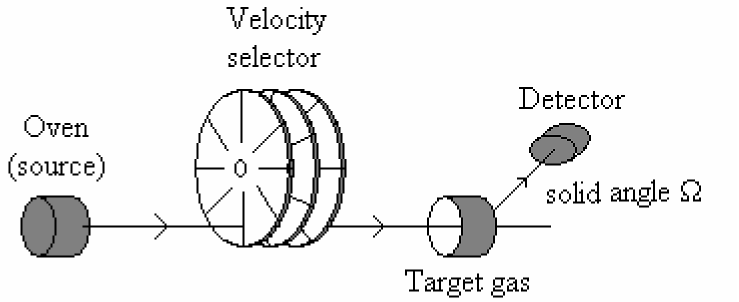
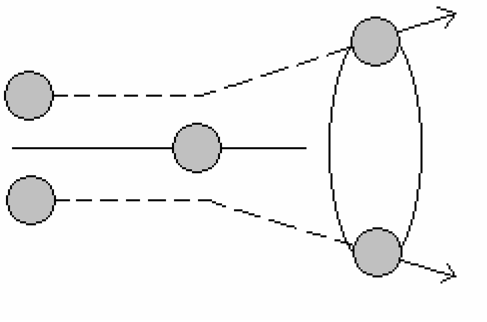
Molecular interactions in beams

A notable advancement in the experimental study of intermolecular forces has come from the development of molecular beams, which consist of a narrow beam of particles, all having the same velocity, traveling through an evacuated vessel. The beam is directed towards other molecules, and the scattering of molecules that occurs on impact is used to study intermolecular interactions.

The basic arrangement for a molecular beam experiment is shown in the figure. The slotted disks make up the **velocity selector**. They rotate in the path of the beam and allow only those molecules having a certain velocity to pass through. Any desired velocity can be chosen by altering the speed of rotation. The target gas may be enclosed in a container, or may be in the form of another molecular beam in a perpendicular direction. The latter is called **crossed beam technique** and gives a lot of useful information because the velocities of both target and projectile molecules can be controlled. The intensity of the incident beam is measured by the incident beam flux, *I*, which is the number of particles per unit area per unit time.



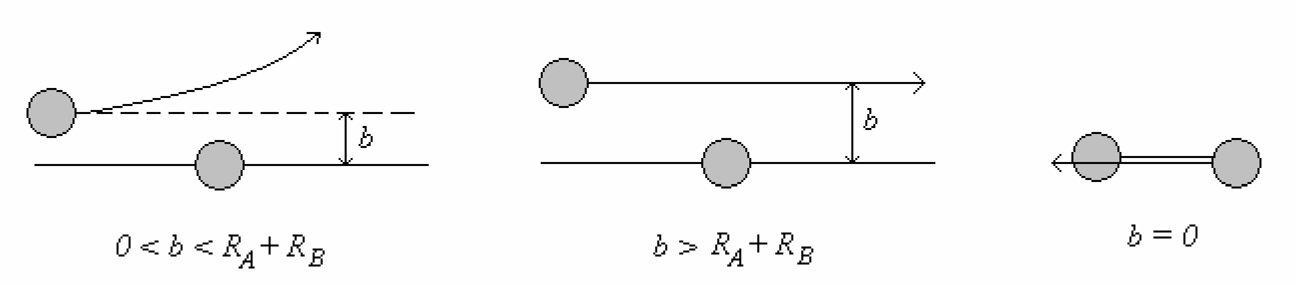
The detectors may consist of a chamber fitted with a sensitive pressure gauge or an ionization detector, in which the incoming molecule is first ionized and then detected electronically. The state of the scattered molecules may also be determined spectroscopically, and is of interest when the collisions change their rotational and vibrational states.



The primary experimental information from a molecular beam experiment is the fraction of molecules in the incident beam that are scattered in a particular direction (angle Ω). The fraction is normally expressed in terms of *dI*, the number of molecules that are scattered per unit time into a cone that represents the area covered by the 'eye' of the detector. This number is reported as the **differential scattering cross section *σ***, and is the constant of proportionality between the value of *dI* and the intensity of the incident beam *I*, the number density of target molecules *N* and the infinitesimal path length *dx* through the sample.

$$dI = \sigma I N dx$$

The differential scattering cross section *σ* has the dimensions of area. Its value depends upon the **impact parameter *b***, which is the initial perpendicular separation of the paths of the colliding molecules, and the details of the intermolecular potential. The role of the impact parameter is most easily seen by considering



