

Lecture-3, Module-1: Part-1

Rate and mechanism of elementary gas phase reactions



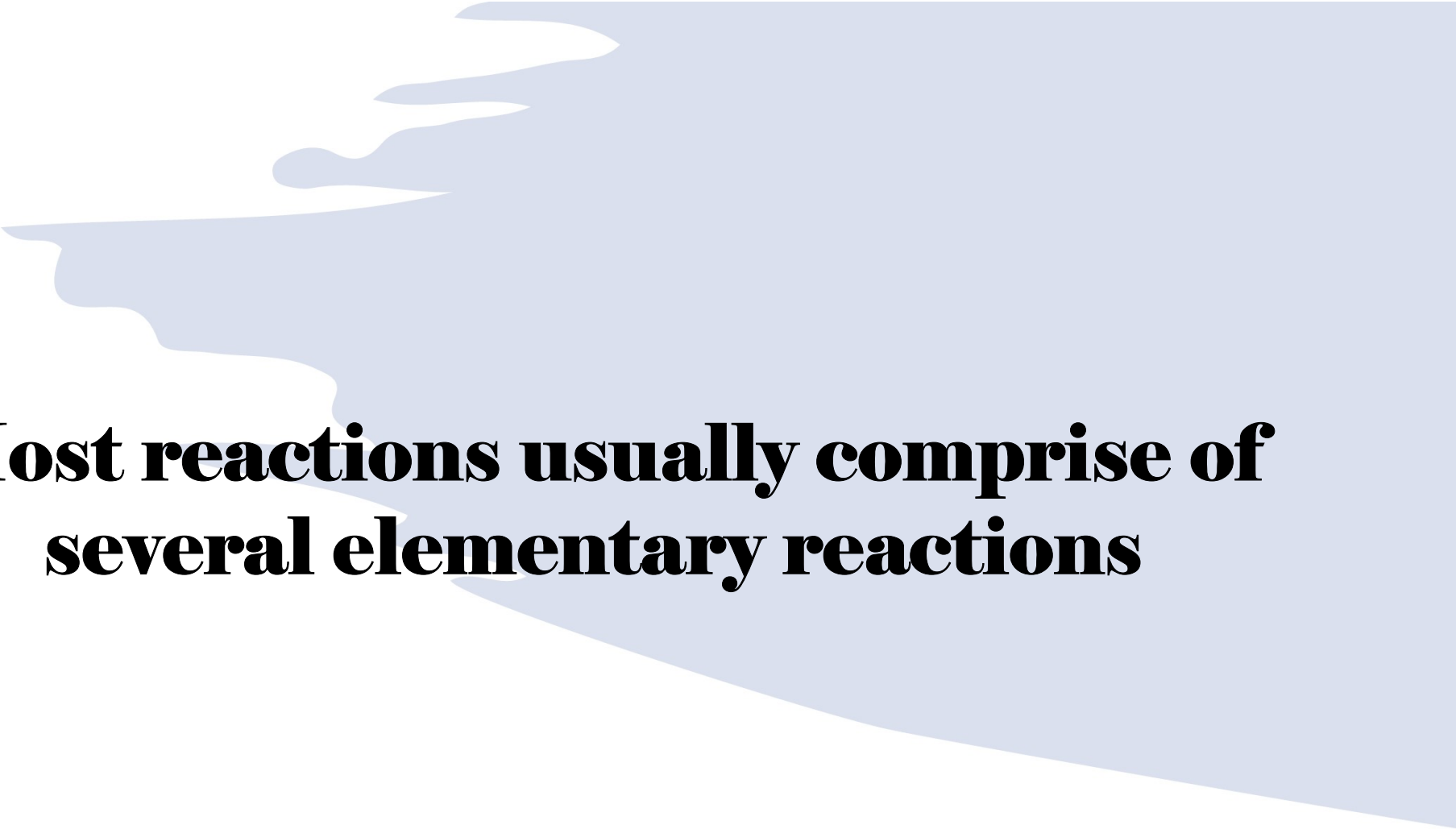
DUDLEY R. HERSCHBACH DEVELOPED THE METHOD OF CROSSED MOLECULAR BEAMS, DIRECTED AND WELL-DEFINED FLUXES OF MOLECULES, TO AND BEYOND THE POINT WHERE DETAILED STUDIES OF CHEMICAL REACTIONS HAVE BEEN POSSIBLE. HE HAS ALSO ELUCIDATED THE DYNAMICS OF THE BASIC TYPES OF REACTION.



YUAN T. LEE, WHO INITIALLY WORKED IN COOPERATION WITH HERSCHBACH, DEVELOPED THE METHOD OF CROSSED MOLECULAR BEAMS FURTHER TOWARDS ITS USE FOR GENERAL REACTIONS. MOST NOTABLY, HE HAS USED THIS METHOD FOR THE STUDY OF IMPORTANT REACTIONS FOR RELATIVELY LARGE MOLECULES.



JOHN C. POLANYI DEVELOPED THE METHOD OF INFRARED CHEMILUMINESCENCE, IN WHICH THE EXTREMELY WEAK INFRARED EMISSION FROM A NEWLY FORMED MOLECULE IS MEASURED AND ANALYSED. HE HAS USED THIS METHOD TO ELUCIDATE THE DETAILED ENERGY DISPOSAL DURING CHEMICAL REACTIONS.

