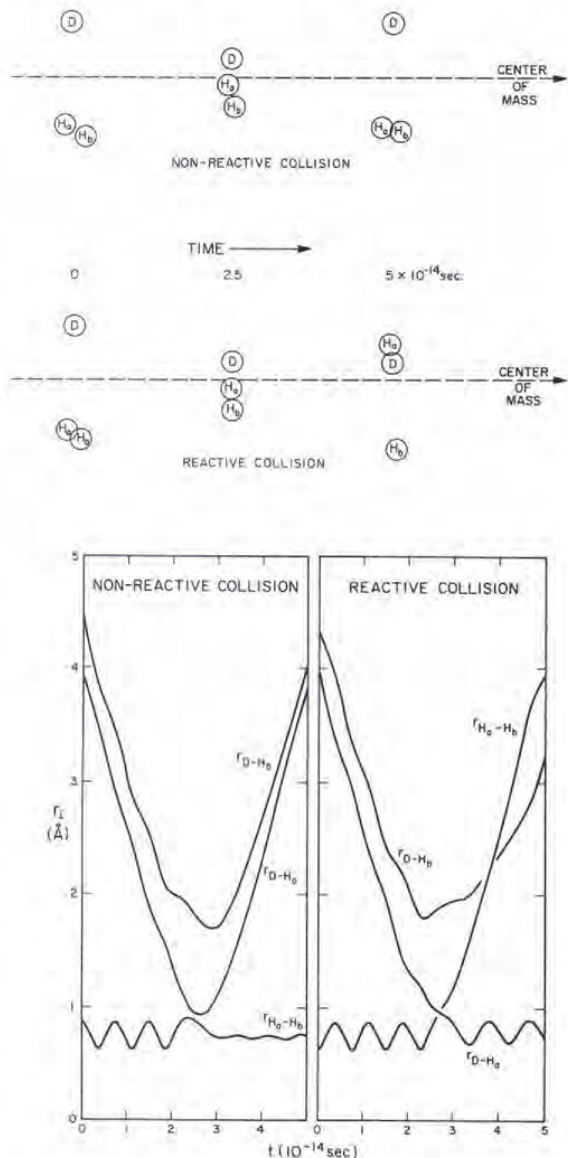


Figure 7. Illustration of nonreactive and reactive collisions between D and H₂. 7a, (above), relative locations of the three particles D, H_a, H_b at three times. 7b, (below), the variation of the three internuclear distances with time for $E = 2$ ev (46 kcal mole⁻¹) reference (8). Note the rotation of the product molecule H₂D after the reactive collision.

approached each other, r_{AB} and r_{AC} are large compared to r_{BC} . After they collide, and if the collision is non-reactive, r_{AB} and r_{AC} again become large compared to r_{BC} as the collision partners move away from each other. However, if the collision is reactive, then after the reaction products have moved away from each other, r_{AC} and r_{BC} are large compared to r_{AB} . Thus, if r_{AB} , r_{BC} , and r_{AC} are known as functions of time, we can decide whether or not a chemical reaction has taken place as a result of the collision simply by inspecting the internuclear distances before and after collision. An illustration of two such kinds of collisions, for the $D + H_2$ system (8), is given in Figure 7. The two atoms in H₂ are labeled H_a and H_b, respectively.

In order to solve the problem of finding out under what conditions a collision between the reactants will or will not be reactive we must decide whether it is necessary to use quantum mechanics, which is presently believed to contain an accurate description of such processes (but which is difficult to apply), or whether classical mechanics may provide an adequate, although not so rigorous, solution to the problem. There is no doubt that the motion of the electrons, which is in general much more rapid than that of the nuclei, is "strongly" quantum mechanical; the use of classical mechanics would lead to completely erroneous conclusions. As a result of this rapid motion, the electrons produce forces of attraction (or, at times, repulsion) between the nuclei. The strength of these forces is described by a potential energy function, or potential energy surface. In the $A + BC$ system, eqn. (44), this surface is a function of the three internuclear distances or any other three equivalent quantities. The potential energy surface can be calculated by solving the Schrödinger equation for the electrons with the nuclei fixed, and then repeating such a solution for a large number of different internuclear distances. Porter and Karplus (9) have done this recently with a fair degree of accuracy for the system $H + H_2$ and, consequently also for all of its isotopic counterparts, such as $D + H_2$, $T + H_2$, $T + HD$, etc. Such a calculation depends only on the charges on each of the three nuclei and the total number of electrons, which are the same for all of these systems.

The next question is whether the motion of the nuclei, subject to the action of the forces described above, is also "strongly" quantum mechanical, or whether classical mechanics may be used instead to a fair degree of accuracy. There seems to be adequate reason to believe that the latter is the case for the calculation of the dependence of reaction cross reactions on relative kinetic energy. The variation of the three internuclear distances with time for the $D + H_2$ system, depicted in Figure 7b, was obtained (8) by solving on a digital computer the classical equations of motion of the three nuclei, under the influence of a theoretical potential energy surface (9) and by using methods developed recently (10).

