1. Introduction

**Thermally averaged rate coefficients**

The thermal rate coefficient, \( k(T) \), is a highly averaged quantity.

Look again at simple collision theory:

- Reactions occur by collisions\(^1\)
- Collision energy\(^2\) \( (E_t) \) must exceed the barrier height \( (E_0) \)

At fixed relative velocity, \( c_{\text{rel}} \) (or collision energy, \( E_t \))

\[
\text{Reaction rate} = \text{Rate of reactive collisions at velocity } c_{\text{rel}} \times \text{Fraction of collisions at velocity } c_{\text{rel}}, \; f(c_{\text{rel}})
\]

\[
\sigma_c = \pi d^2
\]

**Rate of reactive collisions** = \( k(c_{\text{rel}}) \) [A] [B]

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\(^1\) Reactants are structureless spheres, with radii \( r_A \) and \( r_B \) and collision diameter \( d = r_A + r_B \)

\(^2\) The collision energy is the translational energy associated with relative motion \( E_t = \frac{1}{2} \mu c_{\text{rel}}^2 \) with \( \mu = \frac{m_A m_B}{m_A + m_B} \) and \( c_{\text{rel}} \) is the relative speed \( (c_{\text{rel}} = |v_B - v_A|) \).
\( k(\text{rel}) \) defines the **reactive collision volume** swept out per unit time

\[
k(\text{rel}) = \text{rel} \sigma(\text{rel}) ,
\]

where \( \sigma(\text{rel}) \) is the **cross-section** for the process of interest at velocity \( \text{rel} \).

\( f(\text{rel}) \text{d}c_{\text{rel}} \) is the fraction of collisions with velocities in the range \( \text{rel} \) to \( \text{rel} + \text{d}c_{\text{rel}} \):

\[
f(\text{rel}) \text{d}c_{\text{rel}} = \left( \frac{\mu}{2\pi k_B T} \right)^{3/2} e^{-\mu c_{\text{rel}}^2/2RT} 4\pi c_{\text{rel}}^2 \text{d}c_{\text{rel}}
\]

**State-resolved properties**

**Example 1**

\[
\text{K} + \text{HCl}(v) \rightarrow \text{KCl} + \text{H} \quad \Delta H^\circ = 4 \text{kJ mol}^{-1}
\]

HCl(\( v = 1 \)) has an energy of 34.5 kJ mol\(^{-1}\).

Put this energy into HCl(\( v = 1 \)) and rate increases by \( \times 100 \).

Put same energy into relative translation and the rate increases by \( \times 10 \).

**Vibrational energy is \( \sim 10 \) times more efficient at promoting reaction than translational energy.**

**Example 2**

\[
\text{OH} + \text{H}_2(v = 0,1) \rightarrow \text{H}_2\text{O} + \text{H}
\]

Vibrational excitation of the H\(_2\) to \( v = 1 \) increases the rate constant by over a factor of 100 (i.e. \( k_{v=1}(T) \gtrsim 100 k_{v=0}(T) \)).

Vibrational excitation of the ‘spectator’ OH reactant has very little effect on the reaction rate.
Example 3

\[
O + CS \rightarrow CO(v') + S
\]

There is a population inversion in the CO product vibrational levels. Populations cannot be described by Boltzmann distribution (i.e. not at thermal equilibrium).

Reactant energies influence the course of a reaction.

Products can be formed in a non-Boltzmann fashion.

Need to probe the populations over the product states....

....and control the populations in the reactant states.

For example

- Velocities (magnitude and direction)
- Vibrational and rotational (internal) energies
- Orientation

The above examples suggest that reaction cross-sections can depend on all of these quantities.

Conservation laws

Consider

\[
A + BC \rightarrow AB + C
\]

Conservation of energy

\[
E_{\text{avl}} = E_t + E_{\text{vib}} + E_{\text{rot}} - \Delta H^\circ
\]

\[
= E'_t + E'_{\text{vib}} + E'_{\text{rot}}.
\]

So, for example, the fraction of the energy released as vibration would be

\[
f'_v = \frac{E'_{\text{vib}}}{E_{\text{avl}}}.\]

Conservation of angular momentum

Rotational angular momentum

\[
|\mathbf{j}_{BC}| = \sqrt{J(J+1)} \hbar.
\]

Orbital angular momentum

\[
|\mathbf{L}| = \sqrt{L(L+1)} \hbar = \mu_{\text{rel}} b.
\]

\[
\mathbf{J}_{\text{tot}} = \mathbf{j}_{BC} + \mathbf{L} = \mathbf{j}'_{AB} + \mathbf{L}'.
\]

\footnote{It is helpful to define the total energy (with respect to the reactants):

\[
E_{\text{tot}} = E_t + E_{\text{vib}} + E_{\text{rot}} = \Delta H^\circ + E'_t + E'_{\text{vib}} + E'_{\text{rot}}.
\]
Forces and potential energy surfaces

Aim to understand forces which control interactions between atoms.