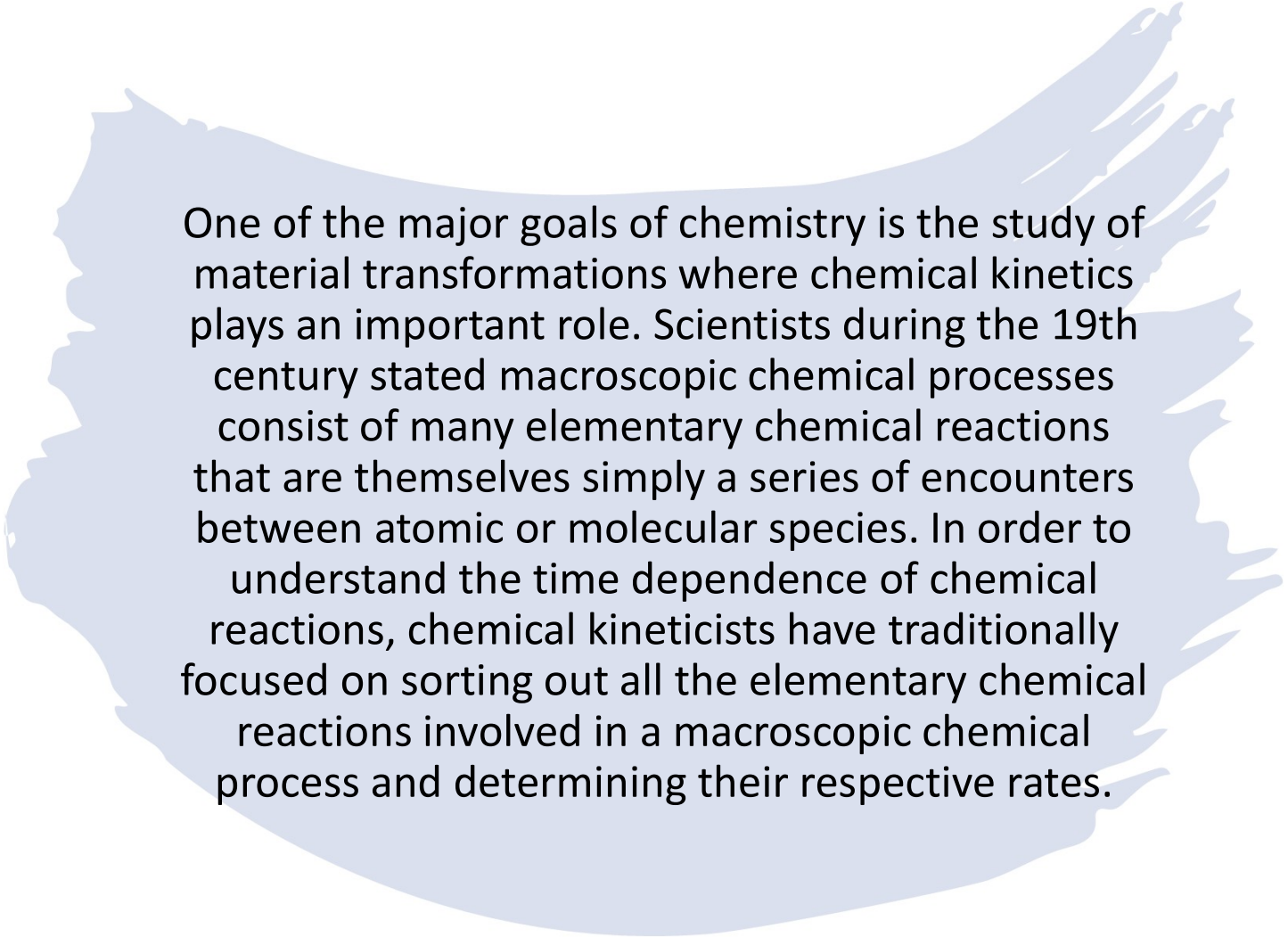


**Most reactions usually comprise of
several elementary reactions**

For example ...



**Rates for elementary reactions
yields overall rate.**



One of the major goals of chemistry is the study of material transformations where chemical kinetics plays an important role. Scientists during the 19th century stated macroscopic chemical processes consist of many elementary chemical reactions that are themselves simply a series of encounters between atomic or molecular species. In order to understand the time dependence of chemical reactions, chemical kineticists have traditionally focused on sorting out all the elementary chemical reactions involved in a macroscopic chemical process and determining their respective rates.

A Long time ago....

During the late 1880s, Swedish chemist Svante Arrhenius stated the relations between reactive molecular encounters and rates of reactions (formulated in terms of activation energies):



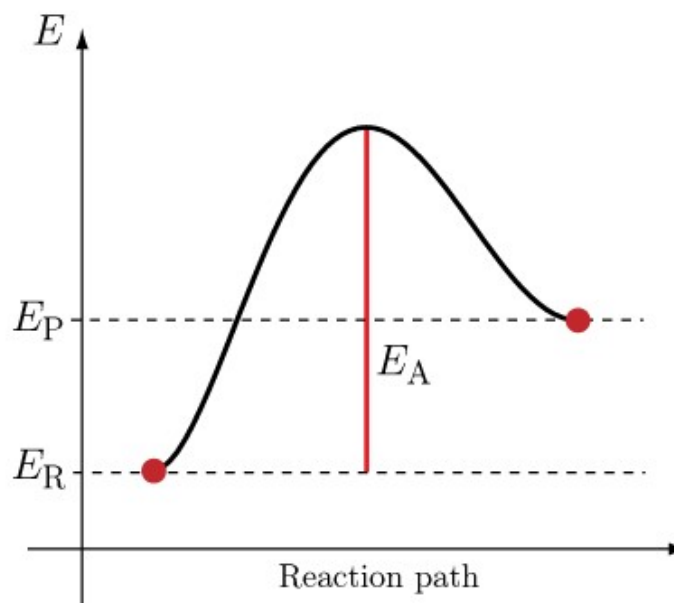
Svante Arrhenius

1859 - 1927

The Nobel Prize in Chemistry 1903

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

Note
T: Temperature



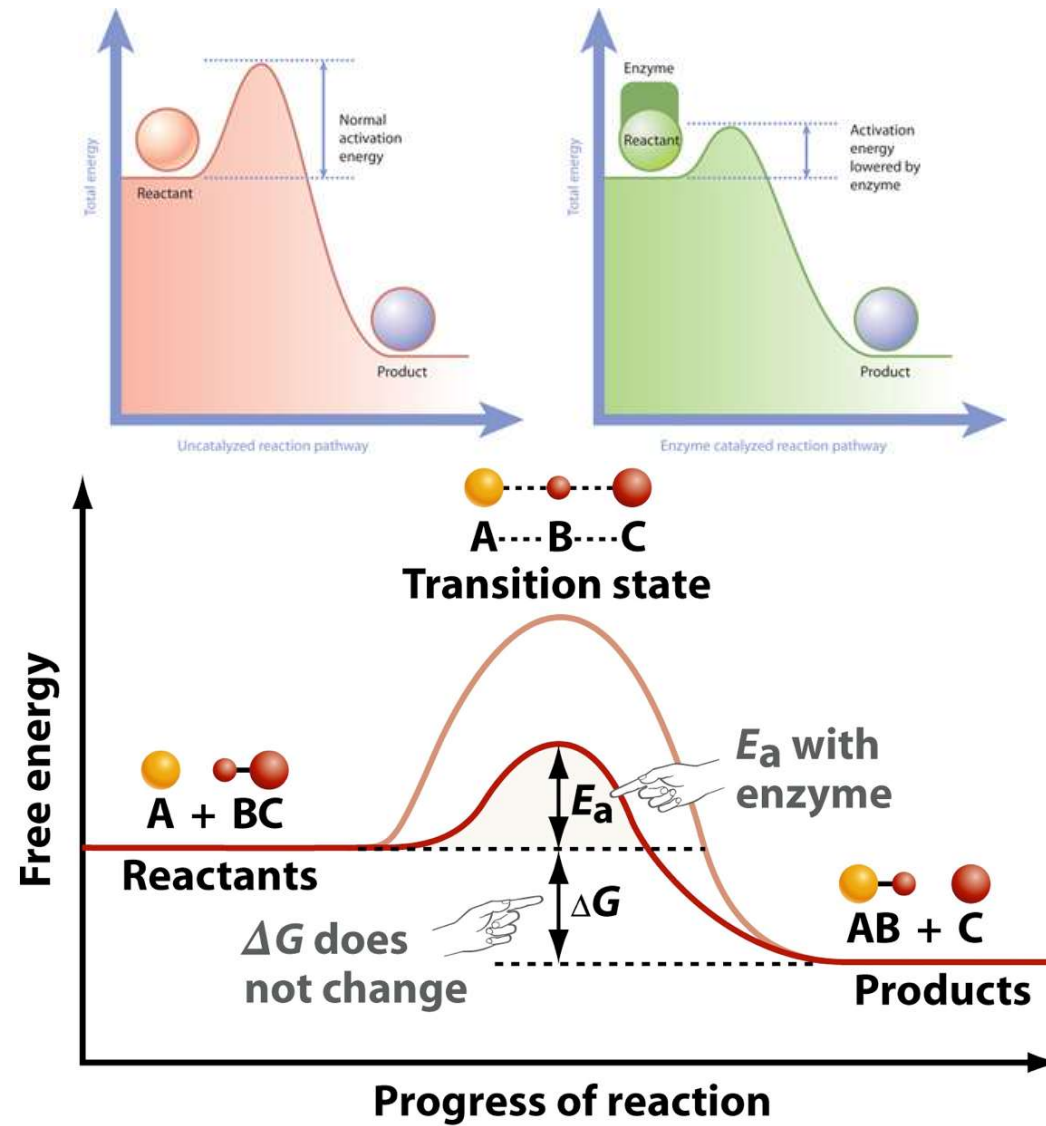


Figure 3-21 Biological Science, 2/e

E_a and $k(T)$ are experimentally determined!

