Molecular Reaction Dynamics

Reference:

1. Molecular Reaction Dynamics and Chemical Reactivity, R. D. Levine and R. B. Bernstein, Oxford University Press, Oxford 1987.
2. Molecular Reaction Dynamics, R. D. Levine, Cambridge University Press, Cambridge, 2005.
3. Femtochemistry-Ultrafast Dynamics of the Chemical Bond, A. H. Zewail, World Scientific, New Jersy, Singapore, 1994.

[Preface: 2-xi]

Molecular reaction dynamics unfolds the history of change on the molecular (atomic) level. It asks what happens on the atomic length and time scales as the chemical change occurs. Not just the static structure, we would also like to know how this structure can evolve in time and what we can do to control this evolution. One would like to write the history of the change or to be a conductor and orchestrate (to arrange or manipulate, esp. by means of clever or thorough planning or maneuvering) the motion.

Kinetics

In physical chemistry we have characterized the dependence of the rate of the chemical transformation on the concentrations of the reactants. This provides the concept of a chemical reaction rate constant *k*. The rate of a bimolecular reaction between species A and B is proportional to the reactant concentrations, [A] and [B]. The proportionality constant is the rate constant, *k(T)*, defined by the rate law as

$$-\frac{d[A]}{dt}=-\frac{d[B]}{dt}=k(T)[A][B].$$

The magnitude of the rate constant depends on a variety of factors under experimental control, most notably the temperature. Arrhenius showed that the temperature dependence of the rate constant often took on the simple form:

$$k(T)=Ae^{-E_a/RT}\ .$$

[2-p1]

It was then realized that the net transformation often proceeds by a series of elementary steps. A key progress was the identification of the reaction mechanism, which is a collection of the elementary processes that leads to the observed stoichiometry and explains how the overall reaction proceeds. The fact that a mechanism "explains" the experimental results, however, is not a proof that the mechanism is correct. Bulk kinetic studies are carried out at a controlled temperature, i.e. under condition of thermal equilibrium. The measured thermal rate constants refer to an average over all accessible reactant states weighted by the populations of those states at that temperature. As a mater of fact such averages hide detailed information about what factors really cause the reaction to proceed. Kinetics study leads to the averaged "macroscopic" properties of the bulk system. What we need is the ability to examine the individual processes and preferably to do so with selection of the energetic state of the reactants.

Molecular reaction dynamics [2-p2,3]

Unlike kinetics, reaction dynamics is the study of the molecular level mechanism of elementary chemical and physical processes. It seeks to understand what actually takes place at the molecular level when a change, chemical or physical, occurs. An understanding of the dynamic behavior of a system at the molecular level is the key to the interpretation of the "macroscopic" kinetics of the bulk system. As an example, when molecular chlorine gas is introduced into a vessel containing bromine vapor, a chemical reaction does take place, and it can be monitored in time by a change in the color. The net chemical change in the vessel is $Cl_2 + Br_2 \rightarrow 2BrCl$. The reaction is observed to be of second order in the concentration of each reactant. Yet on the molecular level the elementary reaction $Cl_2 + Br_2 \rightarrow 2BrCl$ does not take place, which is verified experimentally.

Molecular reaction dynamics is the study of elementary processes and the means of probing them, understanding them, and controlling them. Current rational drug design includes the consideration the approach of the intended drug to its receptor and how both are modified as a result of their interaction. Chemists nowadays require a molecular-level understanding of reactivity. It is not just sufficient to prepare desired product or to optimize conditions such as temperature or solvent or catalyst so as to get high reaction rate and purity.

Kinetic study is relevant to net change, at or near thermal equilibrium, in the bulk. The study of dynamics however, allows us to go beyond that. For example, exciting vibrational motion in either or both the reactants may help the $Cl_2 + Br_2$ to proceed more rapidly by forming a four-center transition state. In bulk, when the reactants are intentionally arranged to be in thermal equilibrium, a particular mode can not be energized preferentially.

We would like to understand how the reactants evolve over time to products. The application of spectroscopy, specifically lasers, to molecular reaction dynamics has allowed us to understand the structural question in time domain, even for time comparable to or shorter than the periods of molecular vibrations.

The concept of the experimental and theoretical methods of molecular reaction dynamics – is all that is necessary to be able to view the very process of chemical change.

"I am grateful to many people who, over the years, joined me to watch the molecules dance to the tune of time. This book is dedicated to Mira who is able to make us join the dance." – Dedication by Raphael D. Levine in him book Molecular Reaction Dynamics.

An example: Energy disposal in an exoergic chemical reaction

Determination of energy disposal in exoergic atom-molecule exchange reactions: one example of such a system is the H-atom transfer reaction

Cl + HI →ClH + I

In the course of this reaction the relatively week HI bond is broken and replaced by stronger HCl bond. The reaction liberates chemical energy.

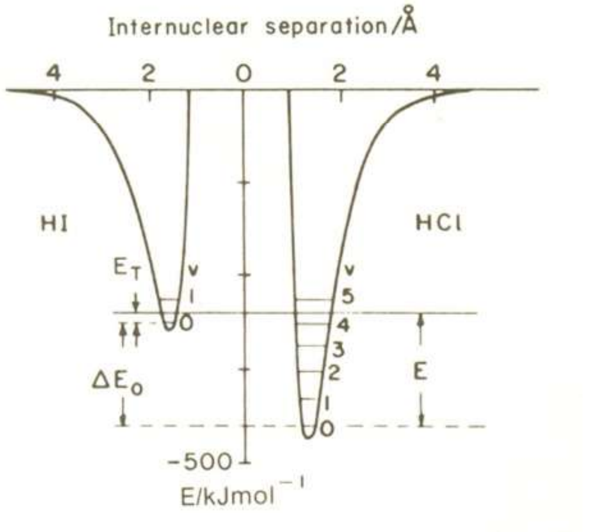


Figure 1:
The energetics of the reaction Cl + HI →ClH + I. The plot is drawn so as to a have zero of energy common to the reactants and products. This is achieved by taking the zero of energy when all the three atoms are well separated and are at rest. The exoergicity, ΔE_0, of the reaction is the difference in bond dissociation energies (= D_0(HI)-$D_{0(\mathrm{HCl})}$ = 134 kJ/mol). E_T is the relative translational energy of the relative motion of Cl and HI.