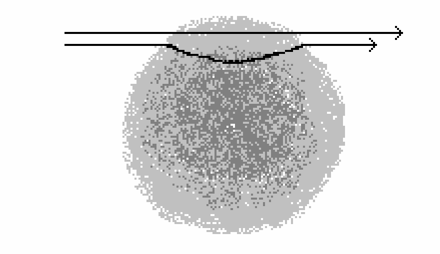
$0 < b < R_A + R_B$ $b > R_A + R_B$ $b = 0$

Effect of impact parameter *b*

the impact of two hard spheres. If $b = 0$, the lighter projectile is on a trajectory that leads to head-on collision, so that the only scattering intensity is detected when the detector is at $\Omega = 180^\circ$. If the impact parameter is so large ($b > R_A+R_B$, where R_A and R_B are the radii of the two spheres respectively) that the spheres do not make contact, there is no scattering and the scattering cross section is zero at all angles except $\Omega = 0^\circ$. Glancing blows with $0 < b < R_A+R_B$ lead to scattering intensity in cones around the initial line of flight direction.

Scattering effects: The scattering pattern of real molecules, which are **not hard spheres**, depends on the details of the intermolecular potential, including the anisotropy that is present when the molecules are non-spherical. The scattering also depends on the relative speed of approach of the two particles: a very fast particle might pass through the interaction region without much deflection, whereas a slower one on the same path might be temporarily captured and undergo considerable deflection. The variation in the scattering cross-section with the relative speed of approach should therefore give information about the strength and range of the intermolecular potential.

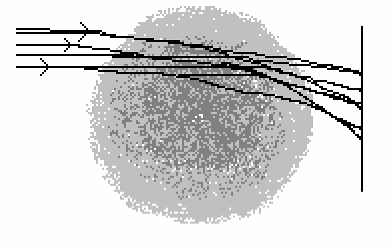
A further point is that the outcome of collisions is determined by quantum, not classical, mechanics. The wave nature of the particles can be taken into account, at least to some extent, by drawing all classical trajectories that take the projectile particle from source to detector, and then considering the effects of interference between them.



Two paths leading to the same destination will interfere quantum mechanically, giving glory scattering in the forward direction.

Two quantum mechanical effects are of great importance. *A particle with a certain impact parameter might approach the attractive region of the potential in such a way that it is deflected towards the repulsive core, which then repels it out through the attractive region to continue its flight in the forward direction. Some molecules, however, also travel in the forward direction because they have impact parameters so large that they are undeflected. The wave functions of the particles that take the two types of path interfere, and the intensity in the* ***forward*** *direction is modified. This effect is called* **glory scattering**. [To see this effect with light rays, look at a bright moon in a sky with thinly dispersed clouds. A bright halo is seen around the moon.]

The second effect is a strongly enhanced scattering in a ***non-forward*** direction. This effect is called **rainbow scattering** because the same mechanism accounts for the appearance of an optical rainbow. *As the impact parameter decreases, there comes a stage when the scattering angle passes through a maximum and the interference between the paths results in a strongly scattered beam*. The **rainbow angle** is the angle for which $d\theta/db = 0$ and the scattering is strong. The detailed analysis of scattering data can be very complicated, but the main outcome is clear: the intensity distribution of the scattered particles can be related to the intermolecular potential, and a detailed picture can be built up of its radial and angular variation. Testing of the effects of van der Waals interaction and Lennard-Jones potential becomes possible.



When b is very small, a maximum scattering angle is reached, and numerous paths interfere, giving rise to rainbow scattering

MOLECULAR COLLISION THEORY & GAS-PHASE REACTION DYNAMICS

Assumptions of the kinetic theory of gases and rates of gas-phase reactions (chemical kinetics):

1. Gases consist of particles moving in all directions with velocities ranging from zero to very high values.
2. The velocities of the particles at any given temperature follow a Gaussian (or Maxwell-Boltzmann) distribution.
3. The mean velocity of the particles is directly proportional to the temperature.
4. The particles collide with each other and with the walls of the vessel during their random motion.
5. These collisions are perfectly elastic (the total momentum is conserved).
6. Reactions take place when molecules collide with each other. Therefore rate of a reaction must be proportional to the collision frequency.
7. The rates of reactions increase with temperature since the velocity of the molecules and therefore the collision frequency increases.

8. All collisions do not lead to reaction. The colliding molecules must have a certain minimum energy called activation energy for successful reaction.