Empirical equation, macroscopic parameters

Result of averaging over microscopic details

**Time (t) is Integrated out
DO NOT confuse Temperature (T) with Time (t)**

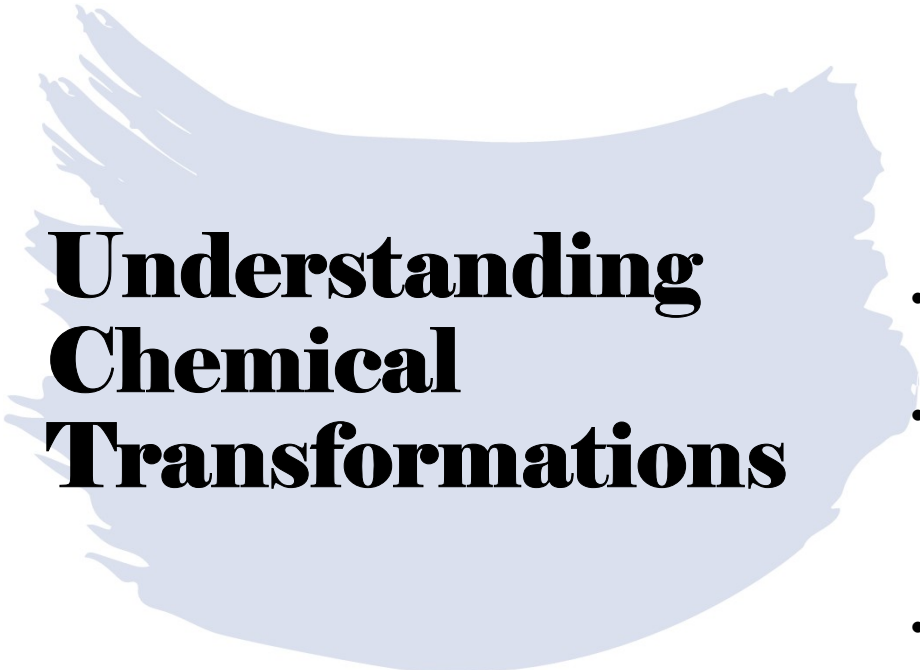
Classical or Quantum?

Unique Mechanism(s)?



Understanding Chemical Transformations

- The molecules are in perpetual motion, and collisions between the molecules in a gas or a liquid occur continuously.
- When molecules come in close enough contact with each other, redistribution of the atoms can take place between or within them.
- New molecules form so-called product molecules, which means that a chemical reaction takes place.
- Nevertheless, for a reaction to occur, the colliding molecules are often required to have some special property such as high velocity or large internal energy.
- The classical description of how chemical reactions occur, and how rates of chemical reaction are measured, belongs to the field of chemical reaction kinetics. This field has developed rapidly during mid-1900s, especially regarding experimental methods. The 1967 Nobel Prize in Chemistry was awarded to M. Eigen, Federal Republic of Germany, R.G.W. Norrish and G. Porter, Great Britain, for their studies of extremely fast chemical reactions.
- In many respects however, fundamental understanding of what molecular features influence the rate of chemical reactions has been slow in developing.



Understanding Chemical Transformations

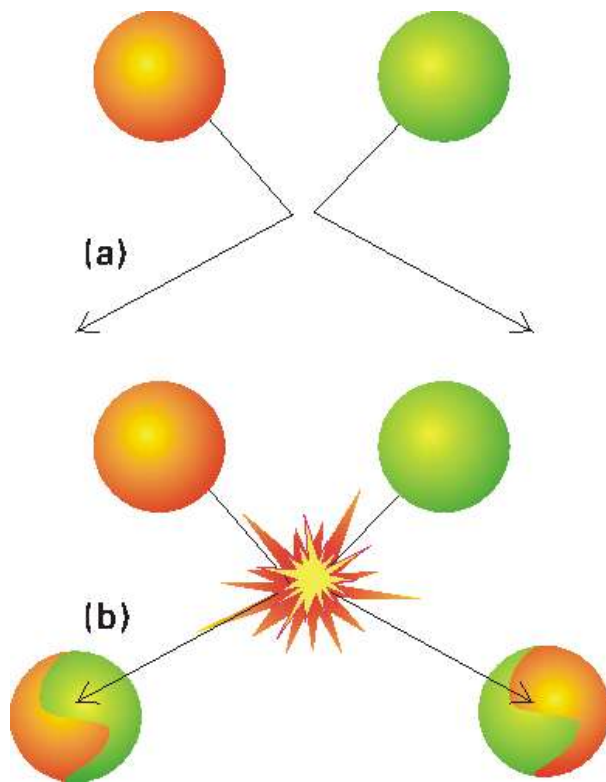
- The directions and velocities of the molecular motion in a gas or a liquid are mainly random. Consequently, the collisions between the molecules are ill-defined as regards, for example, the kinetic energy in the collision. The details of the reaction thus become blurred and cannot be observed precisely enough.
- This problem had not been solved satisfactorily before the development described here.
- It was finally possible to solve the problem by using molecular beams formed of directed and spatially well-defined molecular fluxes of low density, often also with well-defined velocities.
- When two molecular beams are caused to cross each other, the details of the reactions between molecules can be studied. The crossed molecular beam technique is thus one of the most important advances within the field of reaction dynamics.

eters has enabled limited but useful estimates of rate factors. However, these valuable insights were won despite frustrating handicaps. The basic experimental variables of concentration and temperature are not incisive enough to allow further progress. Postulated elementary steps or intermediates often prove incomplete or illusory. The observable rate factors, which represent averages over myriad random collisions, are too remote from the molecular interactions.