Exoergicity is about 134 kJ/mol (~ 32 kcal/mol), this amount energy is large by chemical standards. One should not confuse the exoergicity of the reaction with the exothermicity (or heat release) of a bulk chemical processes. In the bulk there are subsequent collisions where the nascent products collide with other molecules. In reaction dynamics we focus attention on the elementary chemical event. We are dealing with the nascent products of an isolated triatomic system ClHI. We ask when this system of three atoms evolves into the products HCl+I, where is the liberated energy going to go?

We center our attention on the isolated system and ask to probe the products prior to their engaging in any further action. The question is: immediately after the reactive collision of Cl + HI is over, how is the energy distributed among the reaction products? Even if both products are formed in their ground electronic states, we need to determine the partitioning of the excess energy on the chemical reaction into three remaining modes of energy disposal. They are vibration of HCL, rotation of HCl; and relative translation of I and HCl recoiling from each other. But what is the distribution of energy among these three modes?

When a reaction is studied in the “bulk” gas phase, the nascent products soon collide with other molecules, energy is transferred upon collision (thus becoming effectively partitioned among all molecules), and the overall reaction exoergicity is finally liberated in its most degraded form, i.e., heat. In macroscopic terms, the reaction is exothermic, i.e., $\Delta H^0 < 0$. The microscopic approach of molecular dynamics, however, is concerned with the outcome of the individual reactive collisions.

Distribution of products' energy states

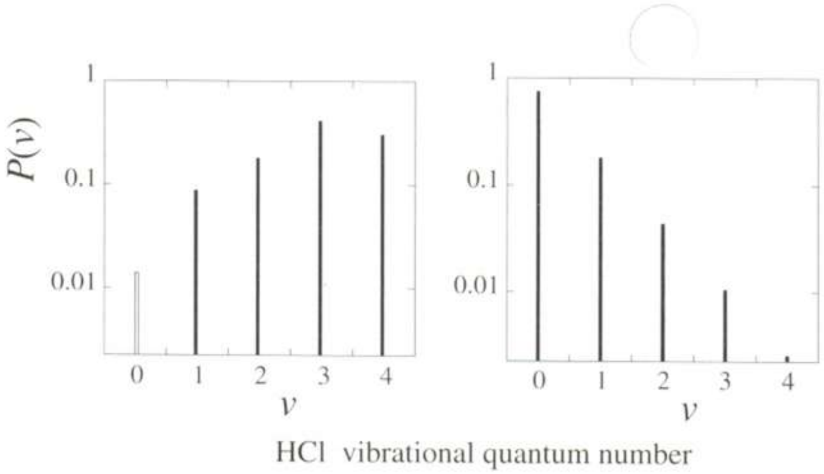


Figure 2:
Left: distribution measured for the nascent HCl product of Cl + HI reaction (Chemiluminescence in the IR), loosely showing a population inversion; P(0) is not available as v = 0 state can not emit infrared. However, P(0)/P(1), P(1)/P(2), and so on, can be deduced from the chemical laser data.
Right: distribution at thermal equilibrium

The figure shows on the left a typical experimental result, illustrating the distribution of energy among the vibrational states of nascent HCl, irrespective of the rotational distribution within a given vibrational state.
Vibrational quantum of HCl is ~35.5 kJ/mol.
Available energy = 134 kJ/mol + thermal energy of the reactants
The large fraction of this available energy goes into vibrational excitation of HCl, and thus by difference, only small fraction into translation recoil of HCl and I or into rotation of HCl.

The vibrational distribution on the left of the figure can be compared with that on the right, which is expected when a reaction is run under "bulk" conditions and the system has run to equilibrium. Then one would expect a Boltzman equilibrium distribution, the most probable state is v = 0, and the relative populations decline exponentially with the vibrational quantum number. The bulk population, of course, does not arise from a single elementary process but rather from a succession of energy-degrading collisions of the vibrationally energy rich HCl molecules with other available molecules.

Molecular dynamics in its "purist" approach tries to seek out and understand the truly elementary events. Thus it is more interested in the left panels of the figure than in the right. It is, however, concerned not only with the primary reactive collision process but also with the subsequent non-reactive, inelastic energy transfer steps that take the system from nascent distribution of the products to the fully relaxed one, i.e. thermal equilibrium. This Cl + HI system is not exceptional. Many exoergic reactions release a substantial part of their energy into internal modes of product excitation. To understand this observation in terms of the forces that act during the collision, we use a ‘spectator’ model.

Spectator model for products’ energy disposal:

Over simplified model of course.

One aspect of the collision is that it involves the transfer of a light atom (H) between two much heavier atoms.

For comparison one can think the CLHI triatomic system is similar in that respect to the H_2^+ molecule ion, where it is the light electron that “mediates” between the two heavy protons.

When a molecule undergoes an electronic transition we obtain insight into the distribution of the final vibrational states from Franck-Condon principle, which says that during the very fast electronic transition the heavy nuclei do not change their momentum, the nuclei merely act as spectators during the rapid electronic rearrangement. A spectator is someone who is not involved, i.e., does not feel any impulse. Naturally, from Newton’s second law one would expect that a spectator is likely to be “heavy”, because its momentum is resilient to change, the mass being the measure of the inertia to change. Thus a spectator has constant momentum.

For the present H transfer reaction we must assume that the H transfer reaction is over in a time short compared to the time required for the heavy nuclei to move substantially. The model is then the heavy iodine acts a spectator during the rapid transfer of the light hydrogen atom to the heavy chlorine atom. This implies that the momentum of the I atom before and after collision essentially the same. $p_I' = p_I$.

It is easy to realize this spectator model account for the observation that very little of the exoergicity is released as translational energy of the products. The Cl atom approaches the HI molecule with particular momentum and “captures” the H. But the H atom is so light that the momentum of the I atom is left nearly unchanged, and so too is that of the Cl atom, which is part of the HCl product. However, to be consistent with energy conservation without altering the translational motion the exoergicity of the reaction must be “deposited” in the internal motion of the HCl.