Dependence of the reaction rate on activation energy and temperature are given by the empirical Arrhenius equation:

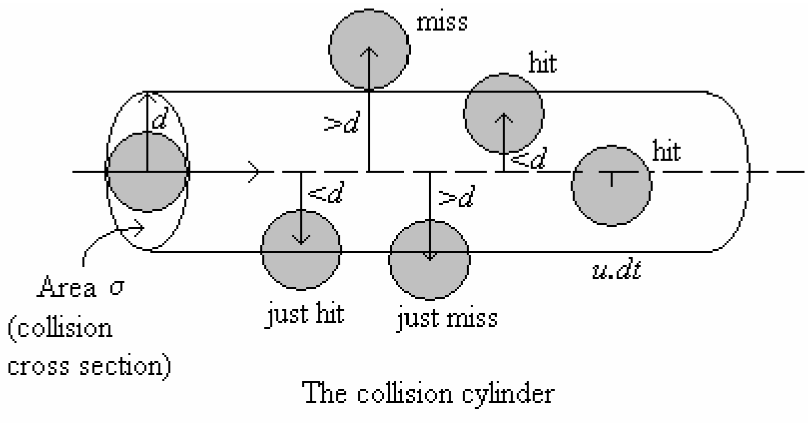
$$\frac{d\ln k}{dT} = \frac{E_a}{\mathrm{RT}^2} \qquad \text{or} \qquad \ln k = \ln A - \frac{E_a}{RT} \qquad \text{or} \qquad k = Ae^{\frac{-Ea}{RT}}$$

The rates of reactions calculated on the basis of the aforesaid assumptions give very high values compared to the experimentally obtained values. Therefore modifications are necessary taking into account the following factors also:

1. Collisions between real molecules are not perfectly elastic.
2. All collisions with the right activation energy cannot be fruitful. The orientations of the molecules at the time of collision are also important.

Till now, examination of kinetics at a molecular level was not possible, and all the above were only intelligent assumptions about the nature of chemical reactions. However, with the development the molecular beam apparatus in the 1950s by Kusch and coworkers at the Columbia University, narrow beams of molecules having a fixed velocity could be obtained (for description and diagram of the apparatus, see earlier discussion on molecular interaction in beams). Using this, the actual number distribution of molecules having different velocities could be obtained and the Maxwell-Boltzmann distribution verified. The other assumptions of the kinetc theory and rates of reactions could also be studied and verified at a molecular level. The ensuing discussion is an introduction to such studies.

The relationship of mean free path and collision frequency to collision cross section:



The collision cylinder

Imagine the molecules to be hard spheres (so that collisions are elastic) of diameter *d*. For the time being, let us also imagine that only the molecule under consideration is moving while all the others are stationary. Then, when our molecule moves along a straight line, it will collide with all other molecules that lie within a cylinder of diameter *2d* surrounding its path. *The area of cross section of this collision cylinder is the* **collision cross section**, σ. The area $\sigma = \pi d^2$. If we are considering the motion of our molecule with a velocity u over an infinitesimal time interval dt, then the length of the collision cylinder is $u.dt$. The volume of the cylinder is $\sigma.u.dt$. If the number density of molecules (ie. number of molecule per unit volume) is ρ, then the number of collisions dN_{coll} in the time interval dt will be

$$dN_{coll} = \rho.\sigma.u.dt$$

Therefore the **collision frequency** (ie. number of collisions per second) z_A is given by

$$z_A = \frac{dN_{coll}}{dt} = \rho\sigma u = \rho\sigma\left(\frac{8\mathrm{k_B}T}{\pi m}\right)^{1/2}$$

where k_B is the Boltzmann constant, T the temperature and m the mass of the particles. If all collisions lead to reactions, then the collision frequency should be equal to the **rate of reaction**.

In the above treatment, we have considered only one particle as moving while all others were fixed. If two different particles of mass m_1 and m_2 are moving relative to each other, then the velocity of one relative to the other can be obtained by considering them as one particle with a reduced mass $\mu = m_1m_2/(m_1+m_2)$ moving with respect to the other being fixed. If both particles are of the same mass, then $\mu = m/2$ and it can be shown that the relative velocity $u_r = 2^{1/2}u$. Therefore:

$$z_A = \rho\sigma u_r = 2^{1/2}\rho\sigma u \qquad (1)$$

Since the velocity (distance traveled per second) is u and the number of collisions per second is z_A, the **mean free path l** (distance between collisions) is given by:

$$l = \frac{u}{z_A} = \frac{u}{2^{1/2}\rho\sigma u} = \frac{1}{2^{1/2}\rho\sigma}$$

Calculation of the rate of a bimolecular gas-phase reaction using hard-sphere collision theory and an energy-dependent reaction cross section

Bimolecular gas-phase reactions are among the simplest elementary kinetic processes that occur in nature. The simplest gas-phase reaction is the hydrogen exchange reaction:

$$H_A + H_B\text{-}H_C \rightarrow H_A\text{-}H_B + H_C$$

Another reaction more convenient to study is:

$$F(g) + D_2(g) \rightarrow DF(g) + D(g)$$

In the following discussions, we will examine some of the current models used in the study of such reactions. The simple general reaction we shall consider is:

$$A(g) + B(g) \rightarrow \text{products}$$

The rate of this reaction is given by: $$v = -\frac{d[A]}{dt} = k[A][B] \qquad (2)$$

