Kinetic Molecular Theory

Part 1

- Distribution of Velocities of Gas Molecules
- Speeds of Gas Molecules
- Molecular Collision
- Transport Phenomena In Gases

Distribution of Velocities of Gas Molecules in One Direction (Boltzmann Distribution)

According to the model on which the kinetic-molecular theory is based, the molecules of a gas are moving with a variety of speeds and directions, i.e., with various velocities.

Since gases behave similarly in all directions,

- We will investigate the distribution along a particular direction, say the x direction.

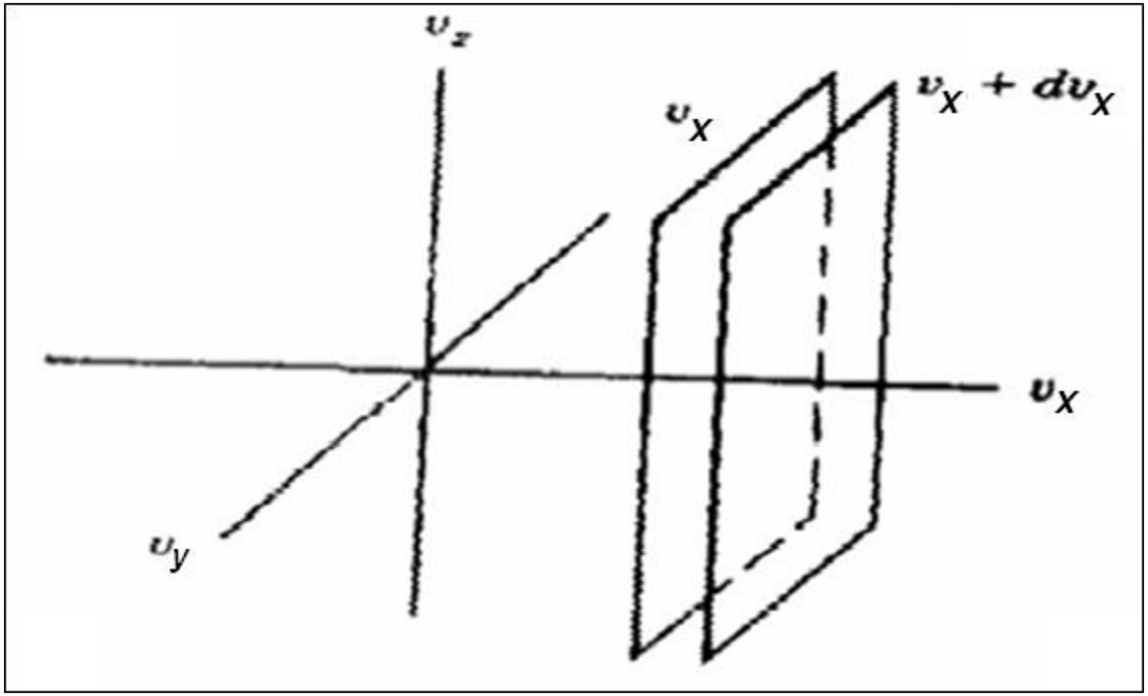
We assume that we have a sample of a gas of:

N total number of molecules .

dN probable number of molecules of velocities in the x direction between U_x and $U_x + dU_x$

dN/N fraction of molecules of velocities between U_x and $U_x + dU_x$ or the probability of finding molecules between the two planes.

This is also the probability of finding molecules with velocity components between two planes



- The probability is expressed also as $f(u_x)\,du_x$ component .

For each molecule $\varepsilon = ½\, mU_x^2$

According to the Boltzmann distribution expression,

$$\frac{dN}{N} \alpha\ e^{-(1/2)mu_x^2/kT} du_x \qquad \therefore \frac{dN}{N} = Ae^{-(1/2)mu_x^2/kT} du_x \qquad (1)$$

- This constant can be evaluated by recognizing that integration of the right side of Eq. (1) over all possible values of u_x, that is, from **$u_x = -\infty$ to $u_x = +\infty$**, must account for all the velocity points. Thus we can write

$$A\int_{-\infty}^{+\infty} e^{-(1/2)mu_x^2/kT}\ \mathrm{du}_x = 1 \qquad (2)$$

$k = 1.380649 \times 10^{-23}$ J/K.

- so that the proportionality constant A is given by

$$A = \frac{1}{\int_{-\infty}^{+\infty} e^{-(1/2)mu_x^2/kT}du_x} \qquad (3)$$

- The value of the integral is seen from the table of integrals to be , $\sqrt{2\pi kT/m}$ and we obtain

$$A = \sqrt{\frac{m}{2\pi kT}} \qquad (4)$$

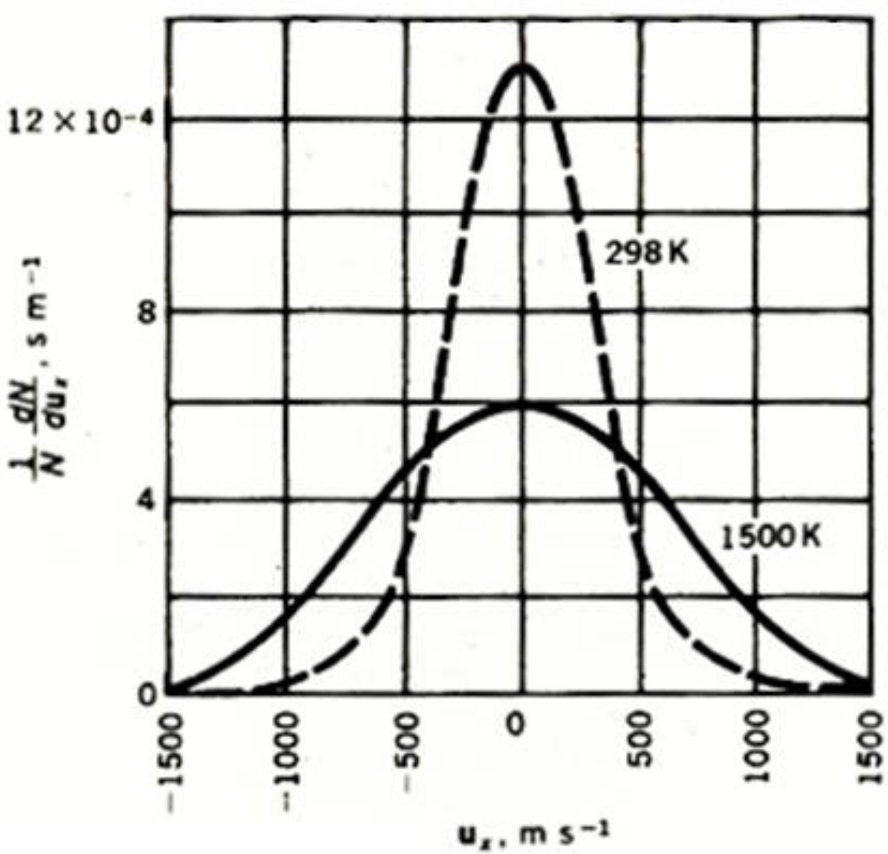
The relation between the Boltzmann constant and the universal gas constant is given by this equation: $R = N_A k$ where R is the ideal gas constant (sometimes called the universal gas constant) and N_A is the Avogadro constant (k is the Boltzmann constant of course).

- Finally, the equation for the distribution over the velocities along the x direction for a sample of N molecules can be written as

$$f(u_x) = \frac{dN/N}{dU_X} = \left(\frac{\mathrm{M}}{2\pi RT}\right)^{1/2} \exp\left(-\frac{\mathrm{M}u_x^2}{2RT}\right) \qquad (5)$$

•Note that **f(u$_x$)** is a velocity **probability density** so that the probability of finding a molecule with velocity components between u$_x$ and u$_x$+ du$_x$ is given by **f(u$_x$)du$_x$**.

•Graphs of this one-dimensional distribution function can be obtained



Probability density $F(U_x)$ for the velocity of N_2 gas in x direction at two different temperatures

Example 1

Calculate the probability density for u_x of N_2 molecules at 300 K.

$u_x = 300\ \mathrm{ms}^{-1}$

Using equation (5)

$$f(u_x) = \left(\frac{M}{2\pi RT}\right)^{1/2} \exp\left(-\frac{Mu_x^2}{2RT}\right)$$

$$= \left[\frac{0.028\,kgmol^{-1}}{2\pi(8.314JK^{-1}mol^{-1})(300K)}\right]^{1/2} \exp\left[-\frac{(0.028\,kgmol^{-1})(300ms^{-1})^2}{2(8.314JK^{-1}mol^{-1})(300K)}\right]$$

$= 8.065 \times 10^{-4}\ \mathrm{s\ m^{-1}}$

Exercise
Calculate the probability density of N2 at 0 and 600 K.

- The speed u of a molecule is related its component velocities by

$$u^2 = u_x^2 + u_y^2 + u_z^2$$

- Therefore, F(u) du is the probability of finding a molecule with a speed between u and u + du .
- The one-dimensional distribution can be combined to give the fraction of the molecules that have velocity components between u_x and u_x+du_x, u_x and u_y+du_y and u_z and u_z+du_z.

- It is given analytically ;

$$f(u_x, u_y, u_z)\, du_x du_y, du_z = \frac{dN}{N}$$

$$\therefore \frac{dN}{N} = \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left[-\frac{m}{2kT}\left(u_x^2 + u_y^2 + u_z^2\right)\right] du_x du_y du_z$$

- The probability of finding a molecule with velocity components between u and u+ du is given by

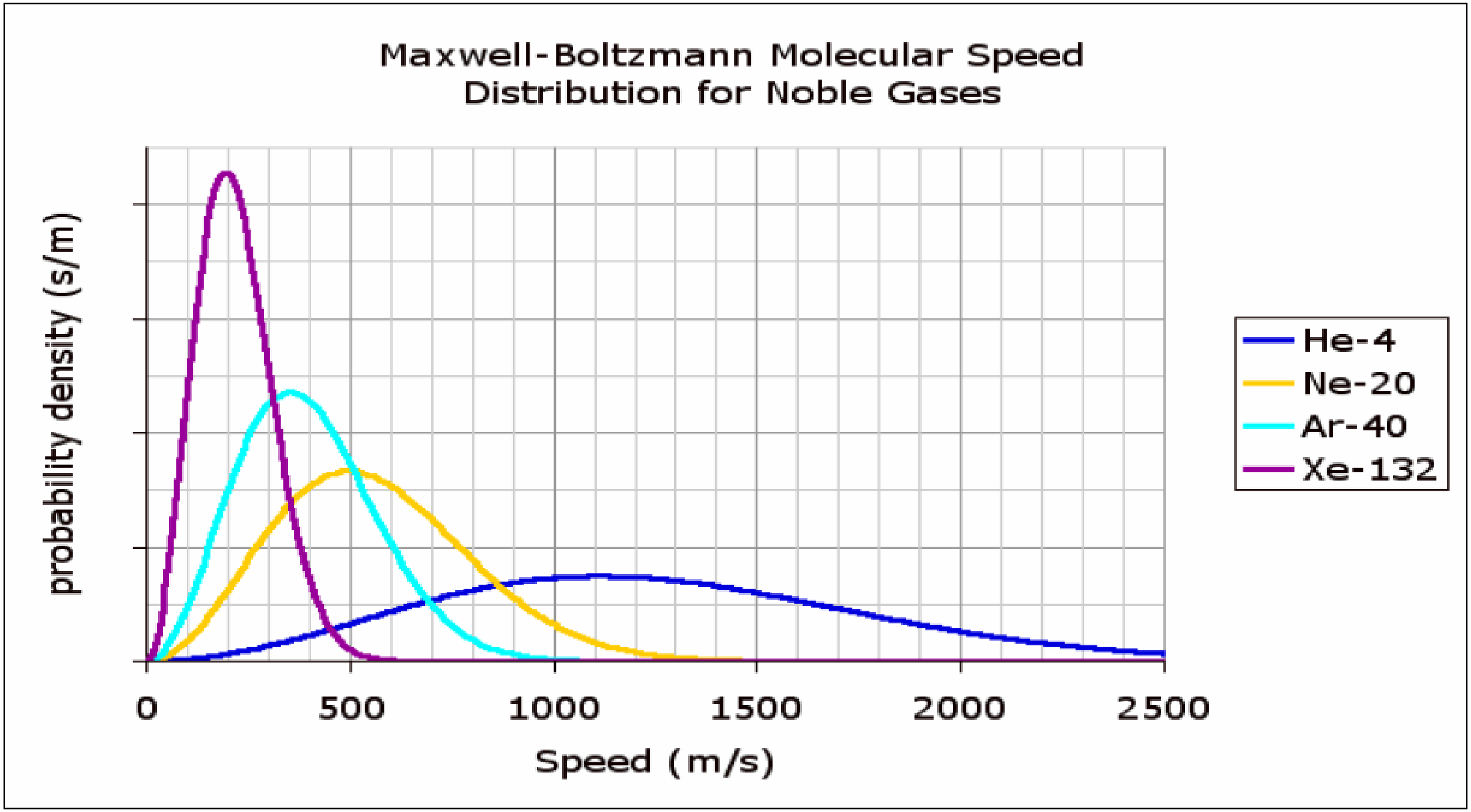
$$F(u)du = 4\pi u^2\left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{-mu^2}{2kT}\right)du$$

- The probability density F(u) is

$$F(u) = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{-mu^2}{2kT}\right)$$

- The probability density at a speed of 0 is zero.