Products’ angular distribution:

According to the spectator model the product I atom should appear in the same direction as that of the incident HI while the product HCl will appear in the direction of the incident chlorine atom. One can say that this description, which has similarity like a spectator stripping picture, is qualitatively the behavior found experimentally. The product HCl appears mainly in the “forward” direction i.e., in the direction of incident Cl atom.

Note that such an argument is only possible for an isolated collision. In the bulk, however, the products would soon collide with other molecules and very rapidly lose all memory of their nascent direction of motion.

Also, one should realize that the angular distribution is rather anisotropic implies that no long-lived ClHI intermediate complex is formed. If the reaction duration were long compared to the period of rotation of such an intermediate, almost all memory of the initial directions of the reactants would be erased and the products' angular distribution would not distinguish between the forward and backward directions. Another way to anticipate the fact is that, if there were a long-lived intermediate we would not expect a very specific energy disposal due to the fact that there would be enough time for the energy to become approximately "equipartitioned" among the different modes of this intermediate.

Mode selective control of chemical reactions:

I + HCl →IH + Cl, the endoergic reaction.
Can we predict the energy requirements of this endoergic reaction and, in particular, can we enhance the reaction rate by a selective preparation of the reactants?

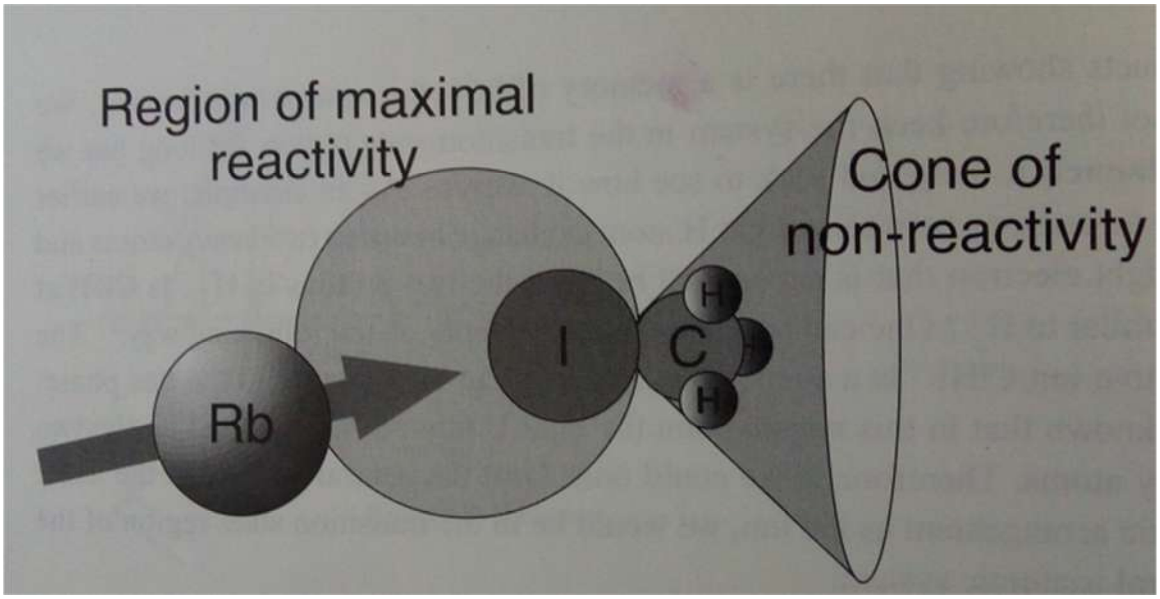
Since we are dealing with an isolated collision, the reaction enedoergicity has to be supplied by the initial energy of the reactants, I and HCl. This energy can be provided by the relative translational energy of the colliding pair and/or by the internal energy of HCl. When the energy of the I and HCl reactants just exceeds the endoergicity, and being consistent with spectator stripping mechanism, i.e., the momentum of the I atom to be nearly unchanged during the collision, the energy required for the reaction can not be provided by the relative translational energy of the reactants, I + HCl, for this would require a high initial momentum of the reactant I relative to the center of mass. The reaction endoergicity, at least just above the energy threshold for the, must therefore, be provided by the initial internal energy of the HCl.

The model based selective energy requirement is much strengthened by consideration of microscopic reversibility. [Loosely phrased, this principle states that if a transition from A to B is possible, then so is the reverse transition from B to A. By implication, if A does not go to B, B does not go to A] [2-p27]
As experiments on Cl + HI showed that at low energies vibrationally cold HI leads mainly to the formation of vibrationally hot HCl, with only a smaller fraction of the energy released as translation. Because vibrationally cold HCl is formed with a very low probability in the forward direction, it follows that for the reverse reaction involving the collision of vibrationally cold HCl with an I atom at high translational energies, most collisions are nonreactive. In contrast, collision vibrationally hot HCl molecules with I atoms will be fruitful even at low translational energies.

The steric requirements of chemical reactions:

One should note that energy, not only, is the requirement for a reaction to drive successfully. Almost always there is also a preferred direction of attack. Like, for Cl + HI reaction, the steric hindrance will be more affective and the cone acceptance for the reaction is expected to be much narrower because the Cl atom needs to reach the small H atom, which is expected to be effectively shielded by the bulky atom I.

One of the early day's examples of the steric requirement is the colliding molecular beam experiments that use oriented MeI molecules. It is found the reaction probability for the "favorable" configuration, in which Rb atom approaches from the I end, is significantly greater than that for "unfavorable" orientation, where Rb attacks from the Me side.