According to the earlier discussion of hard sphere collisions, this should be equal to the collision frequency. Therefore using equation (1), we get

$$v = Z_{AB} = \sigma_{AB}.u_r.\rho_A.\rho_B \qquad (3)$$

where Z_{AB} is the frequency of collision between A and B molecules, σ_{AB} is the collision cross section and ρ_A, ρ_B are the number densities of A and B molecules. The collision cross section is given by:

$$\sigma_{AB} = \pi(d_{AB})^2$$

where d_{AB} is the sum of the radii of the two colliding spheres. The collision frequency Z_{AB} has units of $collisions.m^{-3}.s^{-1}$, where the unit "collisions" is usually omitted. Z_{AB} also gives the number of product molecules formed per unit volume per unit time, which is the rate constant. Comparing equations (2) and (3), we get:

$$k = \sigma_{AB}.u_r \qquad \text{(since [A] = } \rho_A \text{ and [B] = } \rho_B) \qquad (4)$$

The rate constant k has units of $Z_{AB}/\rho_A.\rho_B$ or $molecules.m^{-3}.s^{-1}/(molecules.m^{-3})^2$ or $molecule^{-1}.m^3.s^{-1}$. To convert into the familiar units of $dm^3.mol.s^{-1}$ (1 mole = N_A molecules where N_A is the Avogadro number and 1 m^3 = 1000 litres), k has to be divided by 1000 N_A. Therefore:

$$k = 1000.N_A.\sigma_{AB}.u_r \ dm^3.mol.s^{-1}.$$

The rate constants calculated by the above hard-sphere collision theory equation are found to be about 30 orders of magnitude larger than experimentally observed rate constants! Further, since $u_r \propto T^{1/2}$, this theory predicts that k should show a temperature dependence of $T^{1/2}$, whereas Arrhenius equation and experimental measurements generally show that k is exponentially dependent on ${}^1/_T$. Therefore the above theory requires modification.

Effect of collision energy

We assumed that each pair of reactant molecule approach with a relative speed of u_r, but actually they approach each other with a distribution of speeds. As two molecules collide, the valence electrons of the two molecules repel each other so that no reaction can occur unless the relative speed is sufficient to overcome the repulsive force. The first step in the modification to take the speed dependence into account is to introduce a **reaction cross section $\sigma_r(u_r)$** which depends on the speed of reactant molecules in place of the earlier collision cross section σ_{AB}. The rate constant for all molecules colliding with a relative speed of u_r is given by an equation similar to equation (4).

$$k(u_r) = u_r.\sigma_r(u_r) \qquad (5)$$

To obtain the calculated rate constant k, we must average the right hand side of the above equation over all possible collision speeds ie. integrate the equation within limits 0 to ∞. Further, to compare the result with the traditional Arrhenius form of k, we have to change the dependent variable from u_r to E_r, the relative kinetic energy.

$$E_r = \tfrac{1}{2}\,\mu.u_r^2$$

$$\therefore\ u_r = (2E_r/\mu)^{1/2}$$

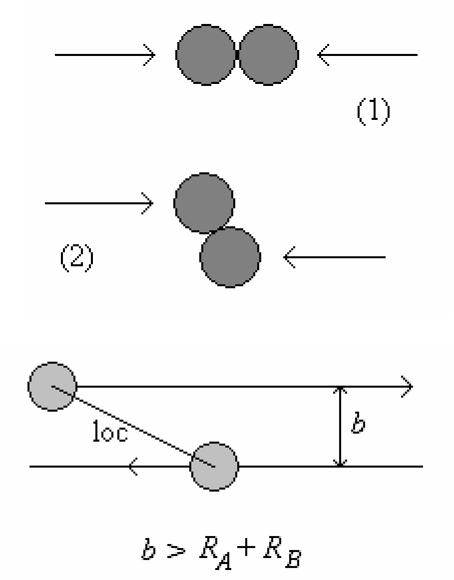
Then the **energy dependence of the reaction cross section** is represented by **$\sigma_r(E_r)$** such that $\sigma_r(E_r) = 0$ when $E_r < E_0$ and $\sigma_r(E_r) = \pi(d_{AB})^2$ when $E_r > E_0$, where E_0 is the threshold energy to overcome repulsion. Introducing these changes and avoiding the involved mathematics, we get an expression for k of the form:

$$k = u_r.\sigma_{AB}.e^{-E_0/k_BT}\left(1+\frac{E_0}{k_BT}\right) \qquad (6)$$

where σ_{AB} is the hard-sphere collision cross section. **The rate constant calculated using this expression gives a value a few orders of magnitude higher than the experimental value**. Therefore the theory has to be further modified. Different models for $\sigma_r(E_r)$ must now be tested which will give different expressions for k. The validity of any model has to be tested experimentally.