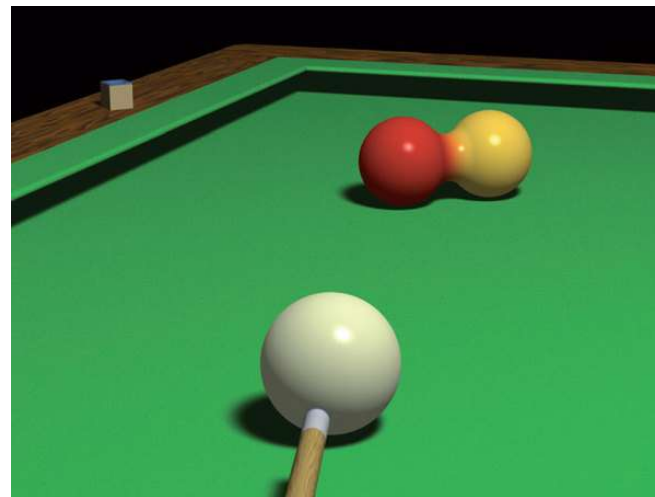
Herschbach

Need for molecular level understanding

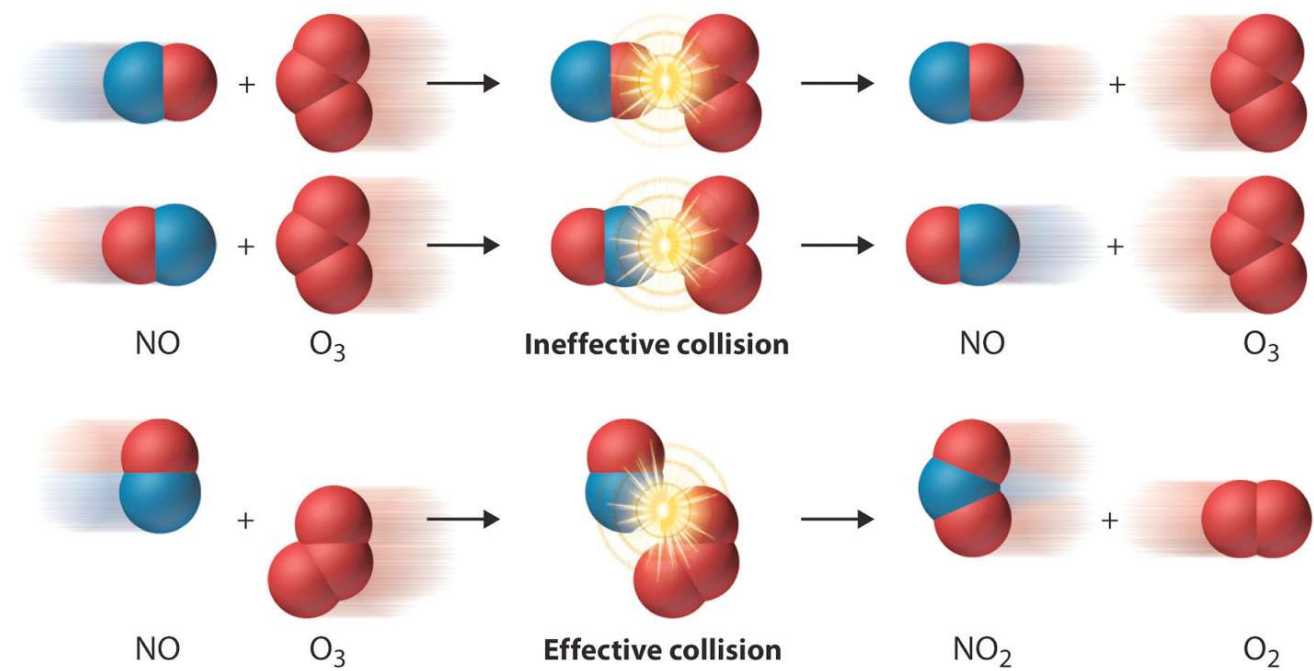
Reaction as collisions



Classical?

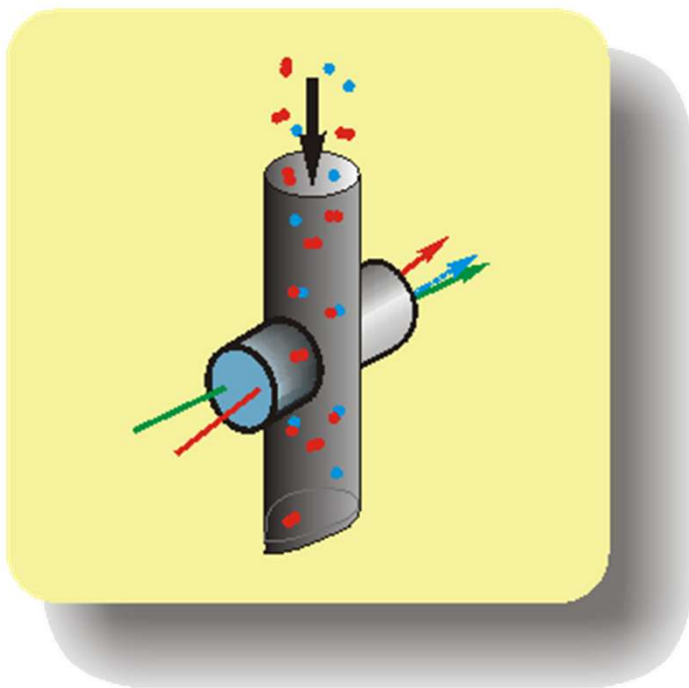


Quantum?



?

Molecular Beam Studies of Elementary Chemical Processes



1. Dilute conditions

2. Controlled collisions

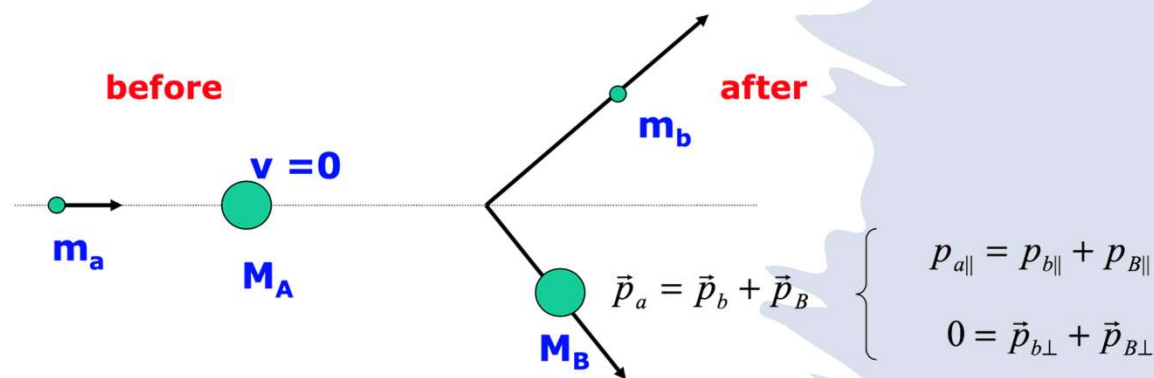
3. Elementary reaction

The first molecular beam experiments were carried out in 1911, immediately after the invention of the high-speed vacuum pump had made it possible to form directed "rays" of neutral atoms or molecules traveling in vessels maintained at sufficiently low pressures to prevent disruption of the beams by collisions with background gas.

Collision kinematics

Conservation laws of:

- **Scalars:** energy, number of particles, electrical charge,...
- **Vectors:** momentum, angular momentum,...



Q value:

Difference of **total kinetic energy** before and after collision

$$Q = (E_b + E_a) - E_a$$

endotherm: $Q < 0$

exotherm : $Q > 0$

- **Dudley R. Herschbach** took part in the development of the crossed molecule beam method almost from the start. His extremely important achievements concerned for example studies of short-lived direct reactions, especially of the two main types, the "rebound" and the "stripping" reaction. He supplemented the commonly-used procedure of detecting the product molecules by deflecting them in magnetic and electric fields, thus circumventing one of the largely-overlooked problems inherent in the early experiments. The discovery of the first long-lived reaction complexes in crossed beams was soon followed by a theoretical description of their formation and decay. The great importance of angular momentum was observed for the first time in these reactions.

- Subsequent, more extensive studies by **Y.T. Lee**, among others, have clearly shown that this type of long-lived reaction is of great general importance. Both Lee and Herschbach, as well as other researchers, have used this type of molecular-beam apparatus for detailed studies of many chemical reactions. Lee has led the development towards chemically important reaction systems by investigating reactions between organic molecules and fluorine or oxygen atoms.

- Another very important method for the detail study of chemical reactions has been developed by **Polanyi**, the infrared -(IR)- chemiluminescence method. This development took place concurrently with the formation of the crossed molecular beam field. This complementary method resembles the crossed molecular beam method in many respects but involves measurement and analysis of the extremely weak infrared emission from the product molecules in some chemical reactions.

Atomic units

Atomic units (a. u.) are a convenient "natural" measure of sizes and magnitudes. The hydrogen atom serves as a standard.