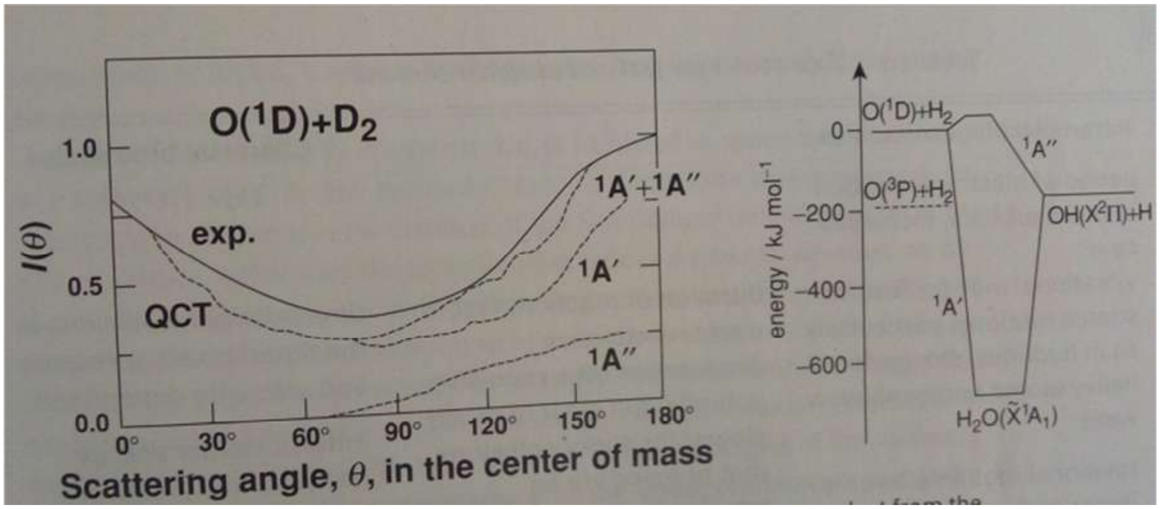
For our earlier example, the Cl + HI reaction, the steric hindrance will be more effective and the cone of acceptance for reaction is expected to be much narrower because the Cl atom needs to reach the small H atom, which we expect to be effectively shielded by the bulky I atom. The computational evidence is that in less than one thir, of all Cl +HI collisions can the Cl atom come within the cone of acceptance for reaction, a cone spanned by the H atom.

The steric requirement is a theme that takes us all the way to the docking of a drug at an active site of an enzyme.

Abstraction vs insertion reaction

The reactions we have discussed so far are all of direct abstraction type. Abstraction reactions typically show either forward or backward scattering predominantly in product angular distribution.

A different behavior shown in angular distribution of the products; a forward-backward symmetry or isotropic in nature is the indication of an insertion reaction. For example, an electronically excited O(^{1}D) atom inserts into the H – H bond. This results in the formation of a water (H – O – H) molecule and we expect the H – O – H bending motion to be energy-rich because in an insertion the O atom needs to attack in a direction perpendicular to the H – H bond and much energy is made available due to replacement of one H – H bond by two O – H bonds. The energy rich molecule can and does fall apart, but will stay bound for more than a rotational period of time. The available energy of the molecule will equally be distributed in all modes, translation, vibration and rotational mode. Because of the insertion mode, the energy is initially made available to the H – O – H bending motion. To form products we need an H atom to separate from OH. In other words, we need energy in an O – H stretch mode. It takes a while before the energy is made available from bending to stretch modes. When an O – H bond is finally broken it hardly remembers if the O atom initially came from the right and H_2 from the left, or vice versa. The products' angular distribution will therefore exhibit a forward-backward symmetry as shown in figure below.



Left: Observed angular distribution (solid line) of the OD product from the O(^{1}D) + D_2 insertion reaction. The scattering angle is defined as the angle that the velocity of the departing OD product makes with the velocity of the incident O atom in the center-of-mass system.

Right: Energetics of the reaction for abstraction (on ^{1}A'' surface) and insertion (on ^{1}A' surface) pathways.

The observed angular distribution shows a slight preference for backward scattering. This is due to the fact that OD can also be formed by abstraction when the O(^{1}D) approaches collinear to D_2. This pathway does not go through the stable intermediate complex D_2O but proceeds via the electronically excited ^{1}A'' state. We expect when the O atom runs head-on into D_2, OD will scatter backwards (which we see from the quasi-classical trajectory calculation results, shown by dashed line in angular distribution plot for ^{1}A'' surface). The OD formed by the insertion reaction indeed shows forward-backward symmetry with respect to the incident O atom (see dashed curve in angular distribution plot for ^{1}A' surface). The sum of these calculated angular distributions corroborates experimental angular distribution.

Molecular collisions:

Consider two-body, A+B, point of view.

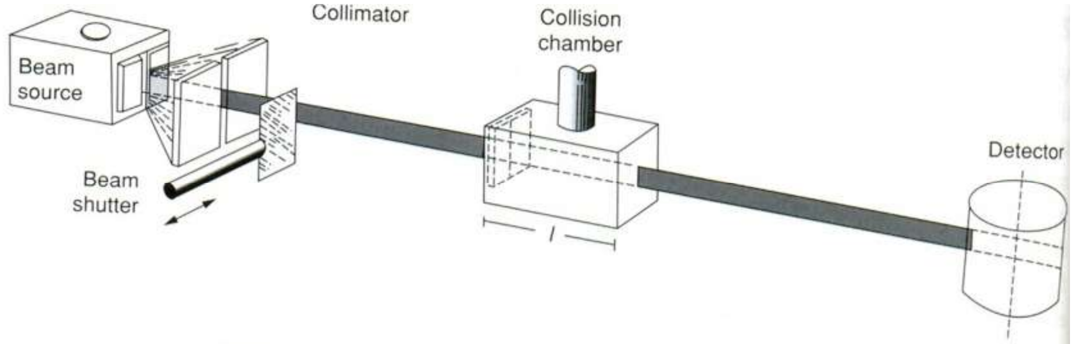


Figure 2.1 Measurement of the mean free path (schematic). A collimated beam[1] of molecules of type A passes through a collision chamber of length *l*, containing a scattering gas of type B molecules. The flux of transmitted beam molecules is measured (at the detector) as a function of the density n_B of the B molecules. From the attenuation of the A beam we can calculate the mean free path via Eq. (2.4) and the collision cross-section via Eq. (2.7).