How can we obtain a reaction cross section from such calculations? Essentially we do an experiment on a computer. We shoot A at BC with a fixed relative speed but a variety of other initial conditions, restricting the impact parameter b to be between 0 and an arbitrarily chosen maximum value b_M . We choose initial conditions at random in a way appropriate to describe

correctly the variety of collisions which is expected to occur between such molecules. Each time we choose a set of initial conditions, we must solve the classical equations of motion and determine whether or not a reaction occurred, according to the internuclear distance criteria described above. We repeat this process a sufficient number of times until the fraction η of "shots" which lead to reaction becomes a constant, i.e., does not change as more shots are tried. The quantity $\eta\pi b_M^2$ is then a first approximation for the reaction cross section at the relative initial speed considered. We now take a larger b_M , and redetermine η , as well as $\eta\pi b_M^2$. When this quantity stops changing as b_M is further increased, we take it as the theoretical reaction cross section. This is the way that the cross section of Figure 7 was computed (7).

Models for the Reaction Cross Section

A simple and sometimes instructive alternative to trajectory calculations is the use of models for $\sigma_R(E)$ which contain some of the important features of reaction cross sections as parameters which may be adjusted to fit experiments or theoretical expressions.

Probably the simplest model for the reaction of A + B (where again A and B can be molecules) is to take both partners as hard spheres with reaction occurring for relative energies above a threshold E_0 . In this case we have

$$\sigma_{AB,R}(E) = \begin{cases} 0 & \text{for } E < E_0 \text{ and } b \text{ arbitrary} \\ \pi(r_A + r_B)^2 & \text{for } E \geq E_0 \text{ and } b \leq r_A + r_B \end{cases} \quad (45)$$

We obtain the corresponding expression for the thermal rate constant from eqns. (38) and (45) after integrating by parts

$$k(T) = 2(r_A + r_B)^2 \left(\frac{2\pi kT}{\mu} \right)^{1/2} \left(1 + \frac{E_0}{kT} \right) e^{-E_0/kT} \quad (46)$$

A slightly more plausible model is one in which the partners are hard spheres as above, but for which reaction occurs only if the relative energy along the line of centers E_{lc} equals or exceeds a threshold value E_0 :

$$\sigma_{AB,R} = \begin{cases} 0 & \text{for } E_{lc} < E_0 \\ \pi[b_{max}(E)]^2 > 0 & \text{for } E_{lc} \geq E_0 \end{cases} \quad (47)$$

E_{lc} is equal to $1/2\mu v^2 v_{lc}$ where v_{lc} is the component of the relative velocity which is parallel to the line of centers of the hard spheres A and B at contact; b_{max} is the impact parameter b for which E_{lc} equals E_0 . For b greater than b_{max} , E_{lc} is less than E_0 and the reaction cannot occur. The value of b_{max} depends on E , as shown below. From Figure 1 we have

$$v_{lc} = v \cos \phi = v \left[1 - \frac{b^2}{(r_A + r_B)^2} \right]^{1/2} \quad (48)$$

or

$$E_{lc} = E \left[1 - \frac{b^2}{(r_A + r_B)^2} \right] \quad (49)$$

As we have just indicated, for E_{lc} equal to E_0 , b is b_{max} . This furnishes

$$b_{max}(E) = (r_A + r_B) \left(1 - \frac{E_0}{E} \right)^{1/2} \quad (50)$$

The corresponding cross section is therefore

$$\sigma_{AB,R}(E) = \begin{cases} 0 & \text{for } E \leq E_0 \\ \pi(r_A + r_B)^2 \left(1 - \frac{E_0}{E} \right) & \text{for } E \geq E_0 \end{cases} \quad (51)$$

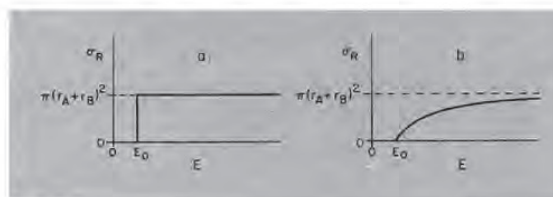


Figure 8. Variation of reaction cross section with energy for two models. 8a, eqn. (45), Hard spheres; 8b, eqn. (47), Hard spheres.

The rate constant obtained from eqns. (38) and (51) is

$$k(T) = 2(r_A + r_B)^2 \left(\frac{2\pi kT}{\mu} \right)^{1/2} e^{-E_0/kT} \quad (52)$$

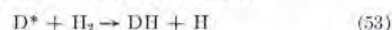
Eqn. (52) shows that this model reproduces the Arrhenius expression for $k(T)$ [see eqn. (3a)]. Unfortunately, in most experiments the errors are large enough so that the factor before the exponential is not significantly different from a constant. For the same reason the difference between eqns. (46) and (52) is difficult to establish experimentally. The energy dependence of $\sigma_R(E)$ for these two hard sphere models is shown in Figure 8.