Effect of collision geometry

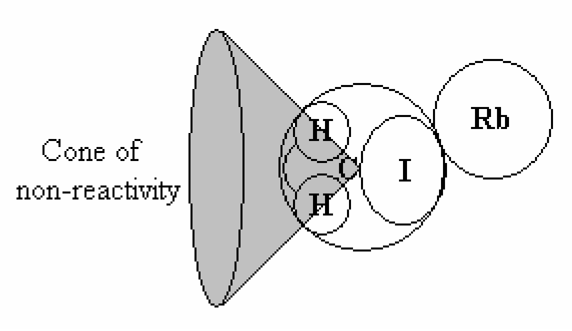
The simple energy-dependent reaction cross section used to derive equation (6) is not realistic. To see why, let us consider the following reaction geometries. The line joining the centres of the two colliding spheres is called the **line of centres (loc)**. In the first case, the molecules approach along the line of centeres and will come to a stop after a head-on collision. The full energy of the impact will be used for reaction. But in the second case, the molecules are not approaching along the line of centres, and will undergo only a grazing collision. Most of the kinetic energy of the molecules still remains with them as they fly apart. Only that component of the kinetic energy which lies along the line of centres will be useful for reaction. Thus a reasonable model for the energy-dependent reaction cross section $\sigma_r(E_r)$ must depend on the component of the kinetic energy which lies along the line of centres. This is called the **line-of-centres model** for $\sigma_r(E_r)$. If we denote the relative kinetic energy along the line of centeres by E_{loc}, then we are assuming that the reaction occurs when $E_{loc} > E_0$. The reaction cross section must depend on the **impact parameter *b***, which is the perpendicular distance between the lines of motion of the two spheres. If $b = 0$, the molecules hit head-on, and if $b > d_{AB}$ ($d_{AB} = R_A + R_B$), the molecules will pass on without colliding and the collision cross section must be equal to zero. The derivation is a bit geometrically involved and is not discussed here. But the result is such that $\sigma_r(E_r) = 0$ when $E_r < E_0$ and $\sigma_r(E_r) = \pi(d_{AB})^2\left(1-\frac{E_0}{E_r}\right)$ when $E_r > E_0$. Then the rate equation for the bimolecular gas-phase reaction becomes:



Effect of impact parameter *b*

$$k = u_r.\sigma_{AB}.e^{-E_0/k_BT} \qquad (7)$$

which differs from equation (6) by a factor of $\left(1+\frac{E_0}{k_B T}\right)$. But the results calculated using equation (7) are still higher than the experimental values by several orders of magnitude. Therefore the theory requires further modifications.

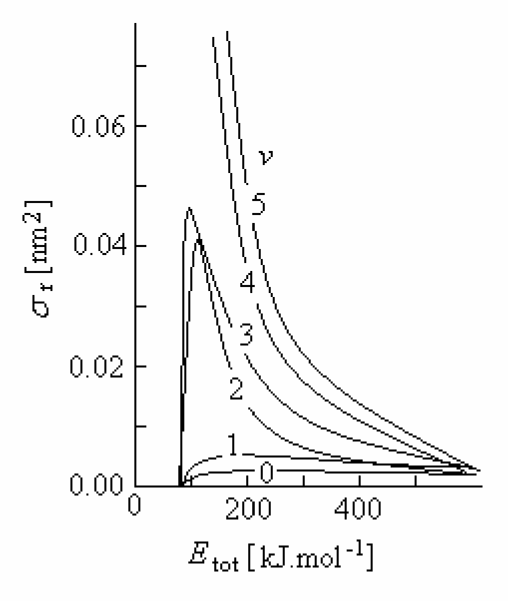


Effect of the orientation of colliding molecules

Results show that the hard-sphere collision theory does not accurately account for the magnitude of the Arrhenius *A* factor. One of the fundamental flaws of this model is the assumption that every collision of sufficient energy is reactive. In addition to an energy requirement, the reacting molecules may need to collide with a specific orientation for the chemical reaction to occur. For example, consider the reaction:

$$Rb(g) + CH_3I(g) \rightarrow RbI(g) + CH_3(g)$$

Experimental studies reveal that this reaction occurs only when the rubidium atom collides with the iodomethane molecule in the vicinity of the iodine atom. Collisions between rubidium and the methyl end of the molecule do not lead to reaction. This is indicated by the cone of nonreactivity in the figure. Since the earlier model does not take the effect of molecular orientation into account, it must overestimate the rate constants for reactions that are orientation dependent. However, this steric factor alone cannot account for the significant differences observed between the experimental and calculated Arrhenius *A* factors. Therefore the theory requires still further modification.