The direction of the beam of A molecule is taken as the x axis. The flux, I(x), [defined as the number of beam molecules crossing a unit area perpendicular to the direction of beam, per unit time] at distance x along the beam $I(x) = vn_A(x)$; v is the velocity of beam molecules and n_A is the number density molecules (number of molecules per unit volume). Owing to collisions with molecules of the target gas, A molecules are deflected from the beam, resulted in decreasing the beam flux along the scattering cell length. The fractional loss in beam intensity when an A molecule traverses a short distance Δx is determined by the likelihood of a collision with a B molecule in the short distance and so must be proportional to Δx.

Probability of a collision between x and x + Δx = $\Delta x / \lambda$.

The fractional decrease in the beam flux, for sufficiently small interval Δx

$$\frac{I(x) - I(x + \Delta x)}{I(x)} = -\frac{\Delta I}{I} = \frac{\Delta x}{\lambda}$$

Taking the limit $\Delta x \to 0$ and integrating $I(x) = I(0)\exp\left(-\frac{x}{\lambda}\right)$.

The collision cross section:

We expect that the probability $\Delta x / \lambda$ of a collision in the short interval Δx to be proportional to the number density n_B of the scattering gas in the cell. Thus $\Delta x / \lambda \quad \alpha \quad n_B \Delta x$. To factor out the dependence of the mean free path on the density of the other molecules we define the collision cross section (σ) as the proportionality constant such that $\frac{1}{\lambda} = n_B \sigma$.

The collision cross section is a measure of the "size" of the two colliding molecules. On the macro scale this means that the larger the cross section, the smaller the mean free path and hence the more likely it is for a molecule in the beam of molecules to experience the collision.

From a micro scale interpretation one molecule collide with another when a force acts between them. Loosely speaking, the longer the range of force, the more likely is a collision. The implication that the cross section depends on the range and strength of the intermolecular force carries with it an obvious corollary: the magnitude of the collision cross section is a property of two molecules that are colliding.

Under standard conditions, let us set d as the range of intermolecular force so that πd^2 is a reasonable guess for the magnitude of the collision cross section.

Rate of molecular collisions:
In the macro world, the physical interpretation of the cross section (σ) is that of an effective area whose size determines the number of collisions that a particular molecule undergoes per unit time as it moves in a gas.

Assuming the cross sectional area (σ) is in a plane perpendicular to the direction of motion, the area σ sweeps, per unit time, a cylinder whose volume is σv. There are $n_B \sigma v$ B molecules in this cylinder.

Collision frequency, the number of collision per unit time of a particular A molecule in a gas of number density n_B is used to operationally define the cross-section:

$\omega = v n_B \sigma$

The number of bimolecular collision per unit time per unit volume (assuming n_A number density for A molecules) is

$Z = n_A n_B v \sigma$.

Loss of flux along the beam $-\frac{dI}{dx} = Z = n_A n_B v\sigma = k n_A n_B$

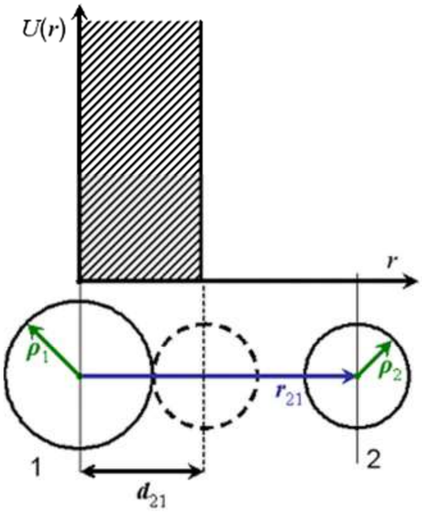
Hence $k(v) = v\sigma$ is called as collision rate constant, is not quite a conventional bimolecular rate constant. It refers to collision for which the relative velocity i.e., the beam velocity is well defined both in magnitude and direction.

At the usual “thermal” equilibrium a gas will have a distribution of velocities of the molecules. So, thermal rate constant

$k(T) = \langle k(v) \rangle = \langle v\sigma \rangle$ average over the relative velocity distribution in a gas at thermal equilibrium at the temperature T.

Molecules as hard spheres

Although unrealistic but is a useful approximation because the model is very simple and appealing one.



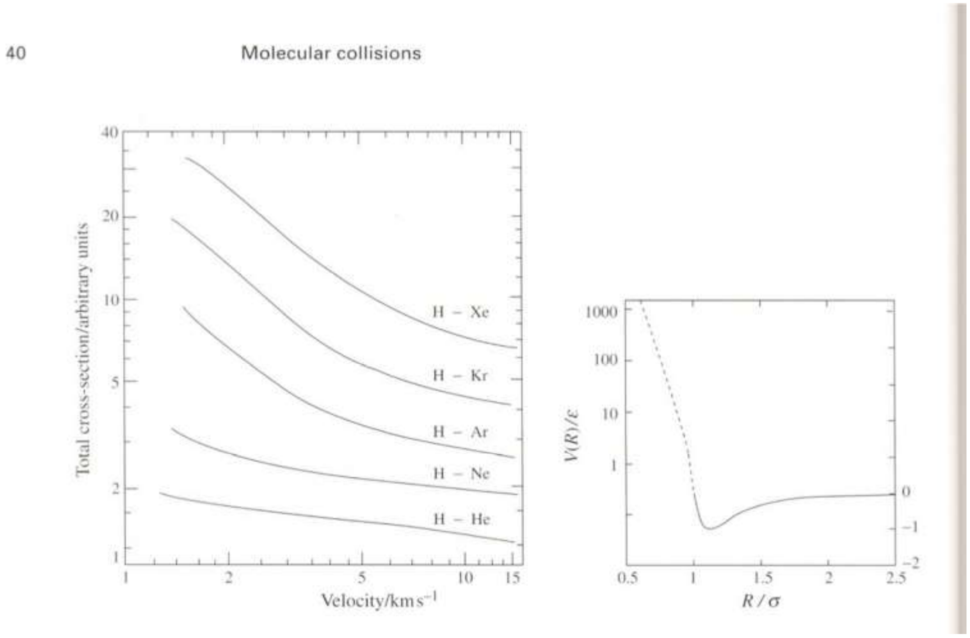
Two molecules interact as hard spheres if no force acts until the separation of the two centers decreases to some definite value, say d_{21} (as shown in the figure above). At that point the molecules cannot approach any closer. They are impenetrable i.e., they repel one another with an infinite force.