- The probability density increases with the speed up to a maximum and then declines.


Maxwell-Boltzmann Molecular Speed Distribution for Noble Gases
probability density (s/m)
0
500
1000
1500
2000
2500
Speed (m/s)
He-4
Ne-20
Ar-40
Xe-132

Example 2

A flask contains of N_2 molecules at 100 K. How many molecules have a velocity in the range 500.0-500.1 ms^{-1}?

Suppose that we have a sample of 1 mol of N_2

$$m = \frac{\text{mol. wt of } N_2}{\text{Avogadro number}}$$

$$m = \frac{28}{6.022x10^{23}} = 4.65x10^{-26}kg$$

$$\frac{dN}{N_A} = 4\pi u^2\left(\frac{m}{2\pi kT}\right)^{1/2}\exp\left(-\frac{mu^2}{2kT}\right)du$$

$$= 4\pi(500ms^{-1})^2\left(\frac{(4.65x10^{-26}kg)(T/kgm^2s^{-2})}{2\pi(1.381x10^{-23}JK^{-1})(100K)}\right)^{1/2}$$

$$Exp\left(-\frac{(4.65x10^{-26}kg)(500ms^{-1})^2(J/kgm^2s^{-1})}{2\pi(1.38x10^{-23})(JK^{-1})(100K)}\right)(0.1\,ms^{-1})$$

$$\frac{dN/N_A}{du} = 5.79x10^{-4}sm^{-1}$$

The number of molecules have velocities in the range 500.0-500.1 ms^{-1}

$$dN = (5.79x10^{-4})(6.022x10^{23})(0.1) = 3x10^{19} \text{ molecules}$$

and the percent of them is given as follows:

$$\frac{dN}{N}x100 = \frac{3x10^{19}}{6.02x10^{23}}x100 = 4.98x10^{-3}\%$$

Kinetic Molecular Theory

Part 2

The speed of the gas molecules is of three types:

- Most Probable Speed (u_p)
- Mean (average) Speed ($\bar{u}$)
- Root mean-square Speed (u_{rms}).

Speeds of Gas Molecules

Most probable speed u_p :

It is the speed at the maximum of F(u). By Differentiating and setting dF/du equal to zero, we find

$$F(u) = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{mu^2}{2kT}\right)$$

$$\frac{dF(u)}{du} = \left(\frac{m}{2\pi kT}\right)^{3/2} e^{-mu^2/2kT}\left[8\pi u + 4\pi u^2\left(-\frac{mu}{kT}\right)\right] = 0$$

$$\therefore u_p = \left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{2RT}{M}\right)^{1/2}$$

Mean speed ($\bar{u}$):

It is calculated as the average of (u) using the probability distribution F(u):

$$\bar{u} = \int_0^\infty uF(u)\,du$$

Substituting

$$F(u) = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{mu^2}{2kT}\right)$$

and performing the integral we find

$$\bar{u} = 4\pi\left(\frac{m}{2\pi kT}\right)^{3/2} \int_0^\infty \exp\left(-\frac{mu^2}{kT}\right)u^2\,du$$

$$\therefore \bar{u} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

Root-mean square speed (u_{rms}):

Which is defined as the square root of $\overline{u^2}$

$$u_{rms} = (\overline{u^2})^{1/2} = \left[\int_0^\infty u^2 F(u)\,du\right]^{1/2}$$

Substituting

$$F(u) = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{mu^2}{2kT}\right)$$

and using tables again, we find

$$u_{rms} = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2}$$

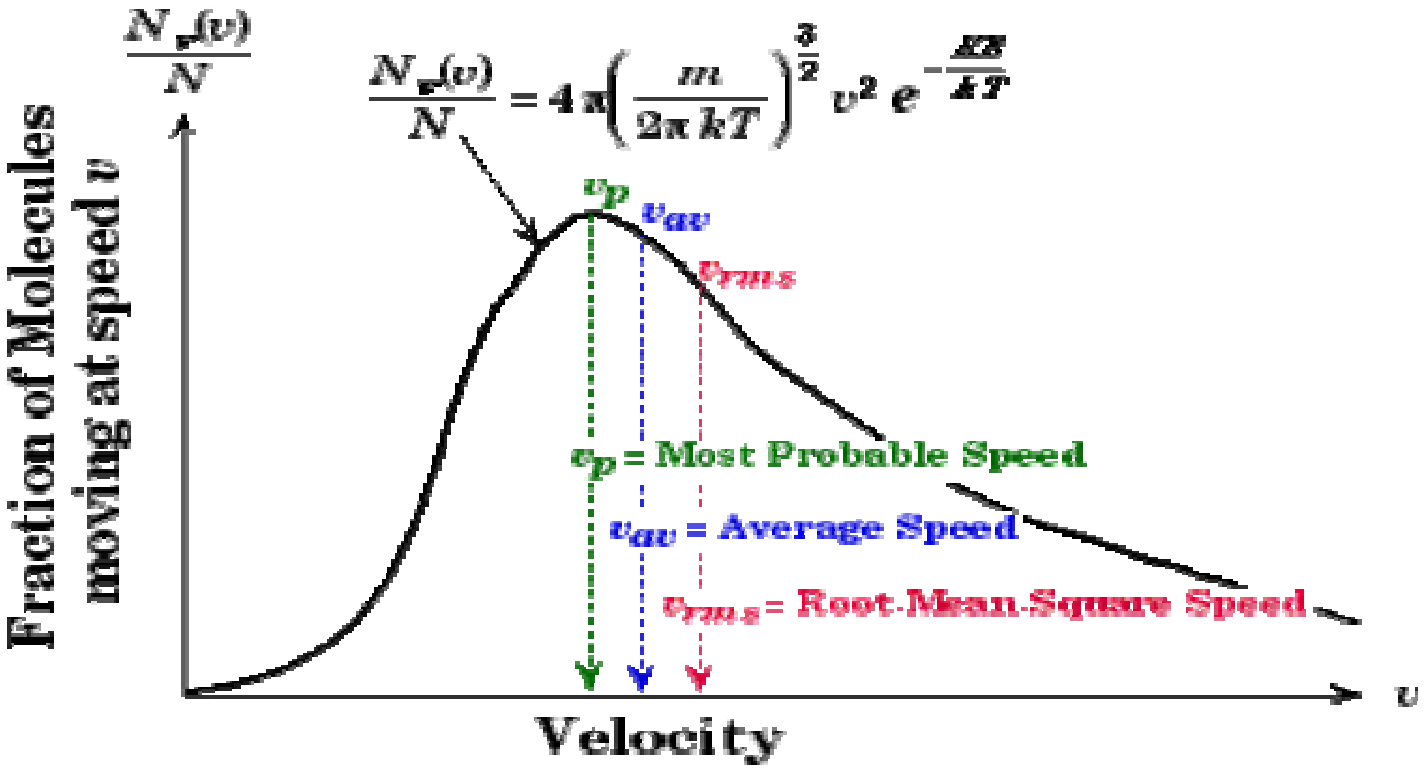
From these three calculations,

$$u_p = \left(\frac{2kT}{m}\right)^{1/2} = \left(\frac{2RT}{M}\right)^{1/2}$$

$$\bar{u} = \left(\frac{8kT}{\pi m}\right)^{1/2} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$u_{rms} = \left(\frac{3kT}{m}\right)^{1/2} = \left(\frac{3RT}{M}\right)^{1/2}$$

We can see that at any temperature $u_{rms} > \bar{\mathrm{u}} > \mathrm{u}_{\mathrm{p}}$



$$v_p = \sqrt{2\frac{kT}{m}} \qquad v_{av} = \sqrt{\frac{8}{\pi}\frac{kT}{m}} \qquad v_{rms} = \sqrt{3\frac{kT}{m}}$$

- ✓ Each of these speeds is proportional to $(T/M)^{1/2}$.

- ✓ Each increases with temperature

- ✓ Each decreases with molar mass. Lighter molecules therefore move faster than heavier molecules on average, as shown in the following table.

Various types of average speeds of gas molecules

Gas	$(u^2)^{1/2}$/m s^{-1}	(u)/m s^{-1}	u_p/m s^{-1}
H_2	1920	1769	1568
O_2	482	444	394
CO_2	411	379	336
CH_4	681	627	556

Example 1

Calculate the The different types of speeds of hydrogen molecules at 0°C.

$$u_p = \left(\frac{2RT}{M}\right)^{1/2} = \left[\frac{(2)(8.314\ Jk^{-1}mol^{-1})(273\ k)}{(2.016\ x10^{-3}\ kg\ \ mol^{-1})}\right]^{1/2} = 1.50 \text{ x } 10^{3} \text{ m s}^{-1}$$

$$\bar{u} = \left(\frac{8RT}{\pi M}\right)^{1/2} = \left[\frac{(8)(8.314\ Jk^{-1}mol^{-1})(273\ k)}{(3.146)(2.016\ x10^{-3}\ kg\ \ mol^{-1}}\right]^{1/2} = 1.69 \text{ x } 10^{3} \text{ m s}^{-1}$$

$$u_{rms} = \left(\frac{3RT}{M}\right)^{1/2} = \left[\frac{3(8.314Jk^{-1}mol^{-1})(273.15k)^{1/2}}{2.06x10^{-3}\,kg\,\text{mol}^{-1}}\right] = 1.84 \text{ x } 10^{3}\ \text{m s}^{-1}$$

The root-mean square speed of a hydrogen molecule at 0°C is 6620 kmh^{-1}, but at ordinary pressures it travels only an exceedingly short distance before colliding with another molecule and changing direction.

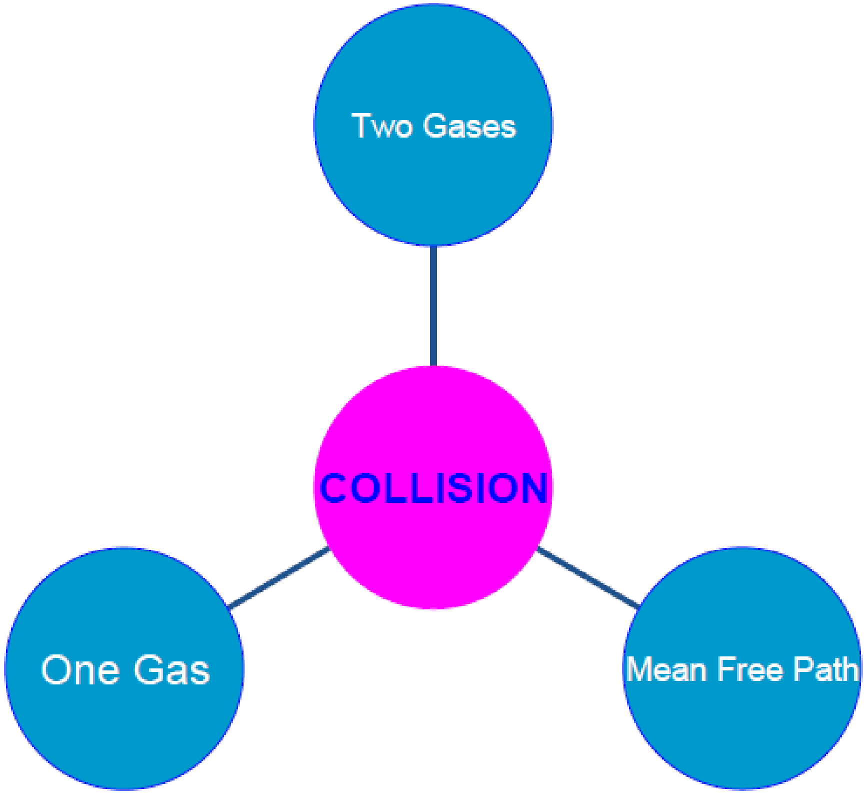
Exercise

How many molecules have a velocity exactly equal to 500 ms^{-1}?