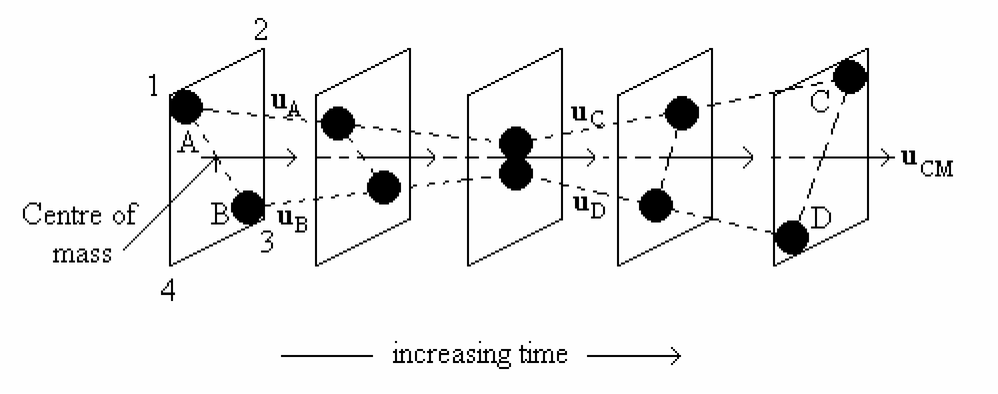
Effect of internal energy of the reactants

Reaction cross sections for hydrogen molecular ion with atomic helium are plotted in the figure.

$$H_2^+(g) + He(g) \rightarrow HeH^+(g) + H(g)$$

Each curve corresponds to the reactant H_2^+ in a specific vibrational state. For vibrational states v = 0 to v = 3, there is a threshold energy of about 70 kJ.mol^{-1}. This is because for H_2^+ molecules with vibrational quantum number v = 0 to v = 3, the total vibratonal energy is less than E_0. Additional translational energy is required to initiate reaction in these states. Molecules having v > 3 do not require additional translational energy sice their vibrational energy is greater than E_0. The internal energy of a molecule is distributed among the discrete rotational, vibrational and electronic states. Data such as in the figure tell us that chemical energy depends not only on the total energy of the reacting molecules but also on how that energy is distributed among these internal levels. Simple hard-sphere collision theory considers only the translational energy of the molecules. Energy can also be exchanged between the different degrees of freedom during the reactive collisions. For example, vibrational energy can be converted to translational energy and vice versa.

A reactive collision can be described by a centre-of-mass coordinate system



Consider the reaction A(g) + B(g) → C(g) + D(g). For simplicity we will assume there are no intermolecular forces. Before collision the molecules A and B are traveling with velocities u_A and u_B respectively. The collision generates products C and D moving away with velocities u_C and u_D respectively. We will describe the collision process in the centre-of-mass coordinate system. The idea is to view the collision from the centre of mass of the two colliding molecules. The centre of mass lies along the vector $r = r_A \rightarrow r_B$ that connects the centres of the two colliding molecules. The location of R, the centre of mass, on this vector depends on the masses of the two molecules and is defined by:

$$R = \frac{m_A r_A + m_B r_B}{m_A + m_B} \qquad \text{and} \qquad u_{CM} = \frac{m_A u_A + m_B u_B}{m_A + m_B}$$

where u_{CM} is the velocity of the centre of mass. Then it can be shown that the total kinetic energy of the reactants consist of two components, one depending on the velocity of the centre of mass, and the other on the relative velocity of the molecules.

$$KE_{react} = \frac{1}{2} M u_{CM}^2 + \frac{1}{2} \mu u_r^2$$

where M is the total mass (m_A+m_B) and μ is the reduced mass $m_A m_B/(m_A+m_B)$.

Alternative treatment of gas-phase reaction dynamics: The symbols used in the equations and the general approach given in Atkins, Physical Chemistry 6th Edn., is slightly different, but gives the same overall results. This treatment is discussed below:

In this treatment, the symbol $\bar{c}_{rel}$ is used to represent relative velocity of the colliding molecules instead of 'u_r' in the earlier discussion. Number density (number of molecules per litre) of molecules of A is given by N_A *[A]*, where N_A is the Avogadro number and *[A]* the number of moles of A per litre. The **collision frequency** '*z*', (which is the number of collisions encountered by a single molecule in unit time) is then given by:

$$z = \sigma \bar{c}_{rel} N_A [A] \qquad (8)$$

which is similar to equation (1) in the earlier discussion. But

$$\bar{c} = \left(\frac{8kT}{\pi m} \right)^{\frac{1}{2}}; \qquad \bar{c}_{rel} = 2^{\frac{1}{2}} \bar{c} \quad \text{and} \quad \mu = \tfrac{1}{2} m \text{ for a single type of molecule A.}$$