The hard-sphere interaction has clearly defined and energy-independent range, namely d, and so the collision cross-section has the exact value πd^2.

Q: Does the collision cross section depend on the relative velocity of two colliding hard-sphere molecules? The clear and loud answer to this is 'NO'.

The real molecules are not of hard-sphere type. Even then the cross-section can be interpreted in such a form, where now *d* is an effective range of the interaction. To do so we need to know more about realistic forces between molecules.

Realistic short-range repulsion:
Looking at short-range collision:
Molecules are not strictly hard spheres. So, the range d of the repulsion decreases with increasing energy of approaching molecules. The direct experimental evidence is that the collision cross section for beam scattering at well-defined relative velocity decreases slowly with relative velocity and thus collision energy.



40 Molecular collisions

There is a steeply increasing repulsion that is often approximated by
$V_{\text{Re}\,pulsive}(R) = A\exp(-R/\rho)$; ρ is the range parameter and A is strength.
Given the potential we can compute the force as

$$F(R) = -\frac{dV(R)}{dR} = \frac{A}{\rho}\exp(-R/\rho)\,.$$

This verifies that short-range potential is repulsive because the force acts so as to increase the separation R.

Realistic interatomic potentials:
Looking at long-range collision:

This observation can be anticipated as follows. As the relative velocity and hence the translational energy increases the effective collision decreases. This may be due to the fact that now beam molecules pass by so quickly that the target molecules do not feel any attraction, which they do at comparatively low relative speed. In other words there is an intermolecular potential.

As the temperature is lowered, bulk gaseous matter shows increasing evidence for attraction between molecules. Collisions at low (thermal-range) energies are sensitive mainly to the long-range attractive part of the intermolecular potential. The energy dependence of the cross-section demonstrates that a realistic intermolecular potential, has an attractive, possibly weak but long-range contribution typically of the form

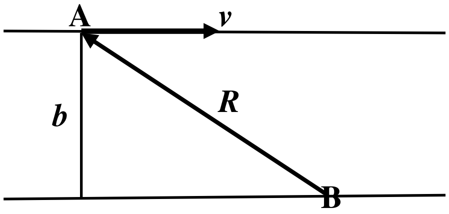
$$V_{attractive}(R) \sim -\frac{C}{R^6}\,.$$

A potential well even in the absence of chemical binding forces results from the competition between the physical long-range attractive and the short-range repulsion.

The approach motion of molecules:

To understand chemical reactions we need to know how close the two molecules will approach and how much energy is available to their relative motion. Our purpose is to argue that in every collision there is a centrifugal force that acts to prevent the molecules from getting too close in. This force is controlled by two variables, the miss distance of colliding molecules, called impact parameter and the kinetic energy of molecules before the collision when they are far apart.

We want to describe the relative motion of two particles, A and B. Connecting the two is a vector, **R,** pointing from B to A. The length of this vector, the relative distance R varies with time. The form of R(t) is nothing but what we mean a classical trajectory.



Conceptually b is miss distance, that is *b* is defined so that it is how near to one another the particles A and B approach, when there is no force acting between them. Technically, *b* is the component of the vector R that is perpendicular to **v** before collision. If b=0 the two particles run into one another. Otherwise, the larger is b the less is the initial velocity directed along **R** and the more will be the two particles miss one another because the approach motion is more off-center.

In absence of a force the **v** will continue to be along the same direction. The distance of closest approach is *b*, which is therefore given the technical name of the impact parameter.

If we allow the two particles to interact, the trajectory will no longer be a straight line and the impact parameter will no longer be exactly equal to the distance of closest approach. But impact parameter will remain well defined as the striking distance: it specifies, before the collision, how large is the component of **R** that is perpendicular to the initial velocity **v.**

Centrifugal barrier and effective potential:

Before the collision, for structureless particles, the total energy $E_T = \frac{\mu v^2}{2}$. There are two contributions to the KE. KE ***during the course of reaction*** is the rate of change of the vector **R** with time, $K = \mu\left(\frac{d\vec{R}}{dt}\right)^2 / 2$.

We have, $R^2 = v^2 t^2 + b^2$. It gives, $\frac{dR^2}{dt} = 2R\frac{dR}{dt} = v^2 2t$.

The KE of the motion along the line of centers is

$$K=\mu\left(\frac{d\vec{R}}{dt}\right)^2/2=\frac{\mu}{2}\left(\frac{v^2t}{R}\right)=\frac{\mu}{2}\left(\frac{v.vt}{R}\right)^2=\frac{\mu}{2}\left(\frac{v\sqrt{R^2-b^2}}{R}\right)^2=\frac{\mu v^2}{2}\left(1-\frac{b^2}{R^2}\right)=E_T\left(1-\frac{b^2}{R^2}\right)$$

In absence of force, the KE before the collision has to equal the KE during the collision. This conservation of energy condition implies that

$$E_T=\frac{\mu v^2}{2}=\mu\left(\frac{dR}{dt}\right)^2/2+\frac{E_Tb^2}{R^2}\quad \text{in absence of force.}$$

This equation equates KE before the collision, where $R\to\infty$, to the kinetic energy at a finite R value. Before collision the kinetic energy is due to the two molecules approaching one another. But when two molecules get closer there is another contribution arising from the rotation of the interparticle distance vector **R.** We identify this centrifugal energy term as $\frac{E_Tb^2}{R^2}$.