Kinetic Molecular Theory

Part 3

Collision properties of gas molecules

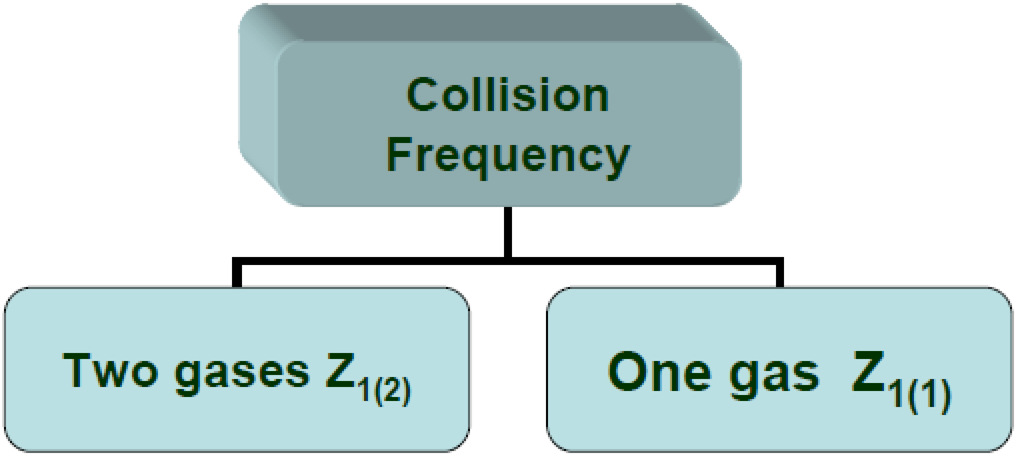


Two Gases

COLLISION

One Gas

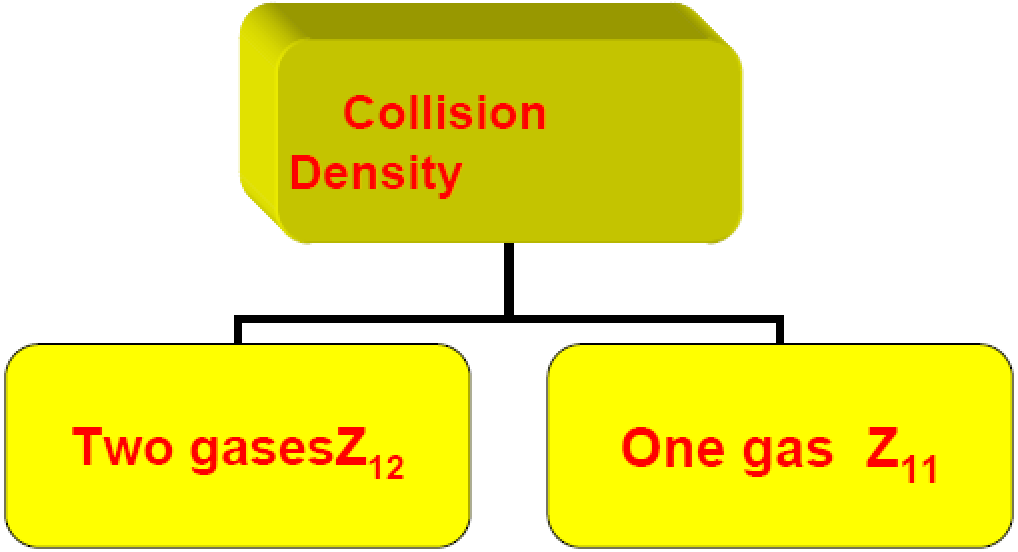
Mean Free Path



Collision Frequency

Two gases $Z_{1(2)}$

One gas $Z_{1(1)}$



Collision Density

Two gases Z_{12}

One gas Z_{11}

Molecular Collision

Collision Frequency:

❑ The collision frequency is ***the number of collisions of molecules per unit time***, where

➢ $Z_{A(B)}$ for the collision between the molecules of two different gases A and B.

➢ $Z_{A(A)}$ for collision between identical molecules.

❑let us consider a cylinder of length l (m) containing N_A and N_B molecules of gas A and gas B, respectively. These molecules have;

➢ Diameters d_A and d_B (m) and collision diamete

$$d_{AB} = (d_A + d_B)/2$$

➢Atomic masses m_A and m_B (kg), molecular masses M_A and M_B (kg) and reduced mass .

Reduced mass μ

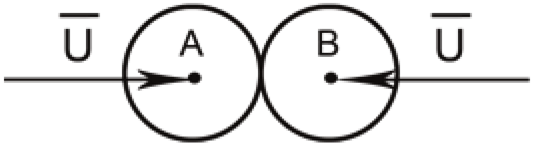
$$\mu = \frac{1}{m_A} + \frac{1}{m_B} = \frac{N_A}{M_A} + \frac{N_A}{M_B} = N_A \frac{M_A + M_B}{M_A M_B}$$

- Densities ρ_A and ρ_B (m^{-3}), number of molecules per unit volume or $\rho = N/V$
- Velocities u_A and u_B (ms^{-1}) and mean relative velocity

$$\overline{u_{AB}} = \left(\frac{8RT}{\pi \mu}\right)^{1/2} \longleftarrow \text{Why?}$$

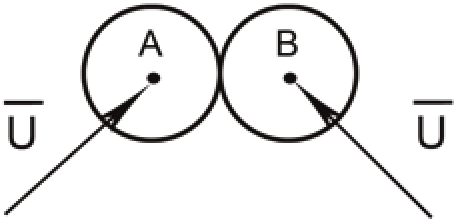
The distribution of relative velocities between two molecules depends on the <u>velocity of each one</u> and <u>the angle of approach</u>:

a



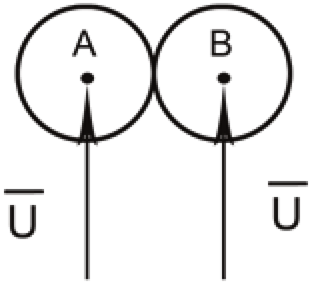
$\overline{U}_{AB} = 2\overline{U}$

b



$U_{AB} = \sqrt{2}U$

c



$\overline{U}_{AB} = 0$

If the velocities of A equals that of B:

a) The two molecules move towards each other

$$\bar{U}_{AB} = \bar{U}_A + \bar{U}_B = 2\bar{U}$$

b) The two molecules move together in the same way

$$\bar{U}_{AB} = \bar{U}_A - \bar{U}_B = 0$$

c) The two molecules move with an angle of 90o (most probable case).

$$\bar{U}_{AB} = \sqrt{(\bar{U}_A)^2 + (\bar{U}_B)^2} = [(\bar{U}_A)^2 + (\bar{U}_B)^2]^{1/2}$$

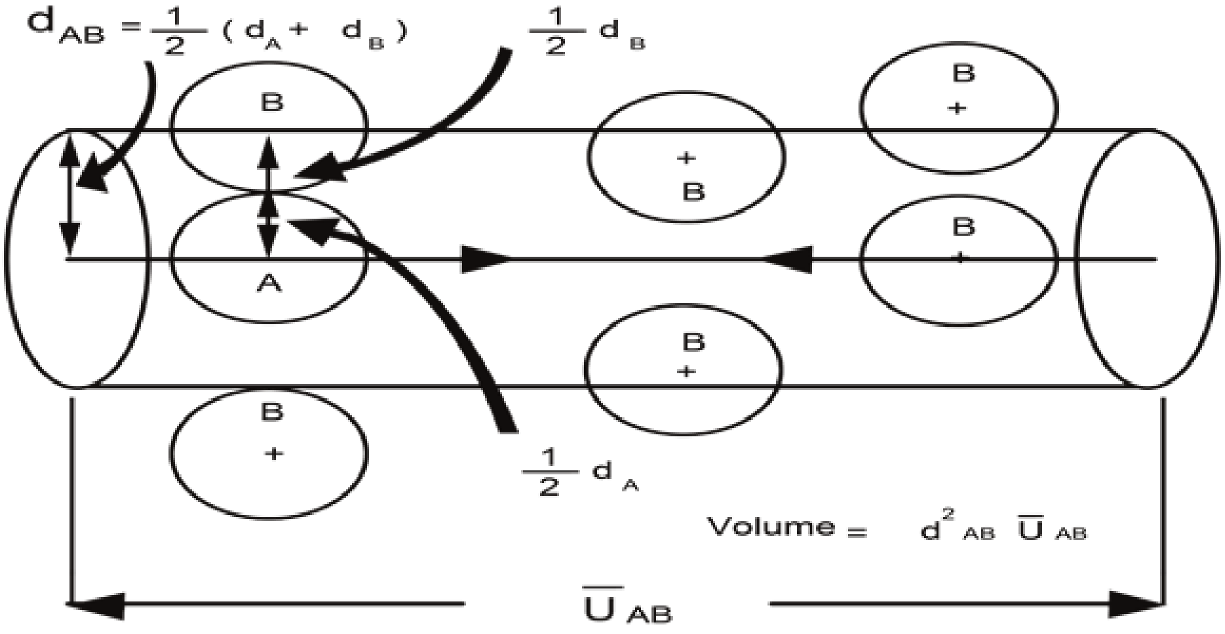
$$\bar{U}_A = \bar{U}_B$$

$$\bar{U}_{AB} = \sqrt{2}\bar{U}$$

$$\overline{U}_{AB} = \sqrt{(\overline{U}_A)^2 + (\overline{U}_B)^2} = [(\overline{U}_A)^2 + (\overline{U}_B)^2]^{1/2}$$

$$\overline{U} = \left(\frac{8RT}{\pi M}\right)^{1/2}$$

$$\overline{U}_{AB} = \left[\frac{8RT}{\pi.\mu_{AB}}\right]^{1/2}$$



- ❑ hard spherical molecules collide with each other if their centers come within a distance

  $d_{AB} = ½ (d_A+d_B)$, **the collision diameter.**

- Molecules of type B are stationary.
- A molecule of type A will collide in unit time with all molecules of type B that have their centers in a cylinder of

Volume = $\pi d_{AB}^{2} u_{A}$

- A molecule of type A would undergo a

number of collisions = $\pi d_{AB}^{2} u_{A} \rho_{B}$

per unit time.

- ☐ Molecules of type B are actually not stationary and so the relative speed $\mathbf{u_{AB}}$ should be used in calculating the rate of collisions $\mathbf{z_{A(B)}}$ of a molecule of type A with molecules of type B. Thus,

$$\mathbf{Z_{A(B)}} = \pi d_{AB}^{2} \bar{u}_{AB} \rho_B \qquad (1)$$

or

$$Z_{A(B)} = \pi d_{AB}^{2} \left(\frac{8RT}{\pi\mu} \right)^{1/2} \rho_B$$

- where $\mathbf{z_{A(B)}}$ is the **collision frequency** of molecules of type A with molecules of type B .

- The collision diameter $\mathbf{d}_{AB}$ has the unit m,
- The relative mean speed ($\mathbf{u}_{AB}$) has the unit m s^{-1},
- The collision frequency has the unit s^{-1}.

- Now a molecule of type A is moving through molecules of type A, rather than molecules of type B, Eq. (1) becomes

$$Z_{A(A)} = \pi d_A^2 \bar{u}_A \rho_A$$

Or $$Z_{A(A)} = \pi d_A^2 \left(\frac{8RT}{\pi \mu} \right)^{1/2} \rho_A \qquad (2)$$

Example 1

What is the mean relative speed of H_2 molecules with respect to O_2molecules (or oxygen molecules with respect to hydrogen molecules) at 298 ?

The molecular masses are:

$$m_1 = \frac{2.016\,x10^{-3}\,kg\ mol^{-1}}{6.022\,x10^{23}\ mol^{-1}} = 3.348\,x10^{-27}\,kg$$

$$m_2 = \frac{32.00\,x10^{-3}\,kg\ mol^{-1}}{6.022\,x10^{23}\ mol^{-1}} = 5.314\,x10^{-26}\,kg$$

$$\mu_{AB} = \frac{1}{m_A} + \frac{1}{m_B} = \frac{m_A + m_B}{m_A.m_B} = 6.022x10^{23}\frac{56.448x10^{-27}}{177.9x(10^{-27})^2} = 1.9x10^{50}$$

$$\bar{u}_{12} = \left(\frac{8kT}{\pi\mu}\right)^{1/2} = \left[\frac{8(1.381\,x10^{-23}\,Jk^{-1})(298\,k)}{\pi(3.150\,x10^{-17}\,kg)}\right] = 1824\ m\ s^{-1}$$

Note that the mean relative speed is closer to the mean speed of molecular hydrogen (1920 ms^{-1}) than to that of molecular oxygen (482 ms^{-1}) .

Kinetic Molecular Theory

Part 4

Collision Density

It is the number of collisions per unit tim per unit volume.