Substituting in equation (8) we get collision frequency for one type of molecules A as:

$$z_A = \sigma \bar{c}_{rel} N_A[A] = \sigma \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} N_A[A] \qquad (9)$$

Then the total **collision density** 'Z' (which is the total number of collisions encountered by all the molecules together) is obtained by multiplying the collision frequency with the number density of A molecules:

$$Z_{AA} = \frac{1}{2} z_A N_A[A] = \frac{1}{2} \sigma \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} N_A[A] N_A[A]$$

The factor ½ is introduced to account for the fact that a single collision of molecule A with another A may be counted as two different collisions (first A with second A, and also as second A with first A). Thus:

$$Z_{AA} = \frac{1}{2} \sigma \bar{c}_{rel} (N_A)^2 [A]^2 = \frac{1}{2} \sigma \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} (N_A)^2 [A]^2 \qquad (10)$$

or if the mass of A is directly used, $Z_{AA} = \sigma \left(\frac{4kT}{\pi m} \right)^{\frac{1}{2}} (N_A)^2 [A]^2$ (11)

If collisions are between two different types of molecules A and B, then the factor ½ is not necessary, and the collision density is given by:

$$Z_{AB} = \sigma \bar{c}_{rel} (N_A)^2 [A][B] = \sigma \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} (N_A)^2 [A][B] \qquad (12)$$

Collision densities may be very large. For example, in nitrogen at room temperature and pressure, with d = 280 pm, $Z = 5 \times 10^{34}$ m^{-3} s^{-1}.

Using the same arguments for the influence of activation energy E_a, and comparing with equation (7),

$$k = z_A = \sigma \bar{c}_{rel} N_A[A] e^{-\frac{E_a}{RT}} = \sigma \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} N_A[A] e^{-\frac{E_a}{RT}} \qquad (13)$$

Correction for all other factors influencing the reaction, such as orientation, internal energy of molecules etc. are introduced through a "**steric factor**" P, so that the **reactive cross section** $\sigma^* = P\sigma$. Thus,

$$k = P \sigma \bar{c}_{rel} N_A[A] e^{-\frac{E_a}{RT}} = P \sigma \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} N_A[A] e^{-\frac{E_a}{RT}} \qquad (14)$$

Comparing with the empirical Arrhenius equation $k = Ae^{\frac{-Ea}{RT}}$ where A is called the pre-exponential factor, the pre-exponential factor as given by molecular dynamical calculations is

$$P \sigma \bar{c}_{rel} N_A[A] \quad \text{or} \quad P \sigma \left(\frac{8kT}{\pi\mu} \right)^{\frac{1}{2}} N_A[A] \qquad (15)$$

Collision frequency when pressure of the gas is given:

Form equation (8), $z = \sigma \bar{c}_{rel} N_A[A]$, or $z = \sigma \bar{c}_{rel} N_A$ for 1 mole.

Since number density of molecules (number of molecules per unit volume) is $\frac{N_A}{V}$, and $V = \frac{RT}{P}$,

number density = $\frac{PN_A}{RT} = \frac{P}{kT}$. Therefore, $z = \sigma \bar{c}_{rel} \frac{P}{kT}$ (16)

In dimerisation of methyl radicals at 25°C, the experimental pre-exponential factor is 2.4×10^{10} L mol^{-1} s^{-1}. What are (a) the reactive cross section and (b) the p-factor for the reaction, if C–H bond length is 154 pm. {April 2005}
[Ref: (1) Physical Chemistry, Atkins, 6th edn, page 846, problem 27.1; (2) valuation scheme for this exam.]

d = 2 × 154 pm = 308 pm = 308×10^{-12} m.