One dimension - a diatomic potential energy curve

\[ F(R) = -\frac{dV(R)}{dR} \]

The potential energy surface for H(D) + H₂:

The H—H—H bond angle has been fixed here at 180°.

Experimental requirements

Wish to select the energies and quantum states of the reactants

and/or

probe the energies and quantum state populations of the nascent products

Need to ensure collisional scrambling of the reactants and products does not occur.

One method is to use molecular beams

1. ~5 □ Torr
   high vacuum
   effusive source
   \(<E> = 5 - 10 \text{ kJ mol}^{-1}\)

2. ~10 Torr
   high vacuum
   supersonic nozzle source
   \(<E> = 10 - 50 \text{ kJ mol}^{-1}\)

With 1, velocities can be selected with a mechanical chopper.

With 2, velocities can be tuned by seeding reactant of interest in different carrier gases.
What can be measured?

It is possible to measure cross-sections experimentally.

Cross-section can be thought of as the effective target area for the process of interest (e.g., a reaction).

In simple collision theory it is defined as 
\[ \pi d^2 \], where \( d \) is the sum of the radii of the two spheres \( r_A + r_B \).

In classical mechanics the cross-section is defined more rigorously by the integral
\[ \sigma = \int_0^{b_{\text{max}}} P(b) \pi b^2 \, db , \]

where \( b \) is the impact parameter. \( P(b) \) the opacity function - the dependence of the probability of the process of interest (e.g., reaction) on impact parameter.

The cross-section can therefore be thought of as a ‘dart-board’ average of the reaction probability.

Note that the reaction probability does not depend on angle \( \phi \) provided that BC is not oriented.

The opacity function is difficult to measure (see later), but can readily be calculated.

\[ \sigma = p \pi b_{\text{max}}^2 \]

The above simple example demonstrates that the above definition leads to a cross-section with the correct dimensions of area.

Types of encounter

Cross-sections can be defined, and measured, for many different collisional processes.

Consider three categories of collisions.

1. Elastic scattering: conserves kinetic energy, lead to a change in direction.

2. Inelastic scattering: leads to a change in internal energy of the colliders.

3. Reactive scattering: leads to a rearrangement of bonds.

Focus on reactive collisions.
2. Elastic and inelastic scattering

*Simple measurement of a cross-section*

Example of a ‘beam-gas’ experiment.

When molecules of A collide with B they are deflected. This leads to attenuation of the molecular beam of A.

Use equivalent of Beer-Lambert law for light

\[ I = I_0 e^{-\sigma c_B l}, \]

\( \sigma \) — the scattering cross-section,

\( c_B \) — the concentration of B, and

\( l \) — the path length of B through which A passes.

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**Glory scattering**

Most clearly seen for atom-atom scattering (e.g., K + Rg).

**Glory oscillations** arise from quantum mechanical interference between two pathways (two de Broglie waves) leading to scattering in the forward direction.

The frequency of the oscillations varies with collision energy because the phase difference between the two pathways varies with velocity.

(i) Low collision energies probe the attractive part of the potential.

(ii) High collision energies probe the repulsive part of the potential.
**Crossed beam experiment**

Measurements with crossed beams provide additional information about the *angular distribution* of the products.

![Diagram of crossed beam experiment](image)

Data are obtained in the laboratory (left)....

....but are usual plotted with respect to the centre-of-mass (cm) (right).

*Need to Transform data from the lab to the cm frames.*

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**The differential cross-section**

The dependence of the cross-section on *scattering angle* is quantified by the *differential cross-section*

\[
\frac{d\sigma}{d\omega}
\]

where \(d\omega\) represents the cm solid angle volume element \(\sin \theta d\theta d\phi\).

The integral of the differential cross-section (DCS) over scattering angles gives the total (integral) cross-section

\[
\sigma = \int_0^{2\pi} \int_0^\pi \frac{d\sigma}{d\omega} \sin \theta d\theta d\phi
\]

Dimensions of the DCS are of area per steradian.

The angular distribution of the products can be expressed as

\[
P(\theta, \phi) = \frac{1}{\sigma} \frac{d\sigma}{d\omega}
\]

where \(P(\theta, \phi)d\omega\) is the probability of finding products scattered into solid angles between \(\omega\) and \(\omega + d\omega\).

Provided the reactants are not oriented, the differential cross-section, and angular distribution, are independent of the angle \(\phi\) (due to dart-board averaging over impact parameter).
**Rainbows**

Again, expect to see *interference*.

At the *rainbow angle* the gradient $d\theta/db = 0$. Classically obtain a discontinuity in differential cross-section at $\theta_R$.