For two gases:

To calculate the number of collisions of molecules of type 1

with molecules of type 2 per unit time per unit volume of gas

$$Z_{12} = Z_{1(2)} x \rho_1$$

$$Z_{12} = \rho_1 . \rho_2 . \pi . d_{12}^2 . \bar{u}_{12}$$

For only one gas:

The number of collisions of molecules of type 1 with other molecules of type 1 per unit time per unit volume of gas will be reduced to

$$Z_{11} = \frac{1}{2}\rho^2.\pi.d^2.\bar{u}_{11}$$

The factor of 1/2 has been introduced to avoid double counting of the collisions. (so one A molecule colliding with another A molecule is counted as one collision regardless of their actual identities). For collisions of A and B molecules present at number densities ρ_A and ρ_B the collision density is

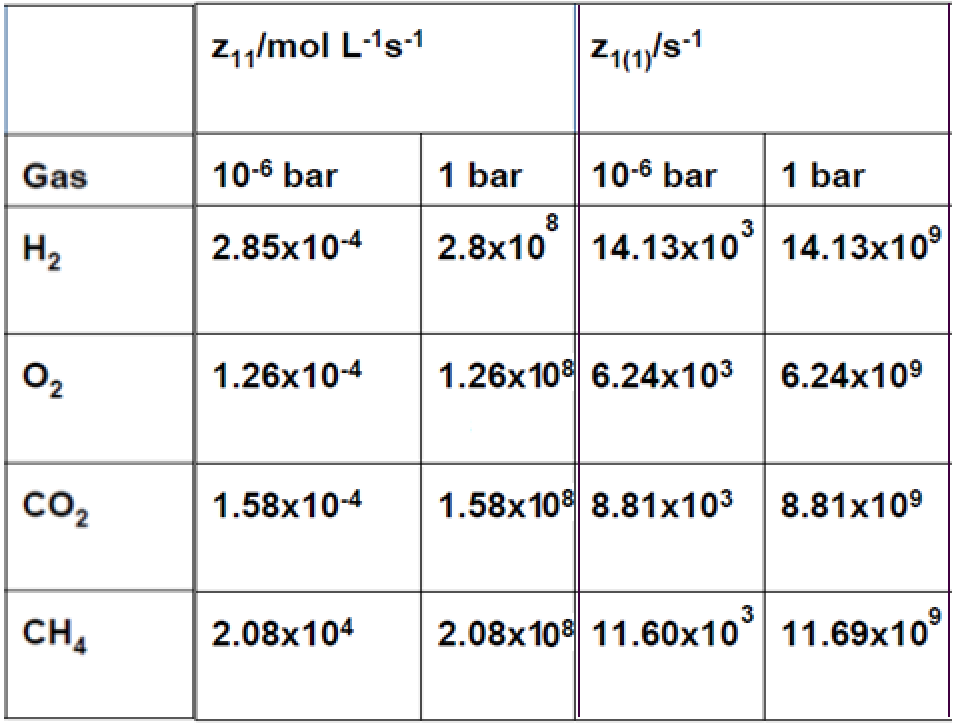
$$Z_{12} = \pi.d^2.\bar{u}_{12}\rho_1.\rho_2$$

The collision density is expressed in mol m^{-3} s^{-1}

The collision density is on interest because it sets an upper limit on the rate with which two gas molecules can react. Actual chemical reaction rates are usually much smaller than the collision rates, indicating that not every collision leads to reaction.

Collision frequencies z1(1) and collision densities z11 for four gases are given In next Table at 25 °C. The collision densities are expressed in mol $L^{-1} . s^{-1}$ because it is easier to think about chemical reactions in these units.

1 Pa = 1 N / m^2 = 10^{-5} bar = 7.5×10^{-3} Torr = 0.987 atm



	z_{11}/mol $L^{-1}s^{-1}$		$z_{1(1)}/s^{-1}$	
Gas	10^{-6} bar	1 bar	10^{-6} bar	1 bar
H_2	2.85×10^{-4}	2.8×10^{8}	14.13×10^{3}	14.13×10^{9}
O_2	1.26×10^{-4}	1.26×10^{8}	6.24×10^{3}	6.24×10^{9}
CO_2	1.58×10^{-4}	1.58×10^{8}	8.81×10^{3}	8.81×10^{9}
CH_4	2.08×10^{4}	2.08×10^{8}	11.60×10^{3}	11.69×10^{9}

Example 1

Calculate the collision frequency and collision density in ammonia, r=190pm, at 25°C and 100kPa. (M_{NH3} = 17.03 g/mol)

Note that he did not mention to ammonia concentration or volume (there is no n or V variables)

The collision frequency is

$$Z = \pi d_{NH_3}^2 \bar{U}_{A(A)} \rho_{NH_3}$$

$$\bar{U}_{A(A)} = \left(\frac{8kT}{\pi m} + \frac{8kT}{\pi m} \right)^{1/2} = 4\left(\frac{kT}{\pi m} \right)^{1/2}$$

$$\rho_{NH_3} = \frac{N}{V} = \frac{nN_A}{V} = \frac{PN_A}{RT} = \frac{P}{kT}$$

$$\pi d_{NH_3}^2 = \pi (2r_{NH_3})^2 = 4\pi r_{NH_3}^2$$

$$Z_{A(A)} = \pi d_{NH_3}^2 \bar{U}_{A(A)} \rho_{NH_3} = 4\pi r^2 . 4\left(\frac{kT}{\pi m} \right)^{1/2} . \frac{P}{kT}$$

$$Z_{A(A)} = 16Pr^2\left(\frac{\pi}{mkT}\right)^{1/2}$$

$$Z_{A(A)} = 16\text{x}(100\text{x}10^3\text{Pa})\text{x}(190\text{x}10^{-12}\text{m})^2\text{x}\left[\frac{\pi}{(17.03\text{x}1.66\text{x}10^{-27})^2\text{x}(1.381\text{x}10^{-23})\text{x}298}\right]^{1/2}$$

$$;1\text{u} = 1.66\text{x}10^{-27}\text{ kg}; \text{u}: \text{atomic mass unit}$$

$$Z_{A(A)} = 9.49x10^9 s^{-1}$$

The collision density $Z_{A(A)}$

$$Z_{AA} = Z_{A(A)}\rho_{NH_3} = \frac{1}{2}Z_{A(A)}.\frac{P}{kT} = \frac{1}{2}x9.49x10^9 s^{-1}x\left(\frac{100x10^3 pa}{1.381x10^{-23}\text{J.K}^{-1}\times(298\text{K})}\right)$$

$$Z_{AA} = 1.15x10^{15}s^{-1}.mol.m^{-3}$$

Mean Free Path

- The mean free path λ is the average distance traveled between collisions.
- It can be computed by dividing the average distance traveled per unit time by the collision frequency.
- For a molecule moving through like molecules.

$$\lambda = \frac{1}{2^{1/2} \rho \pi d^2}$$

Assuming that the collision diameter d is independent to temperature,

the temperature and pressure dependence of the mean free path may be obtained by substituting the ideal gas law in the form $\rho = P/kT$:

$$\lambda = \frac{1}{\sqrt{2}} \frac{kT}{P.\pi.d^2}$$

Thus, at constant temperature, the mean free path is inversely proportional to the pressure.

Example 2

For oxygen at 25 °C the collision diameter is 0.361 nm. What is the mean free path at 1.0 bar pressure, and (b) 0.1 Pa pressure?

a)

$$\rho = N/V = PN_A/RT = \frac{(1\ \text{bar})(6.022\ \text{x}10^{23})(10^{3}\ \text{Lm}^{-3})}{(0.083145\ \text{L bar K}^{-1}\ \text{mol}^{-1})(298\ \text{K})} = 2.43\ \text{x}10^{25}\ \text{m}^{-3}$$

$$\lambda = \frac{1}{2^{1/2}\rho\pi d^{2}}$$

$$\lambda = [(1.414)(2.43\text{x}10^{25}\text{m}^{-3})\pi(3.61\text{x}10^{-10}\text{m})^{2}]^{-1} = 7.11\text{x}10^{-8}\text{m}$$

Why he did not use Boltzmann constant k instead of gas constant?

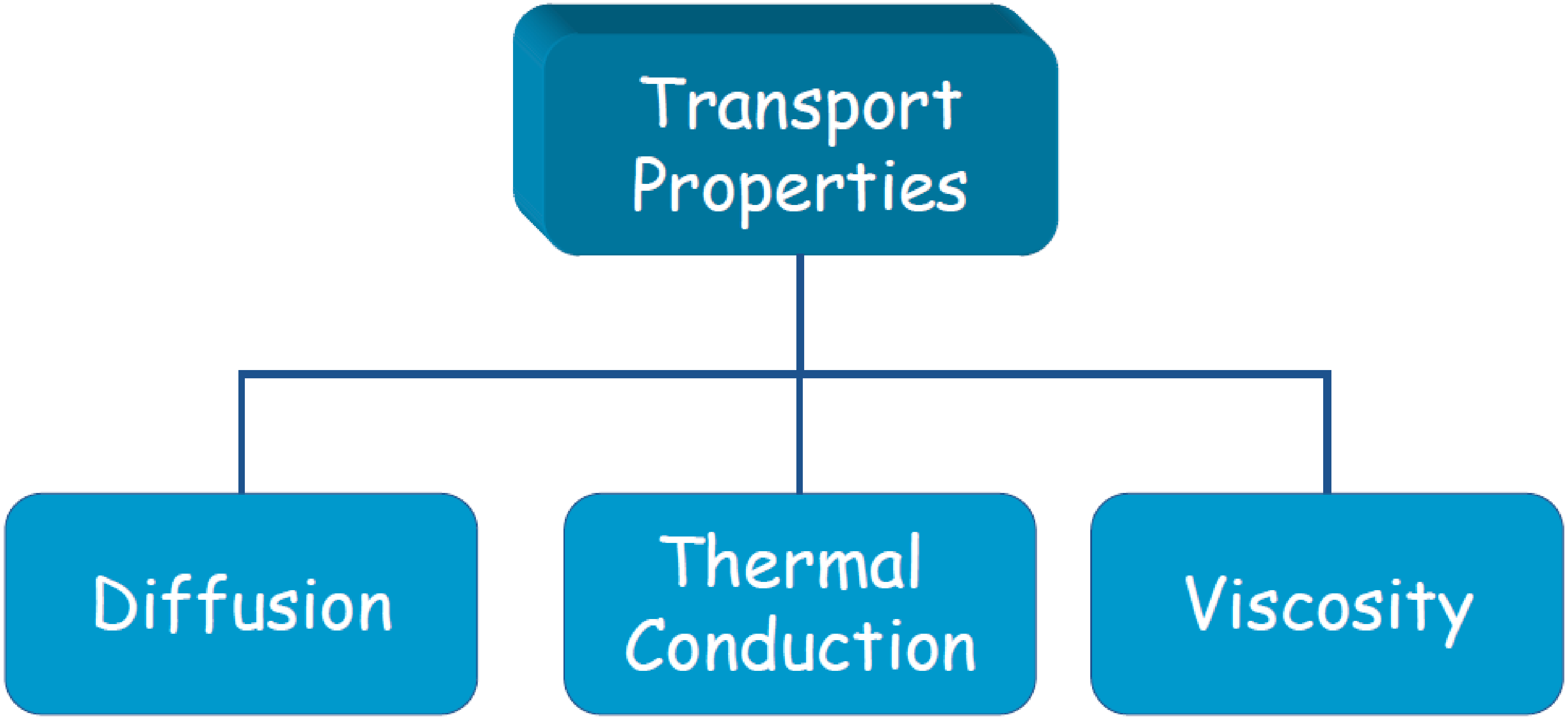
(b)

At pressure so low that the mean free path becomes comparable with the dimensions of the containing vessel, the flow properties of the gas become markedly different from those at higher pressures.

Kinetic Molecular Theory

Part 5

TRANSPORT PHENOMENA IN GASES



Transport Properties

Diffusion

Thermal Conduction

Viscosity

If a gas is not uniform with respect to

- Composition
- temperature, and
- velocity,

transport processes occur until the gas becomes uniform.

Examples:

(1) Open a bottle of perfume at the front of a classroom:

Good smell moves from front row to rear (Diffusion).

(2) Metal bar, one end hot and one end cold:

Heat flows from hot to cold end until temperature becomes (Thermal Conduction)

TRANSORT PROPERTIES

TRANSPORT PROPERTIES OF GASES

DIFFUSION
Transport of (labelled) particles

THERMAL CONDUCTION
Transport of thermal energy

VISCOSITY
Transport of momentum in one direction through a gas in another direction

In each case,

- Rate of flow ∞ Rate of change of some property with distance, a so-called gradient
- All have same mathematical form:

  Flow of_____(per unit area, unit time) = (____x gradient____)

(matter)	(diffusion coefficient)	(concentration)
J_{iz}	$-D$	$\frac{dc_i}{dz}$

The flux of component i in the z direction due to diffusion is proportional to the concentration gradient dci/dz, according to Fick's law:

$$\boxed{J_{iz} = -D\frac{dc_i}{dz}}$$

Diffusion: Fick’s Law

J_{iz} is the flux and

*Expressed in terms of quantity per unit area per unit time.

* J_{iz} has the units mol m^{-2} s^{-1},

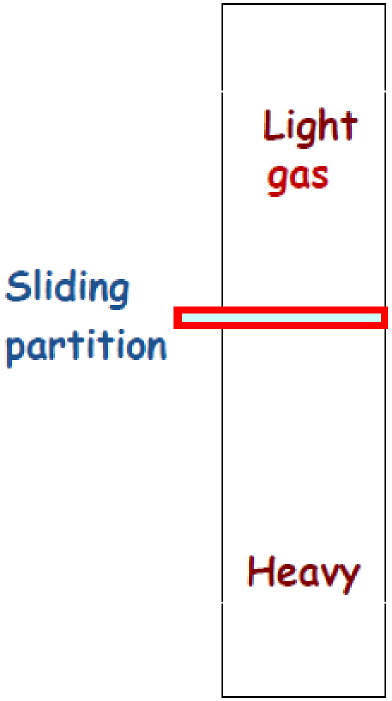
* dc_i/dz has the units of mol m^{-3}

* D has units of m^2 s^{-1}.