(a) Collision cross section $\sigma = \pi d^2 = 3.14 \times (308 \times 10^{-12})^2 \text{ m}^2 = 297872.96 \times 10^{-24} \text{ m}^2$
$= 2.98 \times 10^{-19} \text{ m}^2$

(b) According to Arrhenius' theory, rate constant $k = Ae^{-E_a/RT}$, where 'A' is the collision frequency factor, or the pre-exponential factor. According to reaction dynamics predictions,

$$A = \sigma \bar{c}_{rel} N = \pi d^2 \left(\frac{8kT}{\pi\mu}\right)^{\frac{1}{2}} N$$, where μ is the reduced mass; $\mu = \frac{m_1 m_2}{m_1 + m_2}$.

$$\text{Mass of one methyl radical} = \frac{15}{6.023 \times 10^{23}} \times 10^{-3} \text{ kg} = 2.49 \times 10^{-26} \text{ kg}$$

$$\therefore \mu = \frac{(2.49 \times 10^{-26} \text{ kg}) \times (2.49 \times 10^{-26} \text{ kg})}{2.49 \times 10^{-26} \text{ kg} + 2.49 \times 10^{-26} \text{ kg}} = 1.245 \times 10^{-26} \text{ kg}$$

$$A = 3.14 \times (308 \times 10^{-12} \text{ m})^2 \times 6.023 \times 10^{23} \times \left(\frac{8 \times 1.38 \times 10^{-23} \text{ JK}^{-1} \times 298 \text{K}}{3.14 \times 1.245 \times 10^{-26} \text{ kg}}\right)^{\frac{1}{2}}$$

$$= 3.14 \times 94864 \times 10^{-24} \text{ m}^2 \times 6.023 \times 10^{23} \times 917.39 \text{ m s}^{-1} = \underline{\underline{16.458 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}}.$$

But given that the experimental value of A = 2.4×10^{10} L mol^{-1} s^{-1}
= 2.4×10^7 m^3 mol^{-1} s^{-1} ;

$$P = \text{steric factor} = \frac{\text{experimental value of A}}{\text{calculated value of A}} = \frac{2.4 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}{16.458 \times 10^7 \text{ m}^3 \text{ mol}^{-1} \text{ s}^{-1}}$$
$= \underline{\underline{0.1458}}$.

Then in (a), Reaction cross section $\sigma^* = \sigma \times P = 2.98 \times 10^{-19} \text{ m}^2 \times 0.1458$
$= \underline{\underline{0.4345 \times 10^{-19} \text{ m}^2}}$.

Calculate the collision frequency 'z' and the collision density 'Z' in CO. R = 180 pm at 25°C and 100 kPa. What is the percentage increase when the temperature is raised by 10 K at constant volume? {April 2005}

[Ref: (1) Physical Chemistry, Atkins, 6th edn, page 844, Exercise 27.1(b); (2) valuation scheme for this exam.]

Collission frequency z $= \dfrac{\sigma \bar{c}_{rel} P}{kT}$, where 'P' is the pressure and $\bar{c}_{rel} = \left(\dfrac{8kT}{\pi\mu}\right)^{\frac{1}{2}}$

$\mu = \dfrac{m_1 m_2}{m_1 + m_2} = \dfrac{1}{2} m$ for a single type of molecule;

Therefore $\mu = \dfrac{1}{2} \times \dfrac{28}{6.023 \times 10^{23}} \times 10^{-3} kg = 2.3244 \times 10^{-26}\, kg$. and $\sigma = \pi d^2$.

$$z = \frac{\sigma \bar{c}_{rel} P}{kT} = \pi d^2 \times \frac{8^{\frac{1}{2}} (kT)^{\frac{1}{2}}}{\pi^{\frac{1}{2}} \mu^{\frac{1}{2}}} \times \frac{P}{kT} = \left(\frac{8\pi}{\mu kT}\right)^{\frac{1}{2}} d^2 P$$

$$= \left(\frac{8 \times 3.14}{2.3244 \times 10^{-26} kg \times 1.38 \times 10^{-23} kgm^2 s^{-2} K^{-1} \times 298K}\right)^{\frac{1}{2}} \times (2 \times 180 \times 10^{-12} m)^2 \times 10^5 kgm^{-1} s^{-2}$$

$= \underline{\underline{6.6433 \times 10^9\ s^{-1}}}$.

Collision density 'Z' $= \dfrac{1}{2} z \dfrac{N}{V}$; But $\dfrac{N}{V} = \dfrac{P}{kT}$; Therefore:

$$Z = \frac{Pz}{2kT} = \frac{10^5 kgm^{-1} s^{-2} \times 6.6433 \times 10^9 s^{-1}}{2 \times 1.38 \times 10^{-23} kgm^2 s^{-2} K^{-1} \times 298K} = \underline{\underline{8.0771 \times 10^{34}\ m^{-3}\ s^{-1}}}.$$

Percent increase in collision frequency $= \dfrac{dz}{z} \times 100$; But $\dfrac{1}{z} \times \dfrac{dz}{dT} = \dfrac{1}{\bar{c}} \times \dfrac{d\bar{c}}{dT} = \dfrac{1}{2T}$

Hence $\dfrac{dz}{z} = \dfrac{dT}{2T} = \dfrac{10K}{2 \times 298K} = 0.0167$; Therefore percentage increase $= \underline{\underline{1.67\%}}$