Basic constants:

Angular momentum: \hbar

Electron mass: m_0

Elementary charge: e

Dielectric constant: $4\pi\epsilon_0$

Length: Bohr radius $a_0 = \frac{\hbar^2}{m_0 e^2} (4\pi\epsilon_0) = 0,529 \cdot 10^{-10} \text{ m}$

Energy: potential energy of two elementary charges with distance a_0

$$E_1 = \frac{m_0 e^4}{\hbar^2} \frac{1}{(4\pi\epsilon_0)^2} = \frac{e_0^2}{a_0} \frac{1}{4\pi\epsilon_0} = 4.3 \cdot 10^{-18} \text{ J} = 27.2 \text{ eV}$$

Velocity: classical velocity on 1st Bohr orbit

$$v_0 = \frac{e^2}{(4\pi\epsilon_0)\hbar} = \alpha c \quad \text{Fine structure constant: } \alpha = \frac{e^2}{(4\pi\epsilon_0)\hbar c} \Rightarrow c = 137 a.u.$$

Examples:

Momentum of an electron with 100 eV kinetic energy

$$E_e = p_e^2 / (2m)$$

$$E_e = 100 / 27.2 \text{ a.u.} \Leftrightarrow p_e = \sqrt{2m_e E_e} = \sqrt{2 \cdot 100 / 27.2} = 2.7 a.u.$$

Energy of a He atom with the same momentum $p_i = 2.7 \text{ a.u.}$

$$E_i = p_i^2 / (2M_{\text{He}}) \quad M_{\text{He}} = 4 \cdot 1836$$

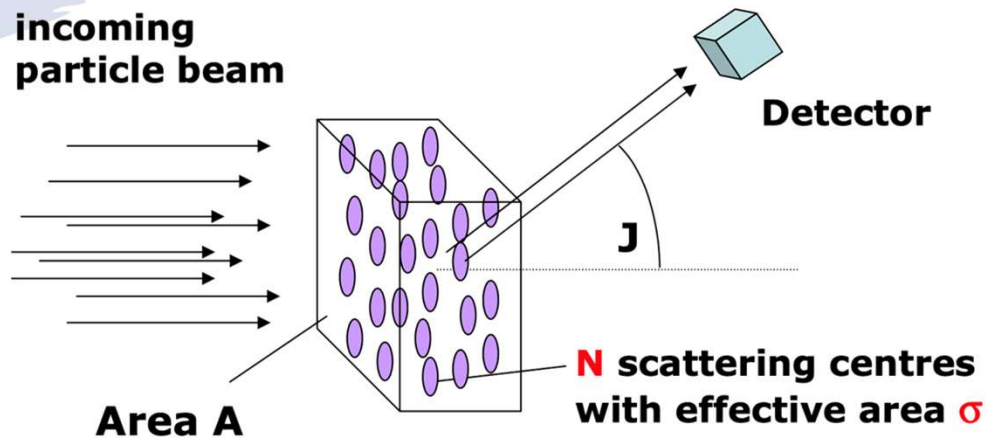
$$E_i = 2.7^2 / (2 \cdot 4 \cdot 1836) = 0.00049 \text{ a.u.} = 13 \text{ meV}$$

or, more directly: $E_i = E_e (m_e / M_{\text{He}}) = 13 \text{ meV}$

Momentum: $p_0 = m_0 v_0 = \frac{m_0 e^2}{(4\pi\epsilon_0)\hbar} = 2 \cdot 10^{-24} \text{ kg m/s}$

Time: $\frac{a_0}{v_0} = \frac{\hbar^3}{m_0 e^4} (4\pi\epsilon_0)^2 = 2.4 \cdot 10^{-17} \text{ s} = 24 \text{ as}$

What is a (collision/reaction) cross section?



Probability for a reaction:

$$P = \frac{N \cdot \sigma}{A}$$

Total cross section:

$$\sigma = \frac{\text{Number of reactions per scattering centre and time interval}}{\text{Current density } j \text{ of incoming particles}}$$

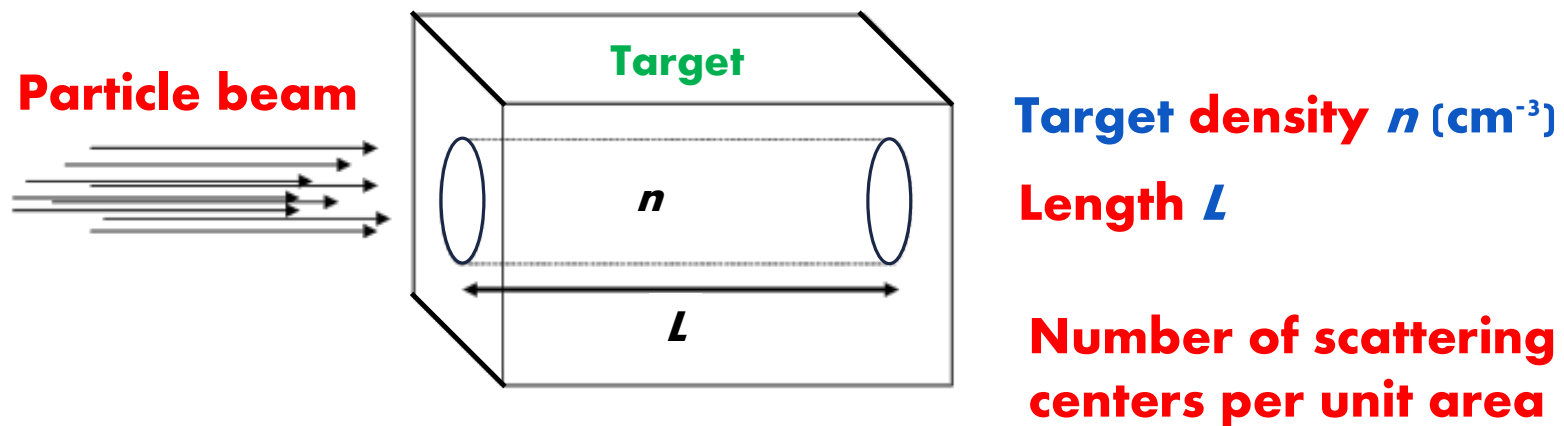
Differential cross section:

$$\left(\frac{d\sigma}{d\Omega} \right)_\vartheta = \frac{\text{Flux of particles scattered in solid angle interval } d\Omega}{\text{Current density } j \text{ of incoming particles}}$$

Total cross-section : $\sigma = \int \left(\frac{d\sigma}{d\Omega} \right) d\Omega$

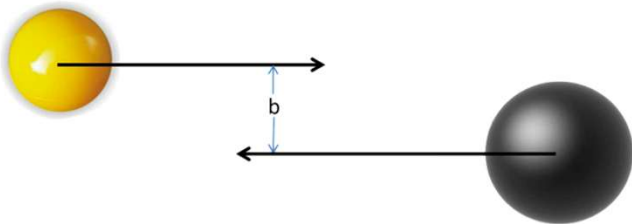
Typical units of area and cross-section :

- Atomic scale : cm^2 ; $1 \text{ a.u.}^2 = 0.88 \times 10^{-16} \text{ cm}^2$

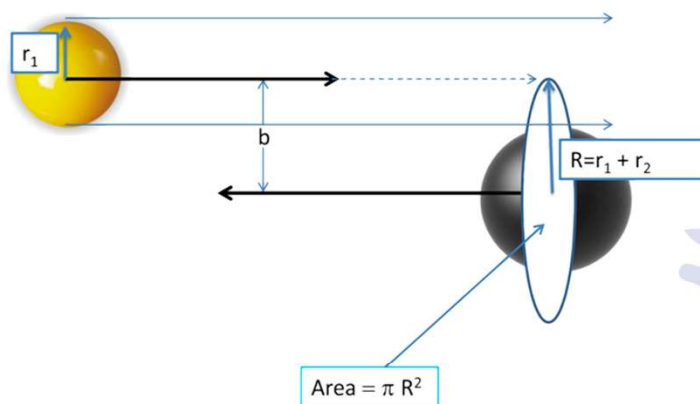


$$\frac{\text{Number of reactions}}{\text{time}} = \frac{\text{Projectiles}}{\text{time}} \cdot n \cdot L \cdot \sigma$$