* The negative sign comes from the fact that if C_i increases in the positive z direction dC_i/dz is positive, but the flux is in the negative z direction because the flow is in the direction of lower concentrations

Determination of D for the diffusion of one gas into another

- The sliding partition is withdrawn for a definite interval of time.
- From the average composition of one chamber or the other, After a time interval, D may be calculated.



Thermal Conduction: Fourier's Law

Transport of heat is due to a gradient in temperature.

(heat)	(thermal conductivity)	(temperature)
q_z	$= - K_T$	$\frac{dT}{dz}$

$$\therefore q_z = -K_T \frac{dT}{dz}$$

- K is the thermal conductivity.
- q_z has the units of J m^{-2} s^{-1} and
- d_T/d_z has the units of K m^{-1},
- K_T has the units of J m^{-1} s^{-1} K^{-1}.
- The negative sign indicates that if d_T/d_z is positive, the flow of heat is in the negative z direction, which is the direction toward lower temperature.

Viscosity: is a measure of the resistance that a fluid offers to an applied shearing force.

- Consider what happens to the fluid between parallel planes
- when the top plane is moved in the y direction at a constant speed relative to the bottom plane while maintaining a constant distance between the planes (coordinate z)
- The planes are considered to be very large, so that edge effects may be ignored.

- The layer of fluid immediately adjacent to the moving plane moves with the velocity of this plane.
- The layer next to the stationary plane is stationary; in between the velocity usually changes linearly with distance,.

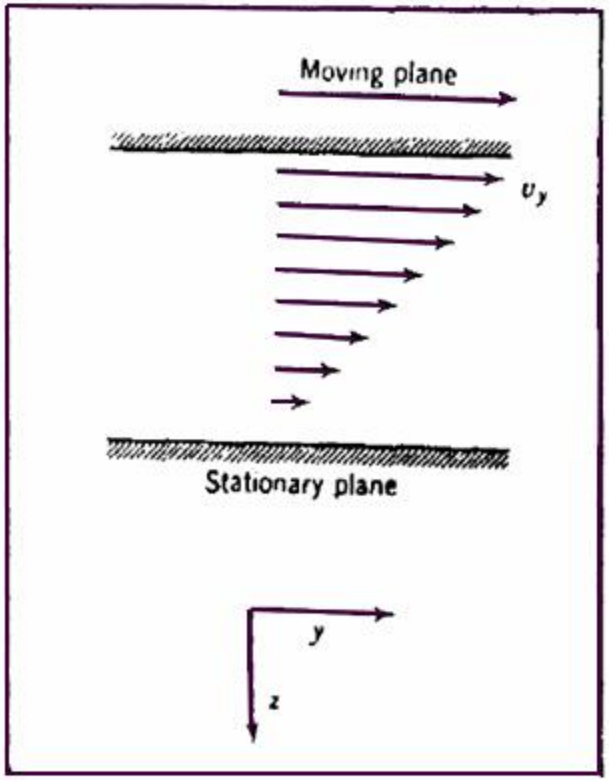
The velocity gradient

Rate of change of velocity with respect to distance measured perpendicular to the direction of flow is represented by

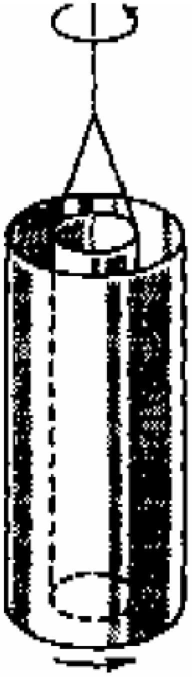
du_y / dz

The viscosity η is defined by the equation

$$F = -\eta \frac{du_y}{dz} \qquad (6.3)$$



- F is the force per unit area required to move one plane relative to the other.
- The negative sign comes from the fact that if F is in the +y direction, the velocity u_y decreases in successive layers away from the moving plane and du_y/dz is negative.
- The thermal conductivity is determined by the hot wire method
- Determination of the rate of flow through a tube, the torque on a disk that is rotated in the fluid, or other experimental arrangement.
- The outer cylinder is rotated at a constant velocity by an electric motor.



(c)

- Since 1N = 1 kg m s^{-2}, 1 Pa s = 1 kg m^{-1} s^{-1}. A fluid has a viscosity of 1 Pa s if a force of 1 N is required to move a plane of 1 m^2 at a velocity of 1 m s^{-1} with respect to a plane surface a meter away and parallel with it.

- The cgs unit of viscosity is the poise, that is, 1 $gs^{-1}cm^{-1}$
  0.1 Pa S = 1 poise.

Kinetic Molecular Theory

Part 6

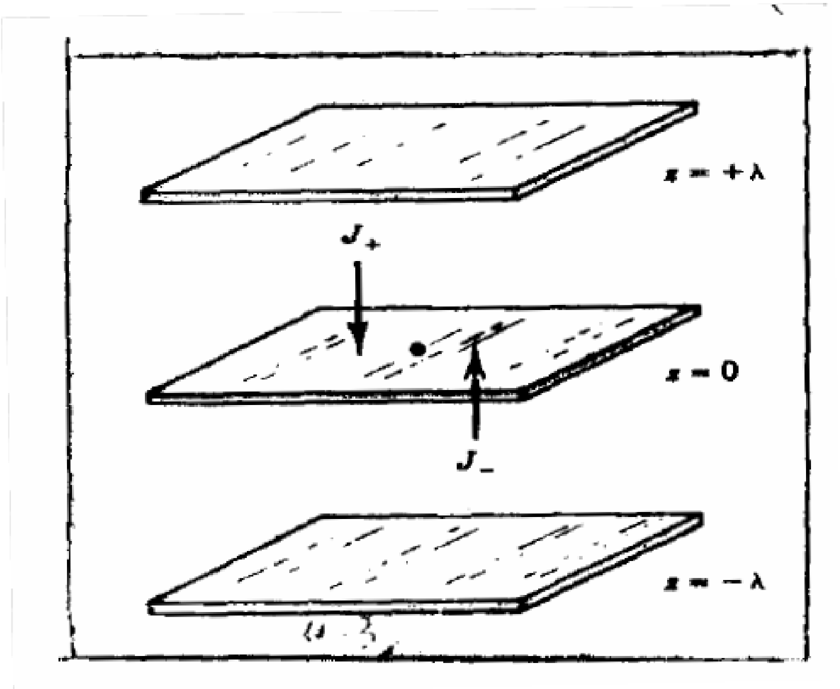
Calculation of Transport Coefficients

To calculate the transport coefficients

D, K_T, and η

even for hard-sphere molecules, needs to consider how the Maxwell-Boltzmann distribution is disturbed by a gradient of concentration, temperature or velocity.

Diffusion Coefficient



Planes constructed at distance ±λ (the mean free path) from the origin. The concentration gradient is in the z direction.

Where ρ_o is the number density of particles in the plane at $z = 0$.

The density of particles at $z = +\lambda$ is given by the term in brackets

- Consider the diffusion of molecules in a concentration gradient in the z direction and we are at $z = 0$.

- Imagine that we construct planes parallel to the xy plane at **x** = ±λ, where λ is the mean free path.

- We choose planes at the mean free path because molecules form more distant points will, on average, have suffered collisions before reaching $z = 0$.

- Calculate the flux of particles across z = 0 due to the molecules above (z>0) and below **(z<0)**. The flux across **z = 0** from above is

$$J_{+} = \left[\rho_{0} + \lambda \left(\frac{d\pi}{dz} \right) \right] \frac{\bar{u}}{4}$$

Similarly, the flux across z = 0 due to the molecules below z = 0 is

$$J_{-} = \left[\rho_o - \lambda\left(\frac{d\rho}{dz}\right)\right]\frac{\bar{u}}{4}$$

The net flux of particles across the plane z = 0 is then

$$J = -\frac{1}{2}(\bar{u})\frac{d\rho}{dz}$$

This equation can be compared with Eq. 5.1 to obtain

$$D_a = \frac{1}{2}(u)\lambda = \left(\frac{kT}{\pi m}\right)^{1/2}\frac{1}{\rho\pi d^2}$$

- where the subscript 'a' indicates approximate value.
- The exact theoretical expression for the diffusion coefficient of hard spheres is:

$$D = \frac{3\pi}{8}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{1}{\rho\pi d^2} = \frac{3}{8}\left(\frac{RT}{\pi M}\right)^{1/2}\frac{1}{\rho d^2}$$

Example 1

Predict $D_{(O2,N2)}$ of an equimolar mixture of O_2 and N_2 gases at 1.00 atm and 0^0C using d_{O2} = 0.353 nm and d_{N2} = 0.373 nm.

$$\rho = \frac{N}{V} = \frac{nN_A}{V} = \frac{N_A P}{RT} \qquad \therefore \rho = \frac{(101.325\ \mathrm{Pa})(6.022\mathrm{x}\ 10^{23}\, mol^{-1}}{(8.314\ \mathrm{m}^3 PaK^{-1} mol^{-1})(273\,K)} = 2.69\,x10^{25}\, m^{-3}$$

$d_{(O_2,N_2)}$ = (0.353 nm + 0.373 nm)/2 = 0.363 nm

$$d_{(O_2,N_2)} = \frac{3}{8}\left[\frac{(0.314\ \ \mathrm{JK}^{-1} mol^{-1})(273\ \ \mathrm{K})}{\pi(32.00\ x10^{-3}\ \ \mathrm{kg}\ \ \mathrm{mol}^{-1})}\right]^{1/2}$$

$$x\frac{1}{(3.63x10^{-10}m)^2(2.64x10^{-3}kg\,\mathrm{mol}^{1})} = 1.59x10^{-5}m^2s^{-1}$$

A similar simplified model for thermal conductivity of hard spheres yield the approximate value

$$K_T = \frac{1}{T}\frac{\overline{C}u}{3N_A}\lambda(u)\rho = \frac{2\overline{C}u}{3N_A}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{1}{\pi d^2}$$

The exact expression for hard sphere is:

$$K_T = \frac{25}{32}\left(\frac{kT}{\mu n}\right)^{1/2}\frac{C_v}{N_A d^2}$$

Example 2

Calculate the thermal conductivity coefficient for water vapor at 25°C

assuming d = 0.50 nm and

C_v = 25.26 $\mathrm{JK^{-1}\ mol^{-1}}$.

Substituting data into Eq. (4.11) gives

$$K_T = \frac{25}{32}\left[\frac{(1.381\mathrm{x}10^{-23}\,\mathrm{J.K^{-1}})(298\,\mathrm{K})}{\pi(18.02\mathrm{x}10^{-3}\,\mathrm{kg\ mol^{-1}})\,/\,6.022\mathrm{x}10^{23}\ \mathrm{mol^{-1}})}\right]^{1/2}$$

$$\mathrm{x}\,\frac{25.26\,\mathrm{JK^{-1}mol^{-1}}}{(6.022\mathrm{x}10^{23}\,\mathrm{mol})(5.0\mathrm{x}10^{-10}\,\mathrm{m})^2} = 0.027\,\mathrm{Jm^{-1}s^{-1}K^{-1}}$$

Finally, the approximate model for the viscosity of hard spheres yields:

$$\eta_a = \frac{1}{3}\rho(u)m\lambda = \frac{2}{3}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{m}{\pi d^2}$$

whereas the exact expression for hard spheres is

$$\eta = \frac{3}{32\sqrt{2}}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{m}{d^2}$$

Note that this does not imply that real molecules are hard spheres; in fact, we are forcing a model on the experiment. Nevertheless, the results in Table 6.1 show that a consistent set of molecular diameters result from this analysis of the data.

Example 3

Calculate the viscosity of molecular oxygen at 273.2K and 1 bar. The molecular diameter is 0.360 nm.