Experimental Methods for the Determination of Reaction Cross Sections

We now describe very briefly two specific experiments to illustrate methods which are suitable for the measurement of the energy dependence of reaction cross sections.

Hot Atom Reactions

When DI in its ground state absorbs light of wavelength 3130 Å, the molecule undergoes a transition to a repulsive, excited electronic state. D and I atoms separate with 0.97 eV (22.8 kcal mole⁻¹) of kinetic energy, 98.5% of which is associated with the D atom as may be shown by requiring conservation of energy and linear momentum. The relative energy of such a D atom with respect to a thermal H₂ molecule is on the average about 0.50 eV (11.7 kcal mole⁻¹). When this photolysis is carried out at room temperature in a large excess of H₂, the fast D* atoms can either react



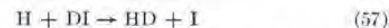
or lose energy by collision without reacting



and then react thermally with DI



The H atoms from eqn. (53) can also react with DI:



Thus the relative amounts of HD and D₂ which are produced depend on the relative magnitudes of the reaction and scattering cross sections for atoms whose initial relative energy is $E = 0.51$ eV (11.7 kcal mole⁻¹). Changing the wavelength of the photolyzing light leads to the production of D* atoms of varying initial relative kinetic energies (11). If the energy dependence of the cross section of the nonreactive collision process represented by eqn. (54) is available (which it is in approximate form), and if proper allowance is

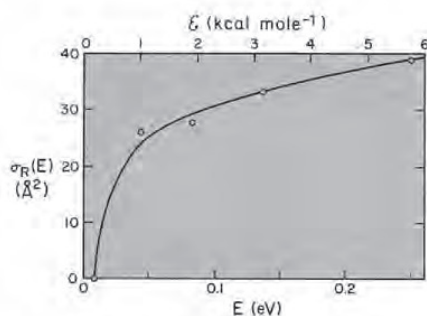
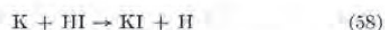


Figure 9. Experimental determination of the variation of the reaction cross-section with energy for the reaction $K + HI \rightarrow KI + H$ by the molecular beam method (points are those labeled "elastic" in Figure 8 of reference (12)). The absolute value of $\sigma_R(E)$ may be in error by a factor of 2.

made for the distribution of relative energies which exists, these measurements give σ_R as a function of E . They show that the threshold energy for this reaction, eqn. (53), is about $1/3$ eV (11).

Molecular Beam Reactions

Another experiment which shows the energy dependence of reaction cross sections involves the use of molecular beams. Such beams are produced when gases effuse through small holes into a vacuum. Only those molecules moving in a desired direction proceed further through a second hole and become what is called a collimated molecular beam. Molecules in the beams which have speeds outside a small range v to $v + \Delta v$ can be filtered out by a velocity selector. The chemical reaction finally has a chance to occur where two such beams consisting of molecules of known relative speed v , intersect. Detectors sensitive to reactants and products indicate the yield of product for collisions of the particular speed or energy. Resetting the velocity selector for other molecular speeds gives further values of $\sigma(E)$. Figure 9 shows some experimental results (12) by the molecular beam method for the reaction



Applications to Reactions in Liquids

So far we have been discussing reactions which occur in dilute gases. The interacting molecules are relatively far removed from other molecules, so the disturbing effects of the latter can be safely neglected or accurately allowed for. The situation for reactions in liquids is far more complicated in detail because of the presence of solvent molecules as well as reactant and product molecules all at close range. In this case, the reagent molecules must diffuse toward each other through the solvent before they can collide. In some reactions in solution the diffusion rate controls the re-

action rate. However, in others, it is the likelihood that the reagent molecules will indeed react once they get together which determines the reaction rate. In these cases, the concept of a reaction cross section still remains useful, as long as complicating factors such as cage effects and other solvent effects are included.

Future Developments

Chemical kinetics is receiving concentrated attention from many people interested in the detailed description of what happens during reactions. Certainly new developments will come rapidly.

The classical mechanical picture we present here seems to be adequate as a first approximation, but for really accurate work quantum treatments will be required in many situations.

Further experiments, particularly those with beams of oriented molecules, will help to make the interpretation of the experiments more straightforward. In various ways more and more of the nature of chemical reactions will be understood.

Conclusions

We end by repeating the points we wish to emphasize. Once the reaction cross section and the distributions are known, they give the rate constant. If the cross section for a reaction is understood, the reaction is understood. The concept of a reaction cross section should help to give a clearer understanding of chemical reactions on a molecular scale.

Acknowledgment

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