Mean free path length : $\langle \lambda \rangle = \frac{1}{n \cdot \sigma}$



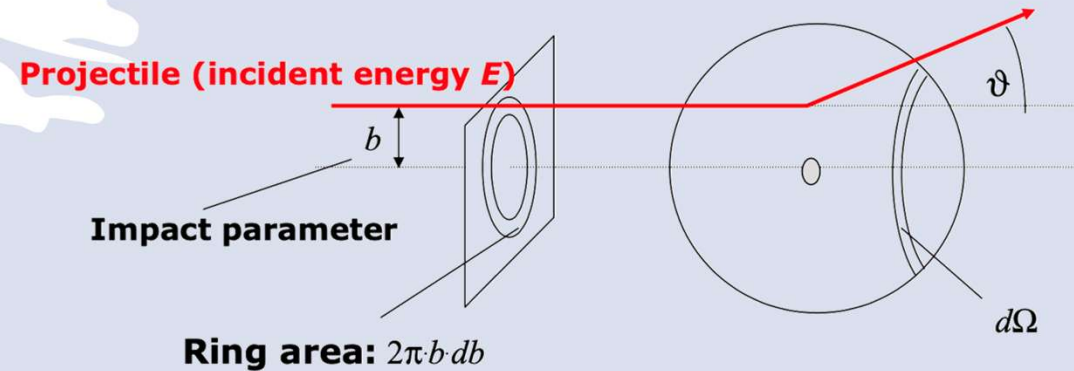
Two atoms colliding, “b” is the impact factor



Grazing collision between two hard sphere atoms illustrating the concept of a collision cross section

Differential cross section

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{1}{2\pi \sin(\vartheta)} \frac{d\sigma}{d\vartheta} \quad \text{with} \quad d\Omega = 2\pi \sin(\vartheta) d\vartheta$$



Ring area: $2\pi b db$

with $d\sigma = 2\pi b db$ follows:

$$\left(\frac{d\sigma}{d\Omega}\right) = \frac{2\pi b}{2\pi \sin(\vartheta)} \cdot \left|\frac{db}{d\vartheta}\right| = \frac{b}{\sin(\vartheta)} \cdot \left|\frac{db}{d\vartheta}\right|$$

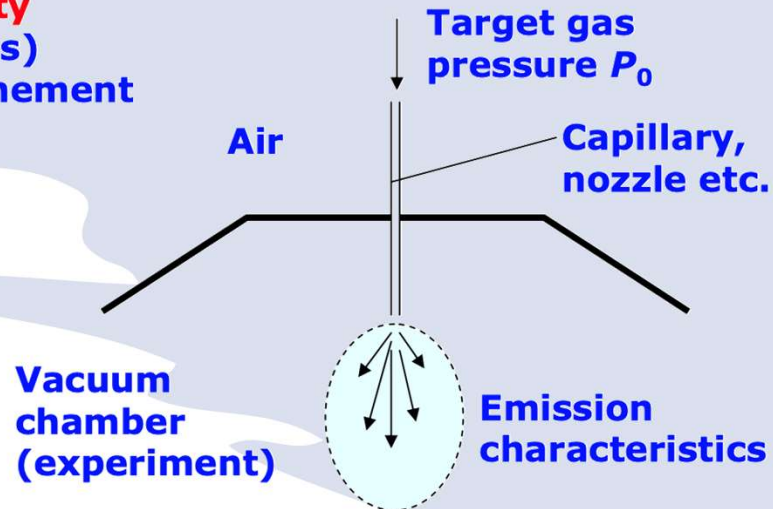
Dependence of scattering angle from impact parameter

$$\vartheta = \vartheta(b, E)$$

Atomic and molecular beams

An ideal target requires:

- **negligible interaction** between the particles of the target gas with the environment
- high (but not too high) **density**
- well defined **velocity** (cold gas)
- **low divergence**, spatial confinement



Important quantities:

- capillary or nozzle **diameter d** and **length L**
- **mean path length Λ** at pressure P

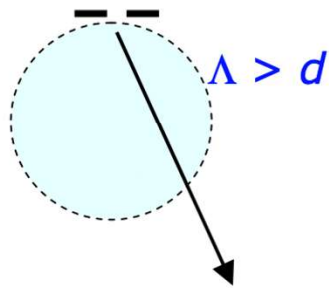
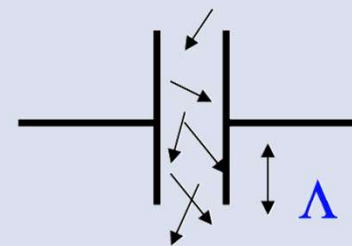
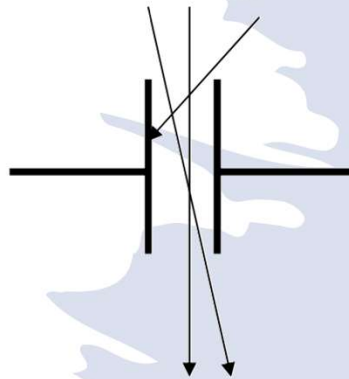
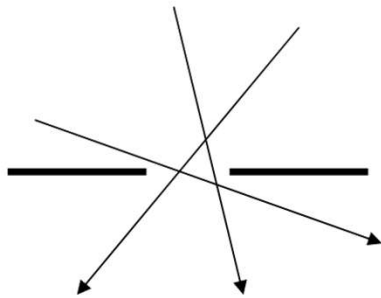
Relation of particle density and pressure (at room temperature)

$$n [\text{cm}^{-3}] = 2.7 \cdot 10^{16} \cdot P [\text{mbar}]$$

Emission characteristics

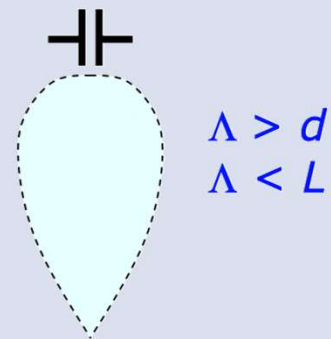
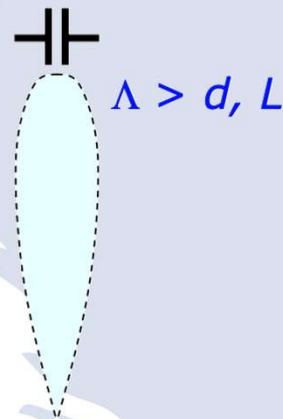
Aperture (diameter d)

Nozzle (diameter d , length L)



$$I(\vartheta) = \cos \vartheta$$

low density



high density

Effusive atomic and molecular beams

Effusive flow: low density

⇒ collisions between the particles can be neglected

$$\Lambda_{\text{Quelle}} \gg d$$

Λ : mean free path length
 d : diameter of the source aperture

The **collision rate R** depends on the **particle velocity v** ,
target density n and **collision cross section σ**

$$R = v_{\text{rel}} \sigma n$$

$$\begin{aligned} \Lambda &= v/R \\ &= \frac{v}{v_{\text{rel}} \sigma n} \\ &= \frac{1}{\sqrt{2} \sigma n} \end{aligned}$$