Using the exact equation for hard spheres, we find:

$$m = \frac{32.00 \times 10^{-3}\ \text{kg mol}^{-1}}{6.022 \times 10^{23}\ \text{mol}^{-1}}$$

$$= 5.314 \times 10^{-26}\ \text{kg}$$

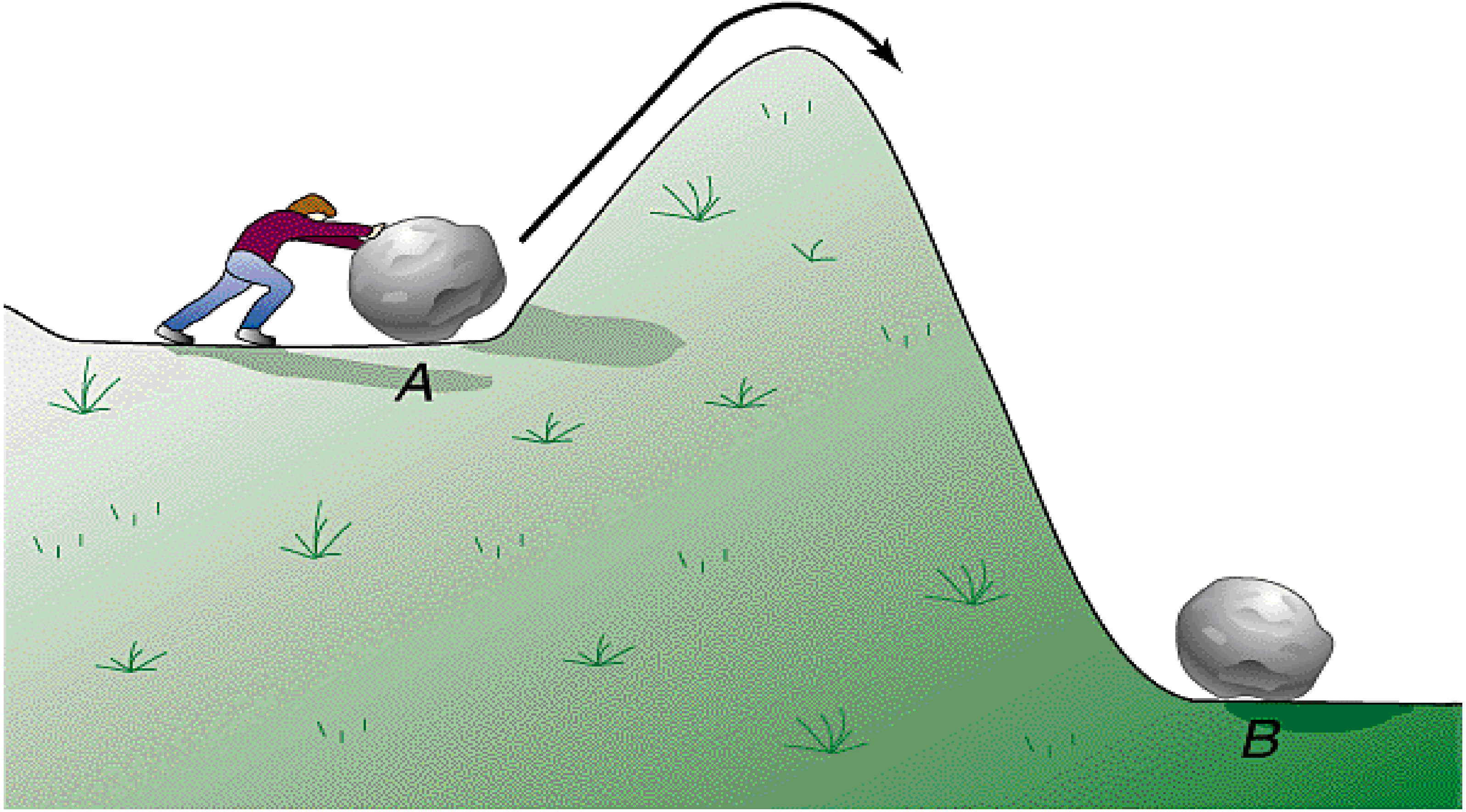
$$\eta = \frac{5\pi}{16}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{m}{\pi d^2}$$

$$= \frac{5\pi}{16}\left[\frac{(1.380\text{x}10^{-23}\text{JK}^{-1}(273.2\text{K})}{\pi(5.314\text{x}10^{-26}\text{kg})}\right]^{1/2}\frac{5.314\text{x}10^{-26}\text{kg}}{\pi(0.360\text{x}10^{-9}\text{m})^2}$$

= 1.926 x 10-5 kg m^{-1} s^{-1}

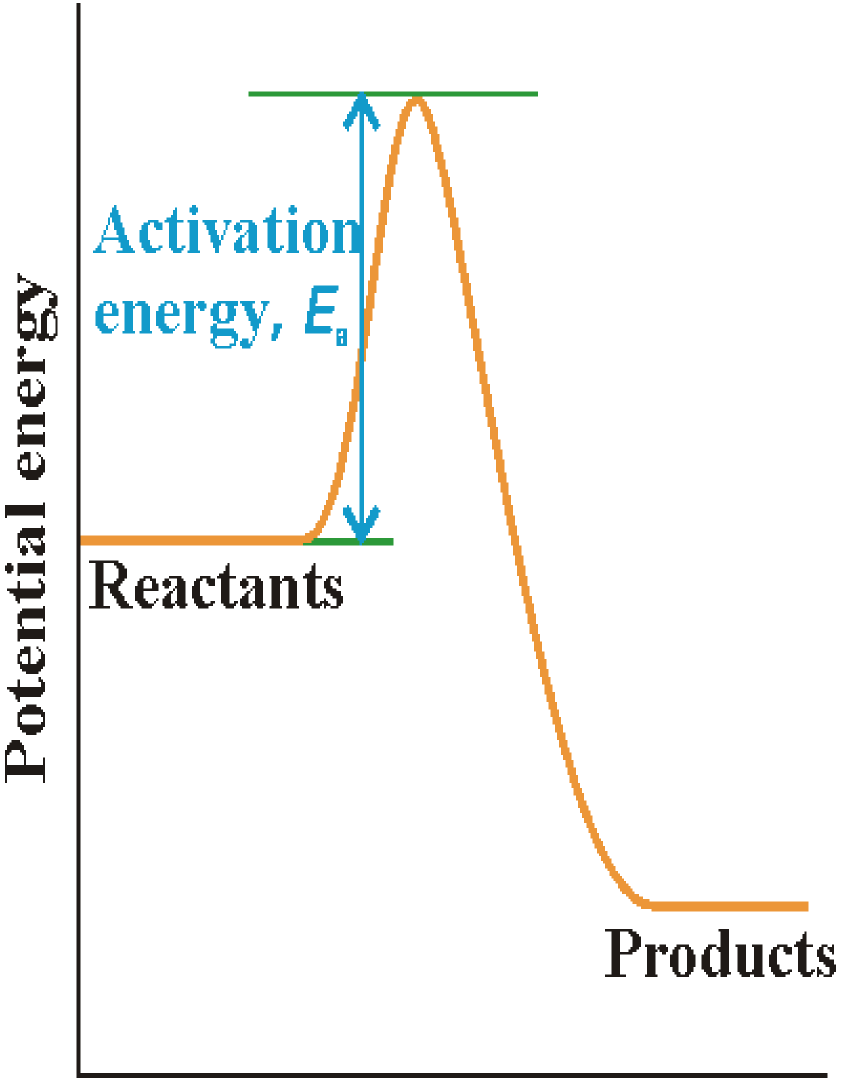
Kinetic Chemistry 1

Activation Energy

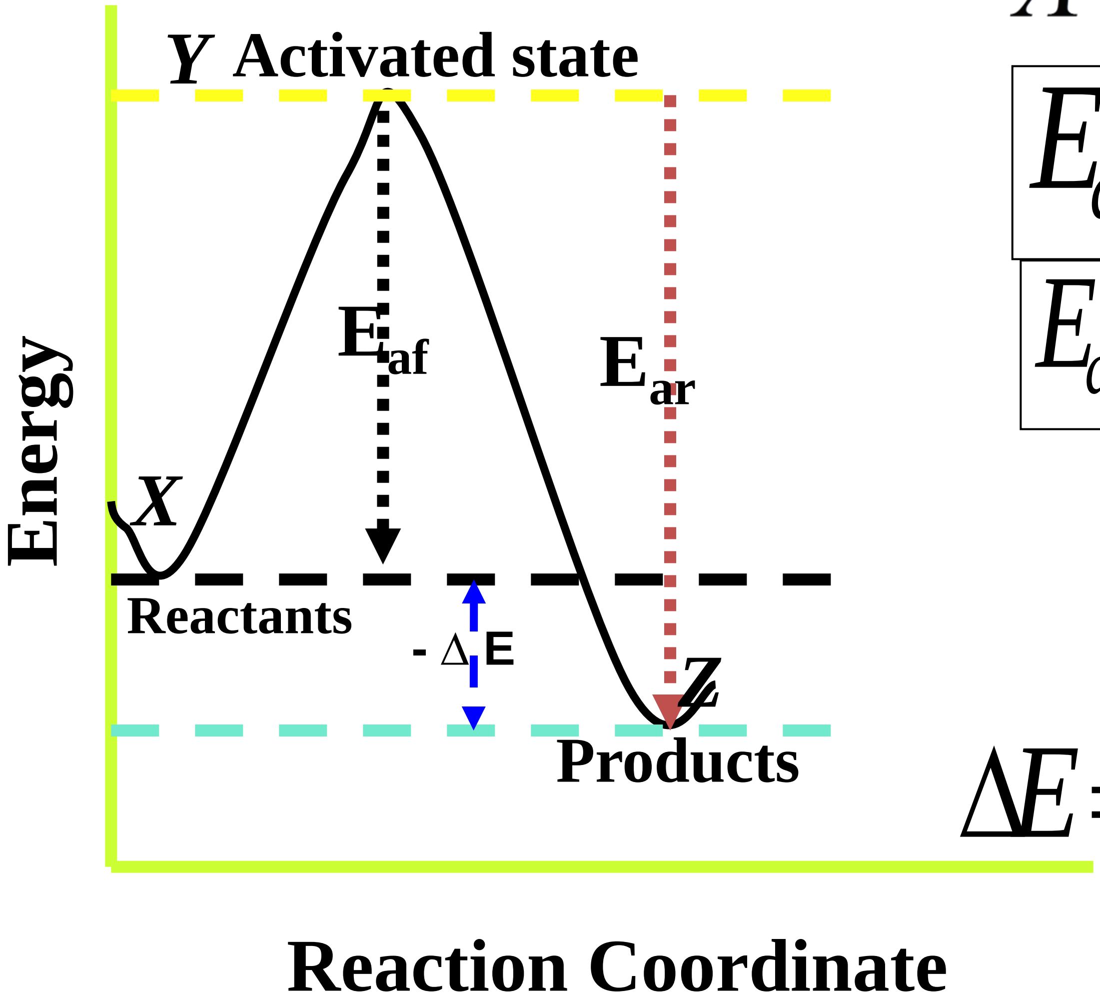


Activated Complex

- it is a state where the collided molecules has a sufficient energy to convert to products
- The activated complex is a intermediate state formed during the conversion of reactants into products. The activated complex is the compound with chemical composition present in the highest point in the energy curve
- Activation energy is the difference between the energy of the activated complex and the energy of the reactants.



If we have a reversible reaction



$$A+B \underset{k_r}{\overset{k_f}{\rightleftarrows}} C+D$$

$$\boxed{E_{af}=E_y-E_X}$$

$$\boxed{E_{ar}=E_y-E_Z}$$

$$\Delta E=E_{af}-E_{ar}$$

$$\Delta E=\cancel{E_Y}-E_X-\cancel{E_Y}+E_Z$$

$$\Delta E=E_Z-E_X$$

$$\Delta E = E_Z - E_X$$

Discussion

1- what is ΔE

it is the difference between the energy of the products and the energy of the reactants and it is the change in reaction energy at constant pressure ΔH