For $\theta < \theta_R$, three values of $b$ lead to deflection through the same scattering angle. Leads to interference known as supernumerary rainbows.

The features in $d\sigma/d\omega$ are directly related to the nature of the potential energy curve.

$\theta_R$ is sensitive to the well depth in potential.

The supernumerary rainbows provide information about the range and shape of the potential near the minimum.

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**Inelastic scattering: energy transfer**

Inelastic collisions lead to a transfer of energy from one form to another, or between one molecule and another:

<table>
<thead>
<tr>
<th>Translation</th>
<th>Rotation</th>
<th>Vibration</th>
<th>Electronic</th>
</tr>
</thead>
</table>

For example:

*Translation $\rightarrow$ Vibration*  \( (T \rightarrow V) \)

\[
\text{Ar} + \text{CO} (v = 0) \rightarrow \text{Ar} + \text{CO} (v = 1)
\]

*Vibration $\rightarrow$ Vibration*  \( (V \rightarrow V) \)

\[
\text{N}_2 (v = 0) + \text{CO} (v = 1) \rightarrow \text{N}_2 (v = 1) + \text{CO} (v = 0)
\]

Huge literature on these types of process.
**General ideas for T, R, V transfer**

\[ T \rightarrow V, R \quad \text{Probability} \uparrow \text{as energy converted into vibration or rotation} \downarrow. \]

\[ T \rightarrow R \quad \text{Usually much more efficient than } T \rightarrow V \]

\[ V \rightarrow V \quad \text{Probability} \uparrow \text{as energy converted into translation or rotation} \downarrow \text{(i.e. as the mismatch between the vibrational levels} \downarrow). \]

**Controlling factors?**

(i) **LOW** efficiency  
E.g., \( T \rightarrow V \)  
Small cross-sections.  
Usually involve small \( b \) collisions.  
Controlled by short range repulsion.

(ii) **HIGH** efficiency  
E.g. \( T \rightarrow R \) or resonant \( V \rightarrow V \)  
Large cross-sections.  
Usually involve a large range of \( b \).  
Controlled by long-range attraction (dipole-dipole, etc.)

**Scattering experiment**

Crossed molecular beam experiment

\[ \text{Li}^+ + H_2(v = 0, j = 0, 1) \longrightarrow \text{Li}^+ + H_2(v', j') \]

Observe the change in velocity as a function of scattering angle (using time-of-flight mass spectrometry detection of \( \text{Li}^+ \)).

(a) **Forward:** Small KE loss in \( \text{Li}^+ \)  
Corresponds to excitation of \( H_2(v = 0, j = 1) \rightarrow H_2(v' = 0, j' = 3) \)  
Large cross-section.

(b) **Backward:**  
KE loss much larger  
Corresponds to excitation of \( H_2(v = 0, j = 1) \rightarrow H_2(v' = 1, 2, 3, j') \)  
Small cross-section
Ne + CO($v = 0, lowj$) $\rightarrow$ Ne + CO($v' = 0, j'$)

CO($v', j'$) probed spectroscopically using an ionization technique called REMPI (see later).

Ions are then detected on a two dimensional detector using a technique called ion-imaging (see later).

**Newton Diagram**

![Newton Diagram](image)


**Dependence on CO($v' = 0, j'$)**

Rings get smaller as $j' \uparrow$, reflecting lower velocity of internally excited CO (energy conservation).

High intensity (high CO number density) shifts position wrt molecular beams as $j' \uparrow$.

\[
\text{Ne} + \text{CO}(v = 0, l_0j) \rightarrow \text{Ne} + \text{CO}(v', j')
\]

**Differential cross-sections**

Angular distribution changes from forward to backward scattering as \(\text{CO}(j')\) ↑.

Oscillations are a manifestation of quantum mechanical interference similar to that described for atom-atom scattering.

3. Angular distributions in reactive scattering

**Molecular beam scattering**

One of the molecular beams is usually chopped or pulsed to provide timing for time-of-flight measurement (from which product lab velocity is calculated).

**Detectors**

- *Hot wire ionization*

  \[ M \text{ or } MX \rightarrow \text{Ions} \rightarrow \text{current} \]

  Good angular resolution, rather poorer speed (energy) resolution

  \[ K + I_2 \rightarrow KI + I \]

- *Electron impact ionization coupled with mass spectrometry*

  Universal detection method.

  Rarely has sensitivity to allow product quantum state resolution.

  \[ F + H_2 \rightarrow HF + H \]

- *Spectroscopic methods*

  Usually based on laser ionization methods (see below).

  High energy resolution, but only recently applied due to low sensitivity

  \[ H + HD \rightarrow H_2 + D \]

**Stripping and harpoon mechanisms**

Early example

\[ K + I_2 \rightarrow KI + I \]

Plot data in the form of a contour plot in the cm system (such that cm is stationary).