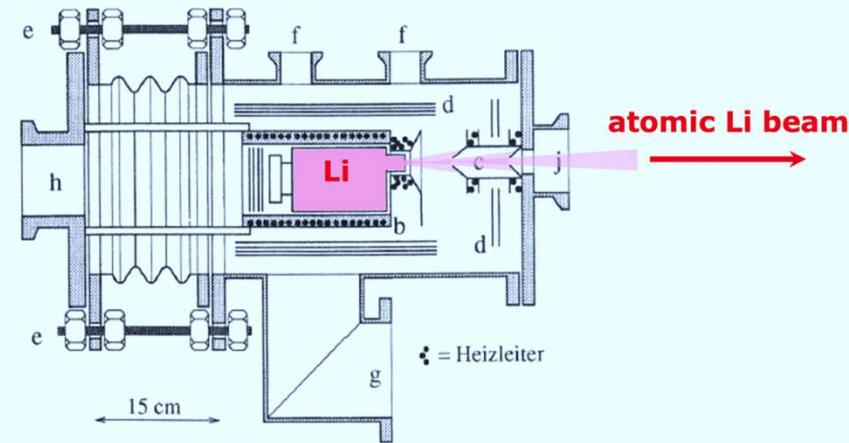
Example:
 at $T = 800 \text{ K}$ and $P = 1 \text{ mbar}$

$$\rightarrow \Lambda = 8 \text{ mm}$$

The cross section σ is of the order of one atomic unit:

$$\begin{aligned} \sigma &\approx \pi a_0^2 \\ &= 10^{-16} \text{ cm}^2 \end{aligned}$$

Lithium atomic (effusive) beam source with oven



- a) Li oven with heated nozzle
- b) Heating wires
- c) Skimmer
- d) Heat shielding

Most probable velocity in a Maxwell-Boltzmann distribution v_w

$$v_w = \sqrt{2kT/m}$$

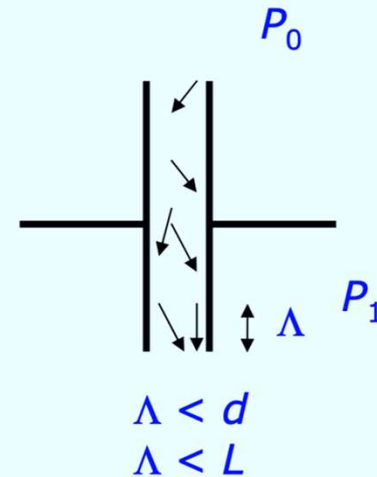
Mean velocity in the gas reservoir

$$\bar{v} = (2/\sqrt{\pi}) v_w \approx 1.13 v_w$$

Supersonic gas jets

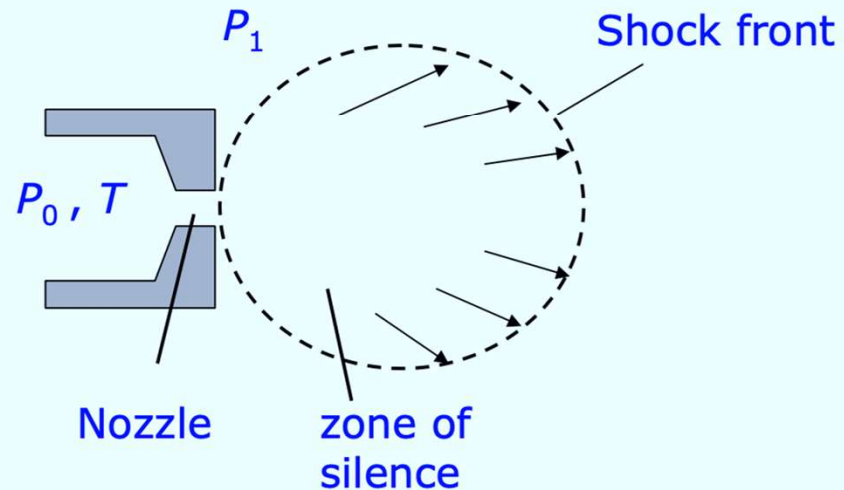
- very low divergence
- high density
- well defined velocity (cold beam: a few K)
- rather complex apparatus (vacuum system)

Gas expands from high pressure (P_0 1-100 bar) through a small nozzle into high vacuum (P_1)



What happens ?

- **acceleration to supersonic speed**
- formation of a **shock front**
(finite pressure P_1 in the chamber)
- **internal energy** (temperature) is transformed into kinetic energy



Supersonic gas jets

During the adiabatic expansion of the gas from initial pressure P_0 to P through the nozzle a **part of the disordered thermal motion** of the particles (given by P_0, T_0) is transformed into directed translational energy.

Energy conservation gives for the enthalpy H (total energy):

$$H = E_{\text{therm}} + PV = 3/2 kT + kT = 5/2 kT$$

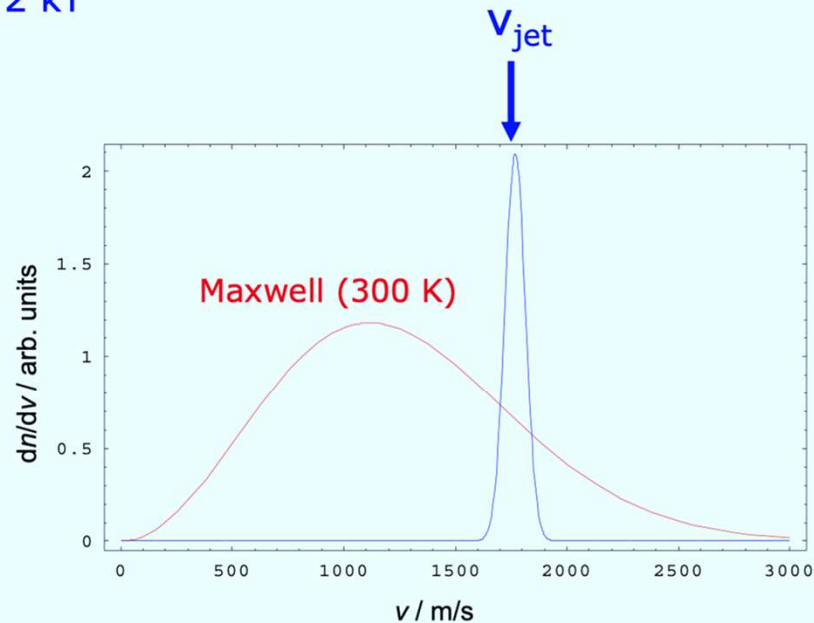
after expansion:

$$E_{\text{kin}} = 5/2 kT$$

$$v_{\text{jet}} = (5kT/M)^{1/2}$$

→ **Temperature decreases**
(adiabatic expansion)