2- what is the meaning of the negative sign of ΔH

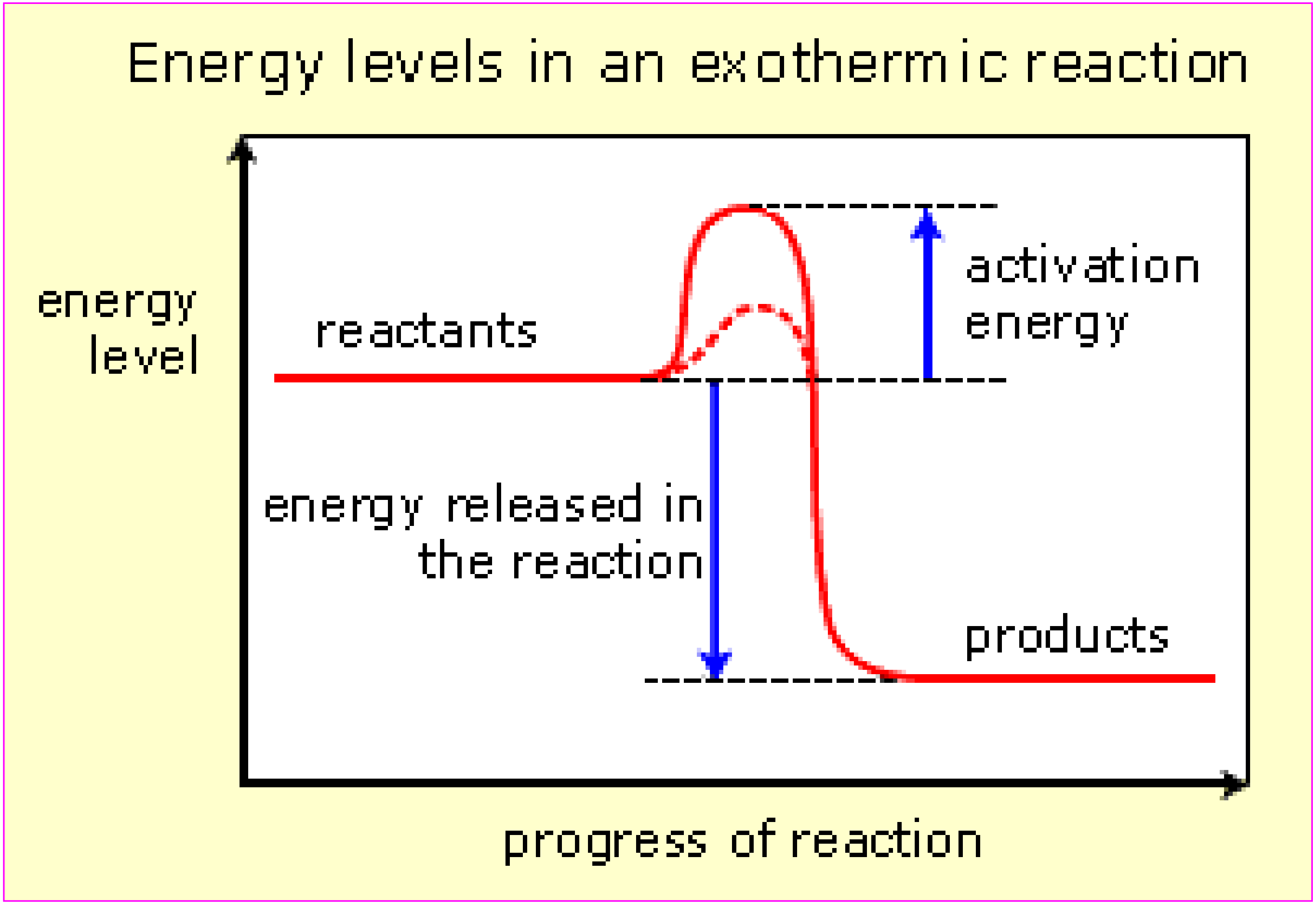
$$E_X \rangle E_Z$$

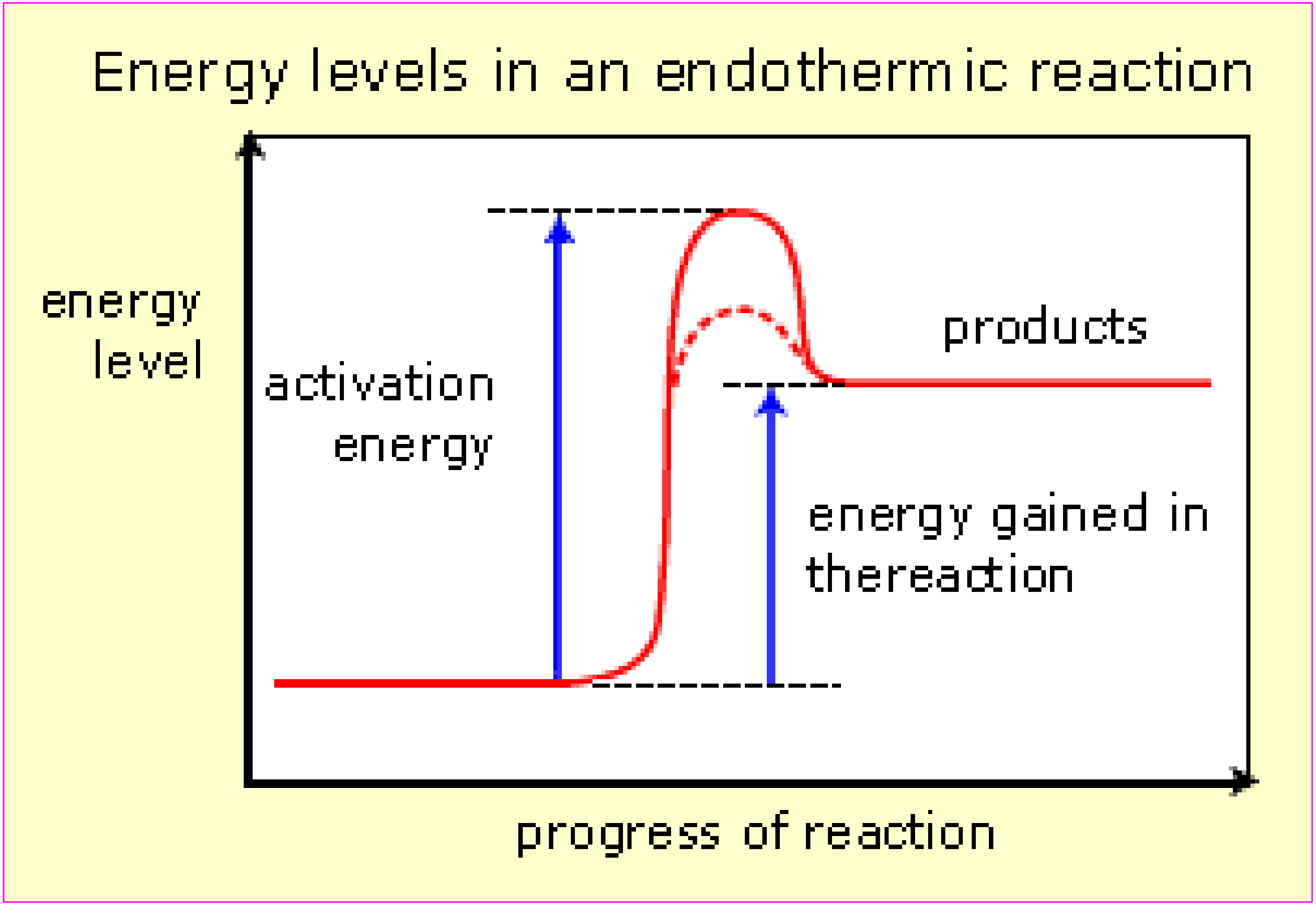
Exothermic reaction

3- what is the meaning of the negative sign of ΔH

$$E_z \rangle E_x$$

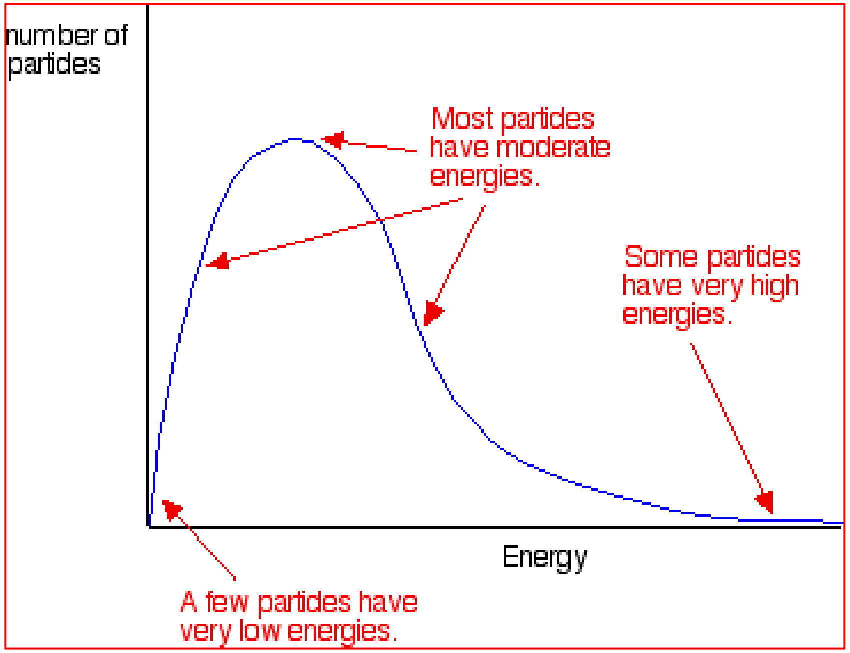
Endothermic reaction

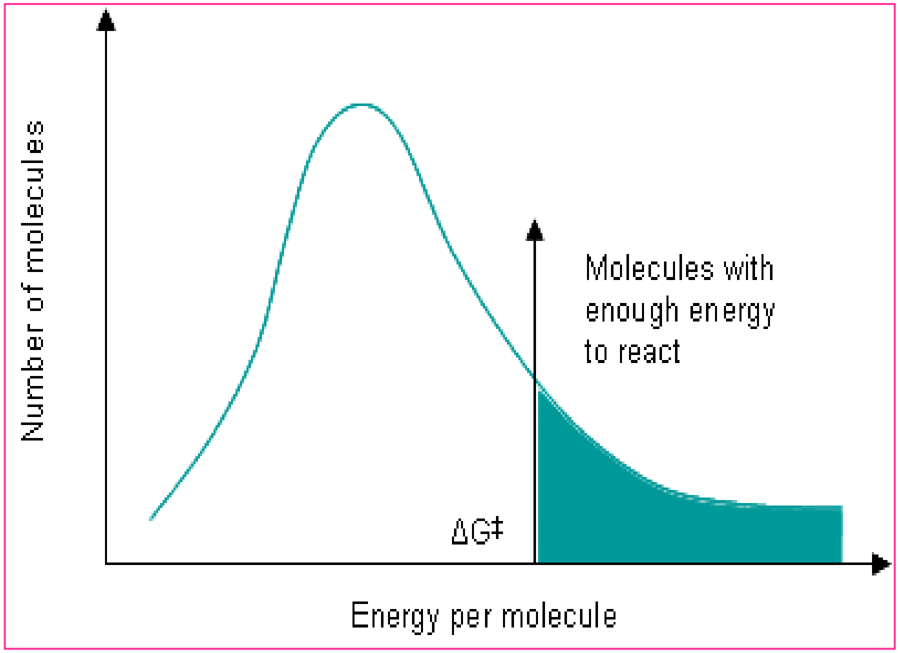

Energy levels in an exothermic reaction
energy level
reactants
activation energy
energy released in the reaction
products
progress of reaction

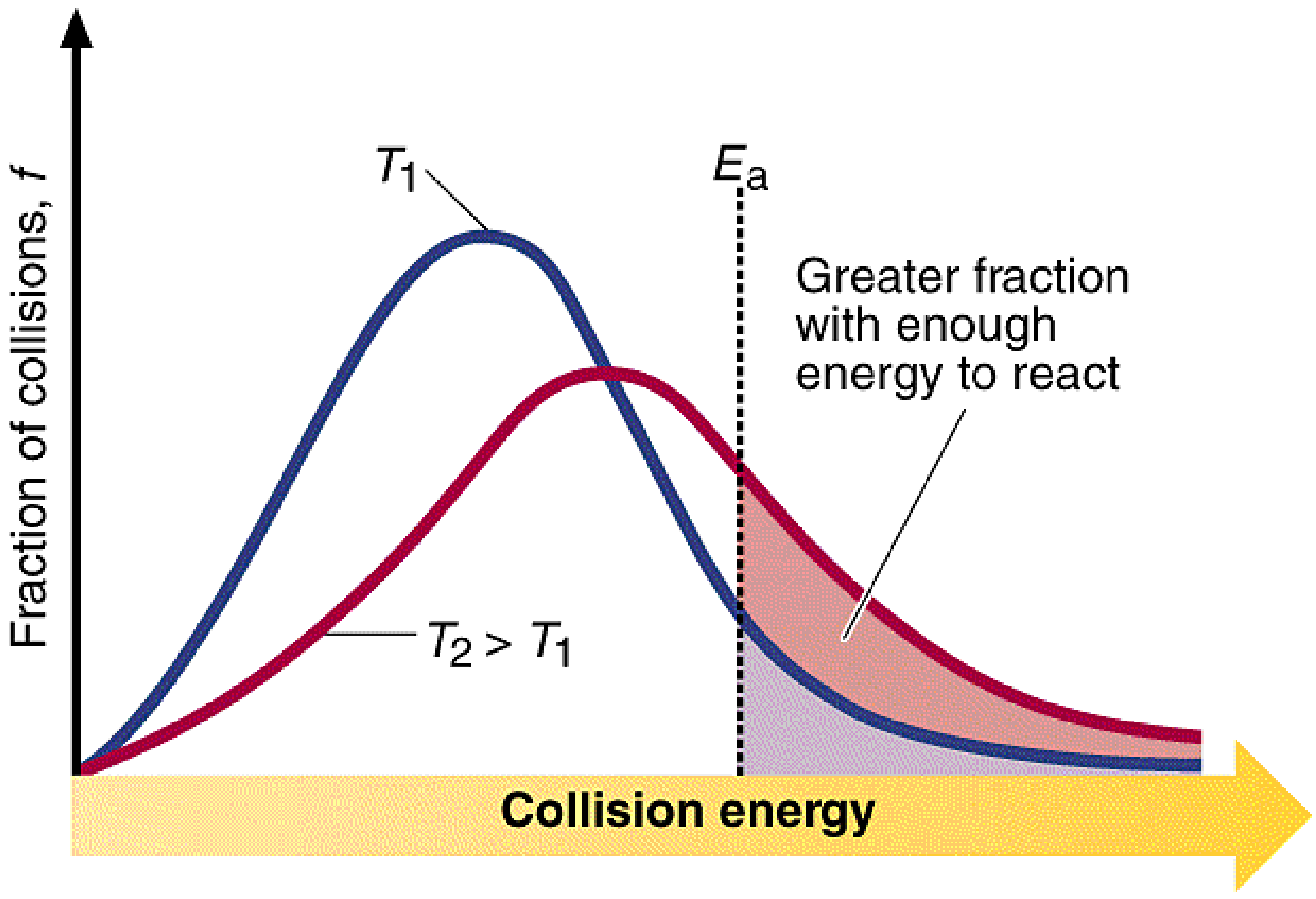

Energy levels in an endothermic reaction
energy level
activation energy
products
energy gained in thereaction
progress of reaction