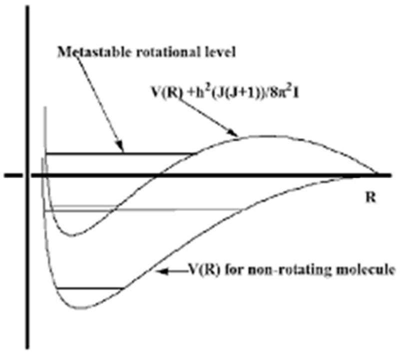
When $R>>b$ the first term dominates, representing the particles approaching one another. However, as they get closer in, more and more of the energy is being spent on the rotation of the relative distance. By R = b, all the kinetic energy is in rotation, and (dR/dt)=0, so that the particles can not get any closer.

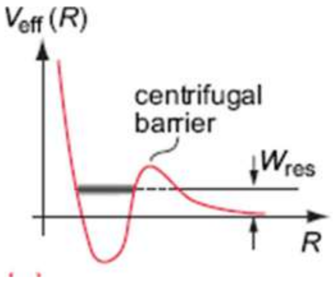
When there is a force acting between the particles, the conservation of energy reads:

$$\text{Energy = K + V(R) = }\mu\left(\frac{dR}{dt}\right)^2/2+\frac{E_Tb^2}{R^2}+V(R)=E_T$$

By our convention we take the zero of the potential energy V(R) when two particles are far apart.

It is convenient to consider the centrifugal energy and the potential energy summed together, and call the sum an effective potential: $V_{eff}(R)=\frac{E_Tb^2}{R^2}+V(R)$. The energy is then sum of the KE along the lines of centers and the effective potential. We have then the energy as a function only of the scalar quantity *R(t).*





Due to centrifugal barrier there are quasibound states those decay after certain time and are called reactive scattering resonances.

Reaction cross section – a macroscopic view:

[2-p75]
For molecules colliding with a well-defined relative velocity *v*, the reaction cross section is defined such that the chemical reaction rate constant is given by

$$k(v) = v\sigma_R .$$

One can imagine measuring it by passing a beam of reactant A molecules through a scattering cell. The loss of flux due to reactive collision

$$-\frac{dI}{dx} = k(v) n_A n_B .$$

One should note that this loss of flux due to reactive collisions only gives the reaction cross section σ_R , not all the collisions.

Experimentally, this is easy for the reactions producing ions: the ions are simply collected by the application of an electric field.

Example:

$K + Br_2 \rightarrow K^+ + Br_2^-$ or $N_2 + CO \rightarrow NO^+ + CN^-$

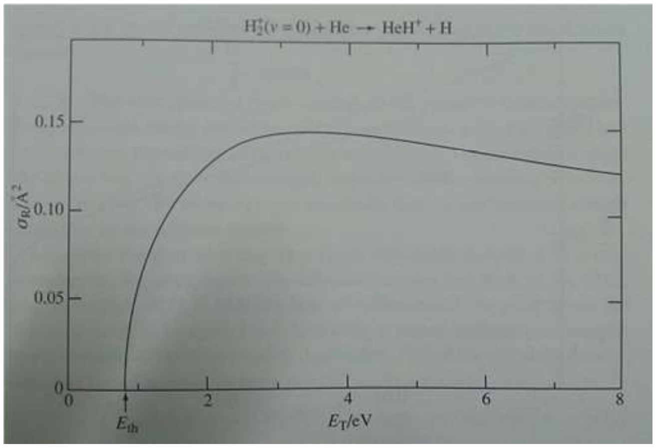
For the reaction of the type

$He + H_2^+ \rightarrow HeH^+ + H$, one has to have mass spectroscopic method to identify reactive and non-reactive channels.

Energy threshold of reaction: [ref. 2 – p76]

What is the role of translational energy on the reaction cross section?

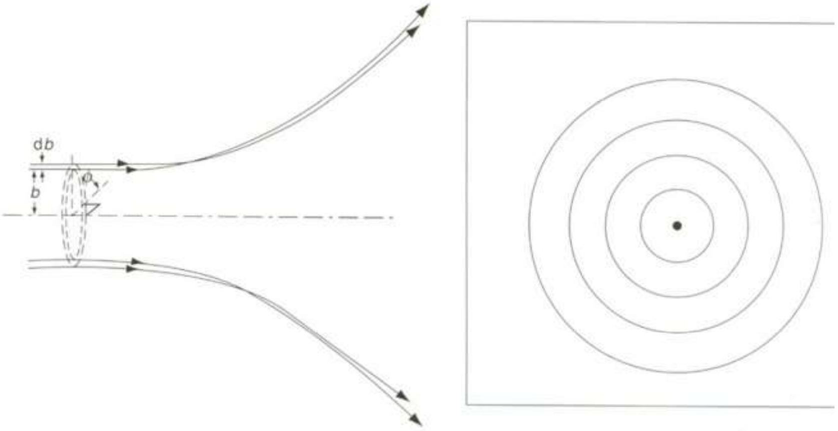
The minimum energy needed for a reaction to take place is defined operationally as the threshold energy, E_0 of the reaction. The cross section vanishes below this threshold value. For endothermic reactions, the conservation of energy implies that there is a minimal energy for reaction to take place. For example, for the ion-molecule reaction $He + H_2^+ \rightarrow HeH^+ + H$, the minimal energy expected on thermochemical grounds is $E_0 = D_0(H_2^+) - D_0(HeH^+) = 0.81$ eV. The experimental results, shown in figure below, are that this minimal energy indeed the threshold. It is further seen that the reaction cross section increases rapidly as the translational energy increases above E_0.



Reactions can have a finite energy threshold that is higher than the thermochemical threshold, meaning that reaction cross section is effectively zero below some threshold energy even though the reaction is thermochemically allowed. One then speaks of an activation barrier that needs to be surmounted for reaction to take place.

Microscopic view of the reaction cross section:

[2-p56,84]



A collision occurs whenever two molecules exercise a force on one another. The outcome of the collision can be that a chemical reaction took place. When a force due to the potential acted, a collision is said to have taken place. The cross section is that area, drawn in a plane perpendicular to the initial velocity, the relative motion of the molecules needs to cross if a collision is to take place.