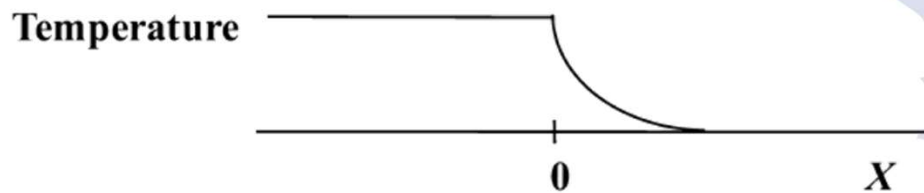
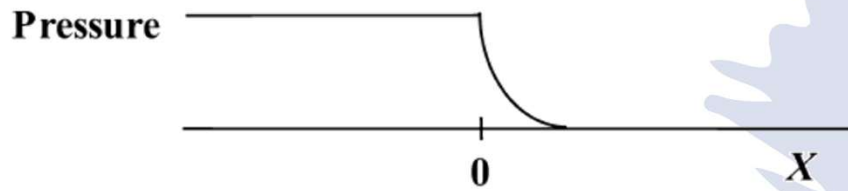
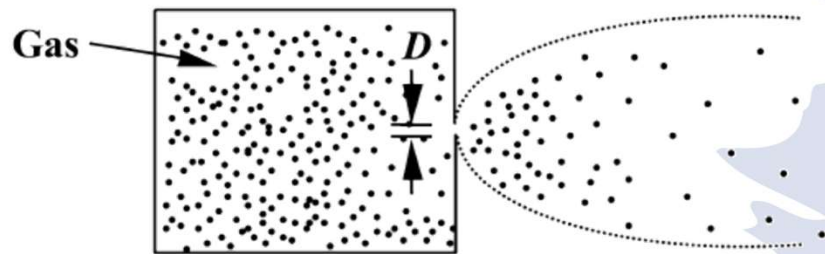
→ **Kinetic energy (directed)**
increases



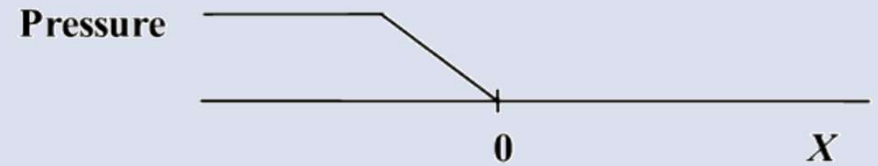
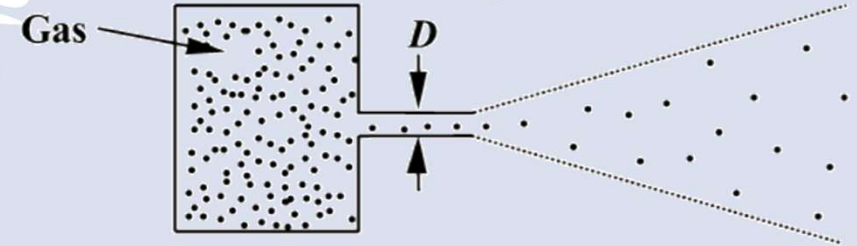
$$E_{\text{kin}} \cong 70 \text{ meV for expansion at } T = 300 \text{ K}$$
$$v_{\text{jet}} \cong 1700 \text{ m/s for Helium}$$

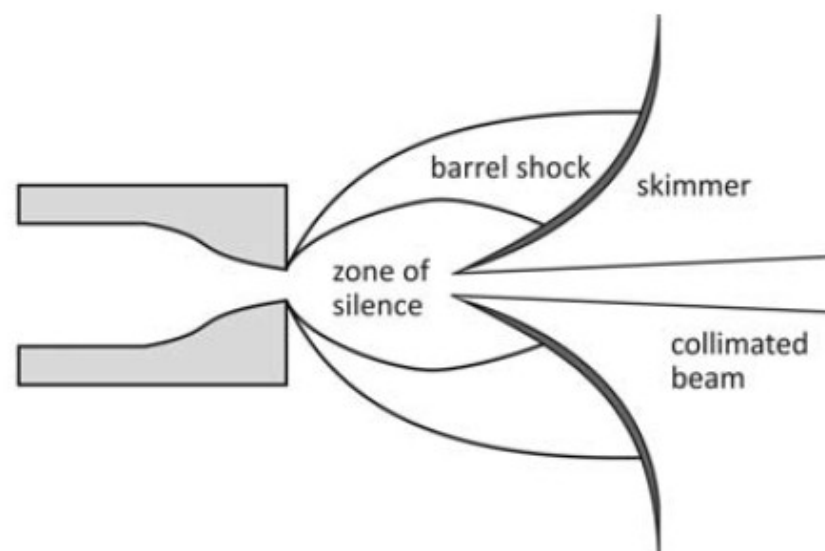
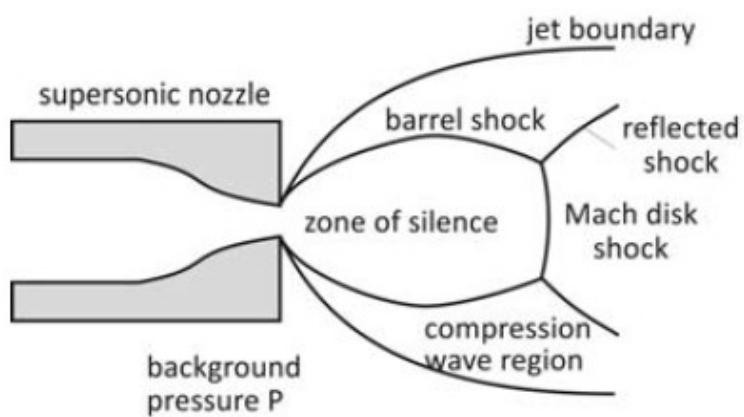
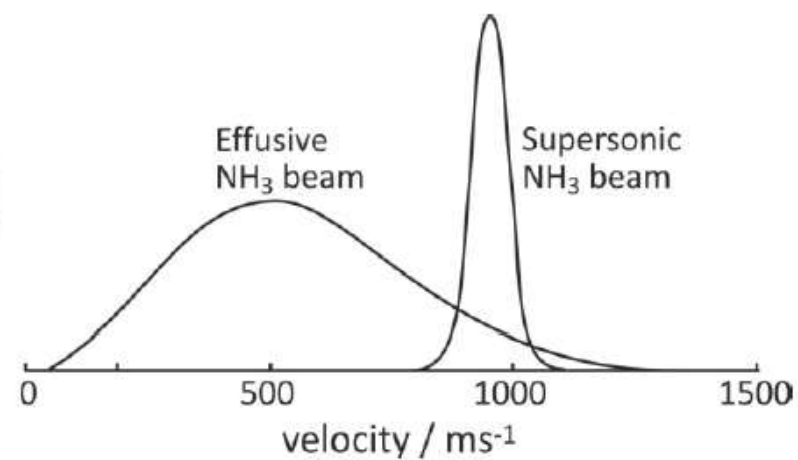
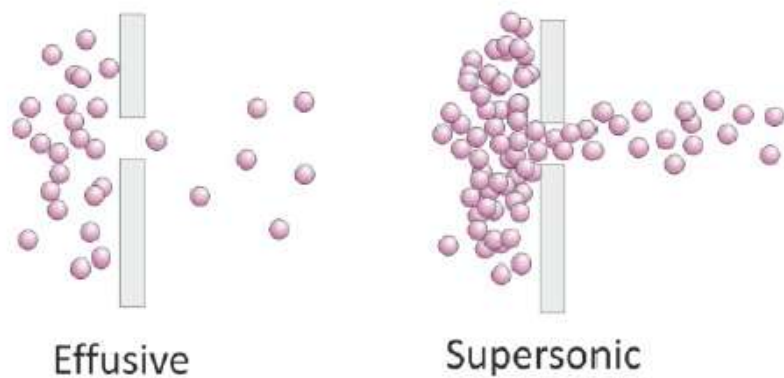
Supersonic expansion reduces target temperature

Thin Pinhole



Long Channel







**Supersonic
Molecular
Beam
Chamber in
SL-216, IIT
Kanpur**

Cross Molecular Beam Experiments