Dependence of the rate of the reaction on temperature

Maxwell and Boltzmann distribution and activation energy

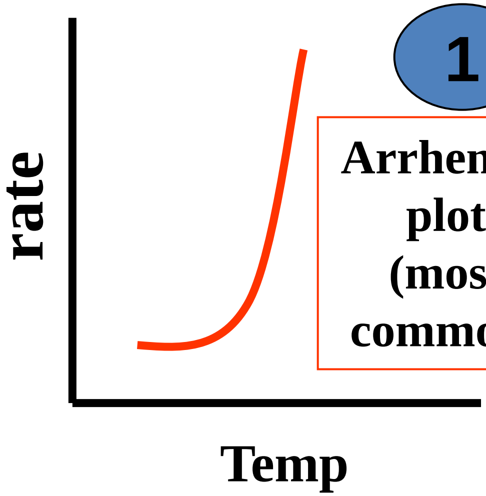





Fraction of collisions, *f*
T_1
E_a
Greater fraction with enough energy to react
$T_2 > T_1$
Collision energy

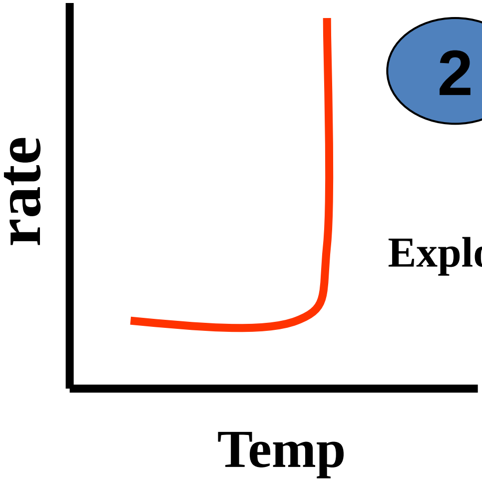
Relation between reaction rate and temperature

1



Arrhenius plot (most common)

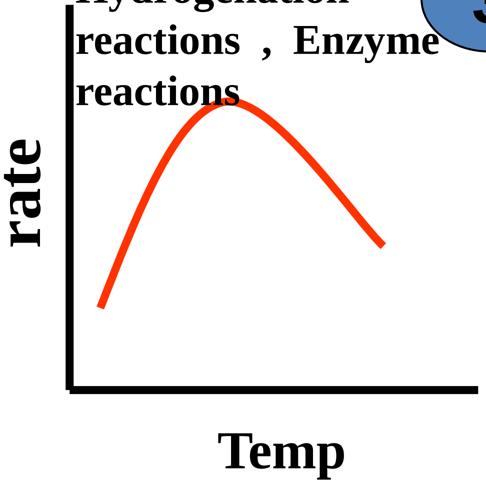
2



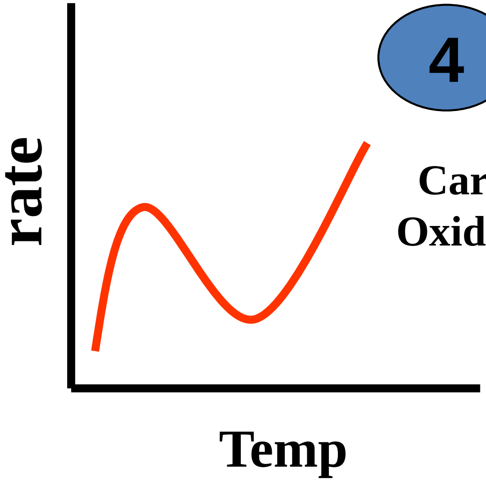
Explosion

3

Catalytic Hydrogenation reactions , Enzyme reactions

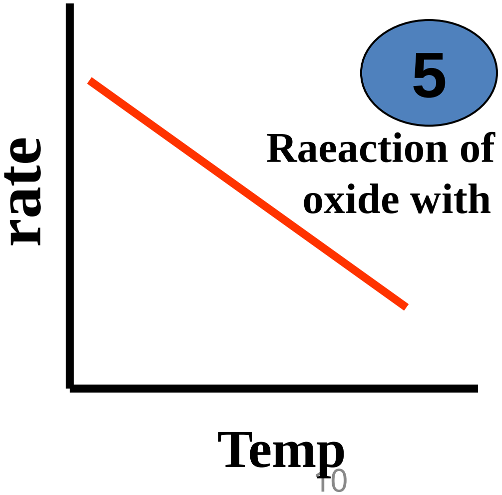


4



Carbon Oxidation

5



Raeaction of Nitrogen oxide with oxygen

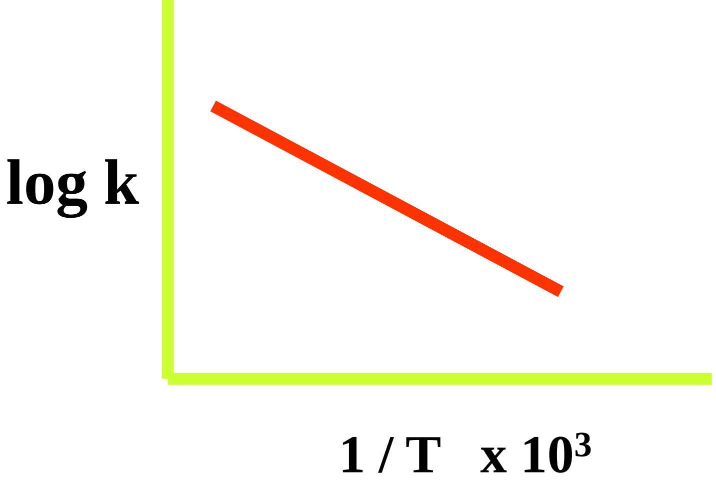
In 1878 Hood presented the first experimental law between the rate constant k and temperature

$$\log k = A' - \frac{B}{T}$$

$A' =$ contant

$B =$ constant

①



……

For any reversible reaction, In 1884 Van’t Hoff proposed a relation between the equilibrium constant and temperature for any reversible reaction و

$$\frac{d \ln K}{dT} = \frac{\Delta U}{RT^2}$$

②

K: equilibrium contan

ΔU: Change in energy

R: gas constant

……

For the following reversible reaction

$$A+B \underset{k_r}{\overset{k_f}{\rightleftarrows}} C+D$$

$$Rate = k_r[C]\,[D]$$

$$Rate = k_f[A]\,[B]$$

k_f is the reaction rate constant for the forward reaction

k_r is the reaction rate constant of the reverse reaction

At equilibrium the rate of the forward reaction equals the rate of the reverse one

$$k_f[A]\,[B] = k_r[C]\,[D]$$

$$\frac{k_f}{k_r} = \frac{[C]\,[D]}{[A]\,[B]} = K$$ **Equilibrium constant**

Equation 2 can be written as follows

$$\frac{d\ln K}{dT} = \frac{\Delta U}{RT^2} \tag{2}$$

$$\frac{d\ln\left(\frac{k_f}{k_r}\right)}{dT} = \frac{\Delta U}{RT^2}$$

$$\frac{d\ln k_f}{dT} - \frac{d\ln k_r}{dT} = \frac{\Delta U}{RT^2} \tag{3}$$

$$\Delta U = E_{af} - E_{ar} \tag{4}$$

From equations 3 and 4

$$\frac{d\ln k_f}{dT} - \frac{d\ln k_r}{dT} = \frac{E_{af}}{RT^2} - \frac{E_{ar}}{RT^2} \tag{5}$$

Arrhenius proposed the separation of equation 5 into two equations

$$\frac{d\ln k_f}{dT} = \frac{E_{af}}{RT^2} + I \qquad \frac{d\ln k_r}{dT} = \frac{E_{ar}}{RT^2} + I$$

The constant I is found to be equals zero experimentally

$$\frac{d\ln k}{dT} = \frac{E_a}{RT^2} \tag{6}$$

Arrhenius equation

$$d\ln k = \frac{E_a}{RT^2}\,dT$$

$$\int d\ln k = \int \frac{E_a}{RT^2}\,dT$$

$$\ln k = -\frac{E_a}{RT} + \mathit{Constan}$$

$$\ln k = -\frac{E_a}{RT} + \ln \mathbf{A}$$ ⑦

$$\int d\ln k = \ln k$$

$$\int \frac{1}{T^2}\,dT = \int T^{-2}\,dT = \frac{T^{-2+1}}{-1} = \frac{T^{-1}}{-1} = -\frac{1}{T}$$

The last equation can be written as follows

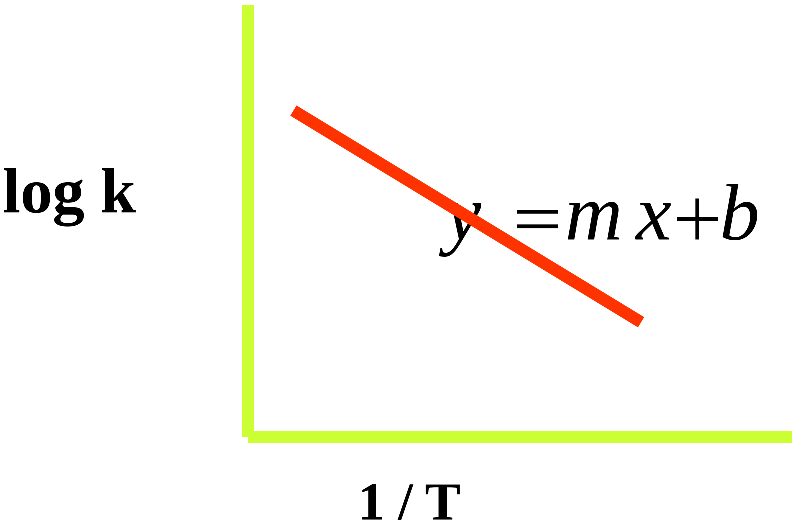
$$\ln k = -\frac{E_a}{RT} + \ln A$$

$$e^{\ln k} = e^{-\frac{E_a}{RT} + \ln A}$$

$$\cancel{e}^{\ln k} = e^{-\frac{E_a}{RT}} \; e^{\cancel{\ln} A}$$

$$k = A \exp\left(-E_a / RT\right)$$ ⑧ **Arrhenius equation**

$$\exp(x) = e^x$$



Slope=-E_a/2.303R

Equation 7 can be written as follows

$$\ln k = -\frac{E_a}{RT} + \ln A \tag{7}$$

$$2.303\log k = -\frac{E_a}{RT} + 2.303\log A$$

$$\log k = -\frac{E_a}{2.303R}\left(\frac{1}{T}\right) + \log A \tag{9}$$

$$y = mx + b$$

If the reaction is carried out at two different tepmeratures

$$\log k_1 = -\frac{E_a}{2.303RT_1} + \log A \quad (10) \qquad \log k_2 = -\frac{E_a}{2.303RT_2} + \log A \quad (11)$$

By subtraction of equation 10 from 11

$$\log k_2 - \log k_1 = -\frac{E_a}{2.303R}\frac{1}{T_2} - \left(-\frac{E_a}{2.303R}\frac{1}{T_1}\right)$$

$$\log\frac{k_2}{k_1} = -\frac{E_a}{2.303R}\frac{1}{T_2} + \frac{E_a}{2.303R}\frac{1}{T_1}$$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_2T_1}\right)$$

N_2O_5 Decomposed thermally between 237K and 338K

$$2N_2O_5(g) \rightarrow 4NO_2(g) + O_2(g)$$

The slope of the relation between log k and 1/T was -5400, what is the value of activation energy

$$\textbf{Slope} = -E_a/2.303R$$

$$\cancel{-}\ 5400 = \cancel{-}\ E_a/2.303R$$

$$E_a = 5400(2.303)(8.314)$$

$$E_a = 103394.57\ \text{J mol}^{-1} = 103.39\ \text{k J mol}^{-1}$$