Contours represent lines of equal product flux as a function of KI velocity (i.e. scattering angle and speed). Outer circle represents the maximum possible product velocity (set by energy conservation).

**Observe forward scattering**
**Harpoon mechanism**

*Observe:*
- very large cross-section (like many other alkali + halogen reactions);
- forward scattered products;
- low energy release into translation (about 1/4 of the available energy). KI must be highly internally excited (see Polanyi’s rules later).

**Electron transfer (harpoon) takes place when**

\[ V_{\text{covalent}}(R_c) = V_{\text{ionic}}(R_c) \approx 0, \]

i.e. when

\[ I_K - E_{A\text{Br}_2} = \frac{e^2}{4\pi\epsilon_0 R_c}. \]

\[ R_c \approx 6\text{ Å} \text{ in this case} \]

Estimate cross-section (assuming \( P(b) = 1 \))

\[ \sigma = \int_0^{b_{\text{max}} = R_c} 2\pi b \, db = \pi R_c^2 \approx 100 \text{ Å}^2 \]

Br\(^-\) formed with internuclear separation such that there is little repulsion between Br and Br\(^-\). K\(^+\) carries off Br\(^-\) in its original direction (forward scattering).

**Rebound dynamics**

\[ \text{K} + \text{CH}_3\text{I} \rightarrow \text{KI} + \text{CH}_3 \]

*Observe*
- Small cross-section
- Backward scattering - consistent with reaction at small \( b \)
- High translational energy release (see later).

This reaction is also a harpoon reaction, but \( E_{A\text{CH}_3\text{I}} \) is negative.

**Curve crossing occurs at short range.**
\[ \text{F + H}_2(v = 0, j = 0, 1) \rightarrow \text{HF}(v') + \text{H} \]

**HF product velocity-angle contour plot**

Crossed molecular beam experiment

Product vibrational resolution. \( v' = 1, 2 \) rebound dynamics.

\( v' = 3 \) forward scattered.

**HF vibrational population distribution**

Vibrational population inversion (see later)

\[ \text{F + H}_2 \rightarrow \text{HF}(v') + \text{H} \]

**Why was the structure observable?**

1. High resolution apparatus (well collimated, *skimmed* molecular beams)

2. **Angular momentum conservation**

\[ J_{\text{tot}} = j_{\text{H}_2} + L = j'_{\text{HF}} + L'. \]

(a) \( j_{\text{H}_2} \) small because of cooling of rotational degree of freedom in the molecular beam, and the large rotational \( B \) constant of \( \text{H}_2 \) (not many states populated even at 300 K).

(b) Reaction has a small cross-section, preferentially occurs at small \( b \), hence \( |L| = \mu c_{\text{rel}} b \) also small (both \( b \) and \( \mu \) small).

(c) Therefore, little angular momentum available to the products. Note that \( |L'| = \mu' c'_{\text{rel}} b' \) tends also to be small because \( \mu' \) is small.

3. HF vibrational levels well-separated in energy - large difference in product velocity.
**Why the forward peak?**

Has been a controversial issue.

Unlike low $v'$, reaction to generate $v' = 3$ arises from high impact parameter collisions.

Reactions at these high $|L|$ are not allowed classically because of the centrifugal barrier.

\[ V_{\text{eff}}(R) = V(R) + E_{\text{cent}} \]

\[ E_{\text{cent}} = \frac{L^2}{2I} = \frac{(\mu c_{\text{rel}}b)^2}{2\mu R^2} = E_t \frac{b^2}{R^2} \]

They are allowed by *quantum mechanical tunnelling* through the centrifugal barrier.

\[ \text{H + HD}(v = 0, j = 0) \rightarrow \text{H}_2(v', j') + \text{D} \]

**Differential cross-section**

State-of-the-art measurements using a laser ionization technique called *Rydberg-tagging* to detect the D atom products.

\[ E_t \sim 0.5 \text{ eV} \]

Rebound

Dynamics

\[ E_t \sim 1.2 \text{ eV} \]

More forward

scattering

Each ring corresponds to a fully resolved rovibrational quantum state of the H$_2$ coproduct (see later).

Formation of complexes

Forward-backward symmetric angular distributions.

\[
O + Br_2 \rightarrow Br_2O^* \rightarrow BrO + Br
\]

\[
S(^1D) + H_2 \rightarrow H_2S^* \rightarrow SH + H
\]

Complex lifetime must be long compared to the rotational period.

Favoured by reactions on attractive potential energy surfaces (see later), which have large cross-sections and \( b \gg 0 \).

Scattering of products is uniform in the plane containing \( c_{rel} \) and \( b \), but \( L \), which lies \( \perp \) to this plane, can lie anywhere on the circle. Leads to

\[
\frac{d\sigma}{d\omega} \sim \frac{1}{\sin \theta}
\]