From the figure it is clear that the center of target is at $b=0$. A collision with an impact parameter that is in the range b to b+db has to cross the target through a ring or radius b and width db. The area of such a ring is, the differential cross section $d\sigma = 2\pi b db$.

When we specify only the (magnitude of the) initial velocity of the colliding particles, collision can occur with all possible values of *b,* hence, total collision cross section

$$\sigma = \int_0^{b\max} 2\pi b db.$$

For hard sphere $b_{\max} = d$ the diameter of the molecule. Hence

$$\sigma = \int_0^d 2\pi b db = \pi d^2 .$$

The ***reaction cross section*** σ_R is a measure of the effective size of the molecules as determined propensity (tendency) to react, at a given collision energy. As the reactants collide at a given energy we characterize their initial approach in terms of the impact parameter. As all the collisions may not lead to chemical reaction, we introduce here the reaction probability or opacity function, P(b), as the fraction of collisions with impact parameter b that lead to reaction.

$0 \le P(b) \le 1$

We expect that reaction will take place only when b is small enough to chemical force to be operated and there will be atomic rearrangements that constitute chemical change can take place. Reaction will fail to occur, i.e., $P(b) = 0$, for higher values of b.

For the collisions with an impact parameter in the range b to b+db, the differential reaction cross section is given in terms of the opacity function by

$$d\sigma_R = 2\pi b P(b) db$$

Due to the possibility of reaction, the total collision cross section, $d\sigma = 2\pi b db$, is partitioned between the cross section for reactive $(d\sigma_R)$ and non-reactive collisions

$$d\sigma_{NR} = 2\pi b[1 - P(b)]db$$

One can say that the non-reactive scattering quenches the reaction.

In case of experimental measurement, if a force is applied, leading to deflection, the molecules in the beam fails to reach the detector. Hence, the experiment measures the total cross section irrespective of how the outcome of the collision is partitioned between different kinds of processes that are possible.

The total reaction cross section is the sum (=integral) over all collisions irrespective of their impact parameter

$$\sigma_R = \int_0^{b\max} 2\pi b P(b) db.$$

One should note that σ_R weights P(b) such that the contributions at higher *b* values tend to contribute more heavily because of the $2\pi b$ term in the area element. Hence, if a reaction has an opacity function that extends to higher *b* values, it will have a particularly large reaction cross section.

Harpoon mechanism:
[2-p86]

The reactions of atoms (or molecules) with rather low ionization potential with molecules with high electron affinity are long-range electron transfer process and have relatively larger reaction cross sections. One type of example is the reaction of alkali atom with halogen molecules, which show very large reaction cross sections (~100Å^2). This can be explained by long-range electron transfer process known as harpoon mechanism. In this mechanism the charge transfer occurs at quite large separation of the reactants, well before what one would customarily think of as the range of chemical forces.

At first stage of the reaction the alkali metal transfers the valence electron to the halogen molecule. Once the transfer takes place and a temporary ion-pair (e.g., $K^+Br_2^-$) is formed, the strongly attractive Coulomb force accelerates the two ions toward each other. This is followed by formation of the stable KBr and rejection of Br atom. The metal atom has, in effect, used its valence electron as “harpoon” in order to pull in the halogen molecule, employing the Coulombic interionic attraction as a “rope”.

[Adapted from Ref. 2 – p86]

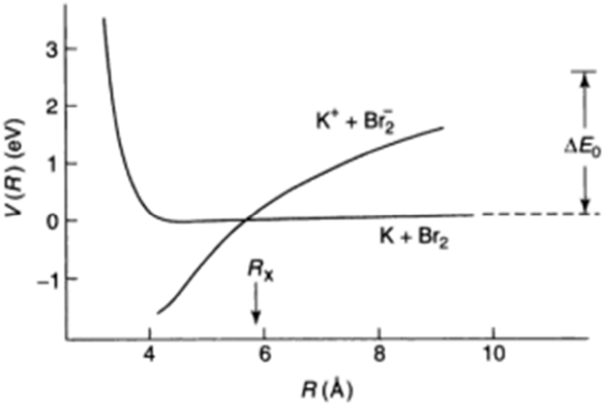


Figure 3.5 Schematic drawing of intersecting potential curves to model the harpoon reaction of $K + Br_2$. The nearly flat curve represents the long-range $K–Br_2$ interaction where both species are neutral. The value of this energy at large separations sets the zero of energy. The upper curve is a coulombic attraction approximating the ionic $K^+–Br_2^-$ potential at long range. As R is decreased to the crossing point R_X, the lowest energy state of the KBr_2 system switches from the covalent to the ionic form and follows the lower curve until K^+Br^- forms, with the ejection of a Br atom. At very large separations the potential energy curve for $K^+ + Br_2^-$ levels out at the difference, ΔE_0, between the ionization potential of K and the (vertical) electron affinity of Br_2. Therefore the asymptotic (= in the reactants' region) separation in energy of the two potential curves is ΔE_0.

Initially, at large distance the ionization potential (IP) of metal exceeds the electron affinity (EA) of the halogen molecule, and charge transfer does not take place. However, as reactants approach each other there is an ion-pair (e.g., $K^+Br_2^-$) formation due to coulomb attraction in newly formed ion-pair.

The largest separation R_X at which the charge separation can take place on energetic grounds can be estimated by solving an equation relating the coulomb attraction between two oppositely charged ions that is sufficient to provide required energy $\Delta E_0 = \text{IP (metal)} - \text{EA(halogen molecule)}$, the endoergicity:

$$-\frac{e^2}{R_X} + \Delta E_0 = 0$$

The above equation gives an approximate value of R_X by the formula

$$R_X \cong \frac{e^2}{\Delta E_0} = \frac{14.4}{\Delta E_0(\text{in eV})} \quad (\text{in Å})$$

For $b > R_X$ the reactants will never get "close enough" and there will not be any charge transfer. When $b < R_X$ charge transfer can occur and then the strong coulomb attraction overcomes the centrifugal repulsion and draws the two ions together, downhill. Thus $b_{max} \cong R_X$ and reaction cross section $\sigma_R = \pi R_X^2$.