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SOUTH VALLEY UNIVERSITY
جامعة جنوب الوادي

Physical Chemistry II
كيمياء فيزيائية II

Code : 321 Ch

For

3rd year Students

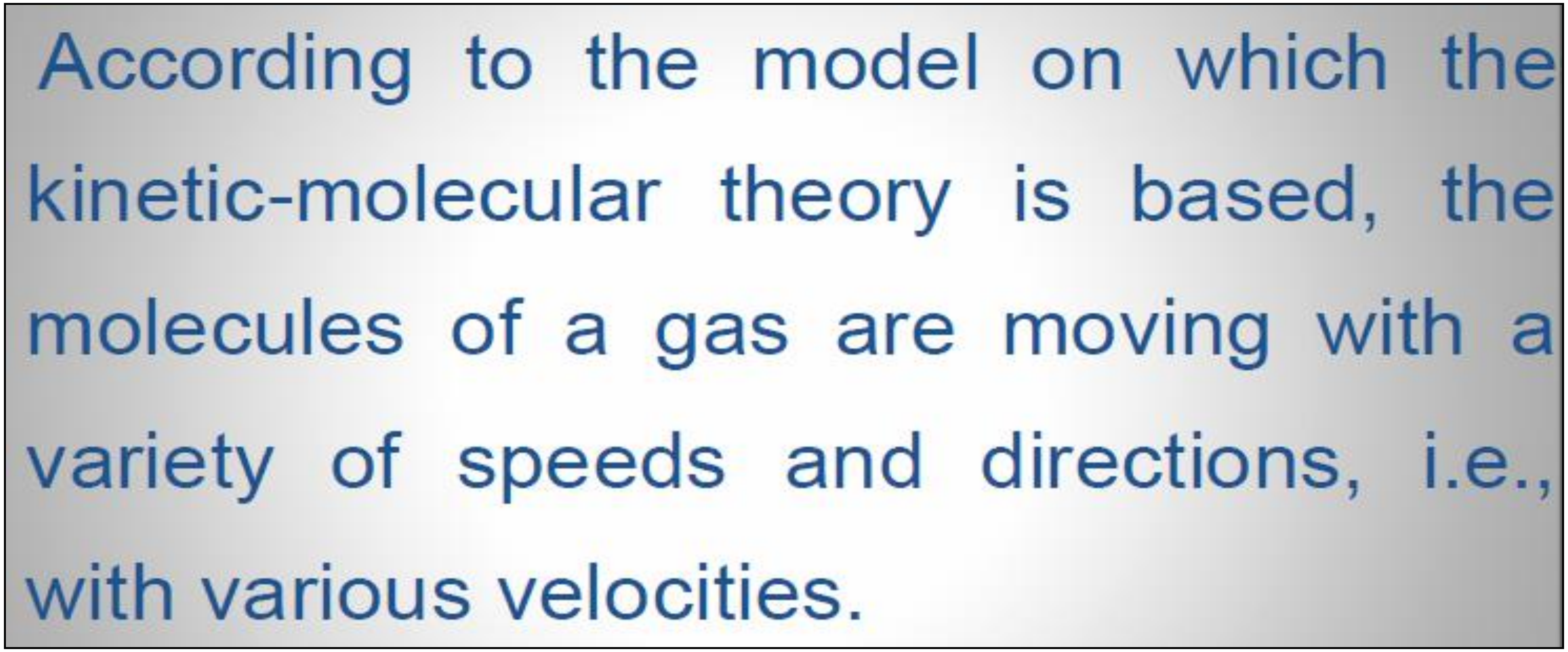
(Chemistry Group)

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.

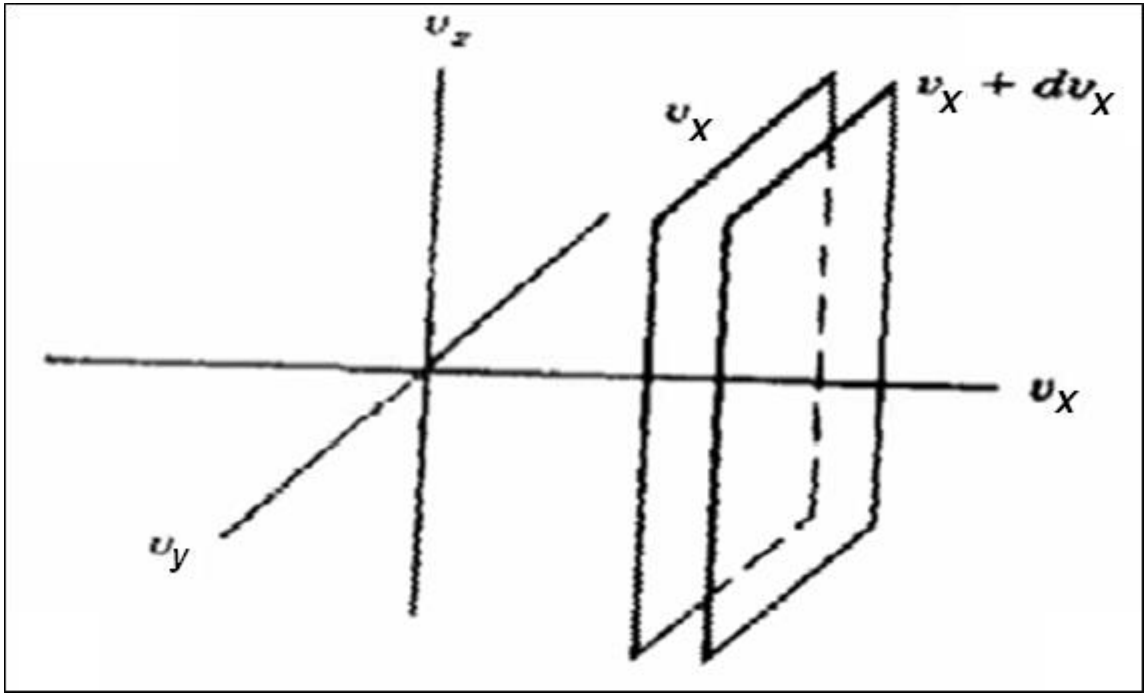
We assume that we have a sample of a gas of:

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 = -∞ to u_x = +∞**, must account for all the velocity points. Thus we can write

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

$k = 1.380649\times10^{-23}$ 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

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

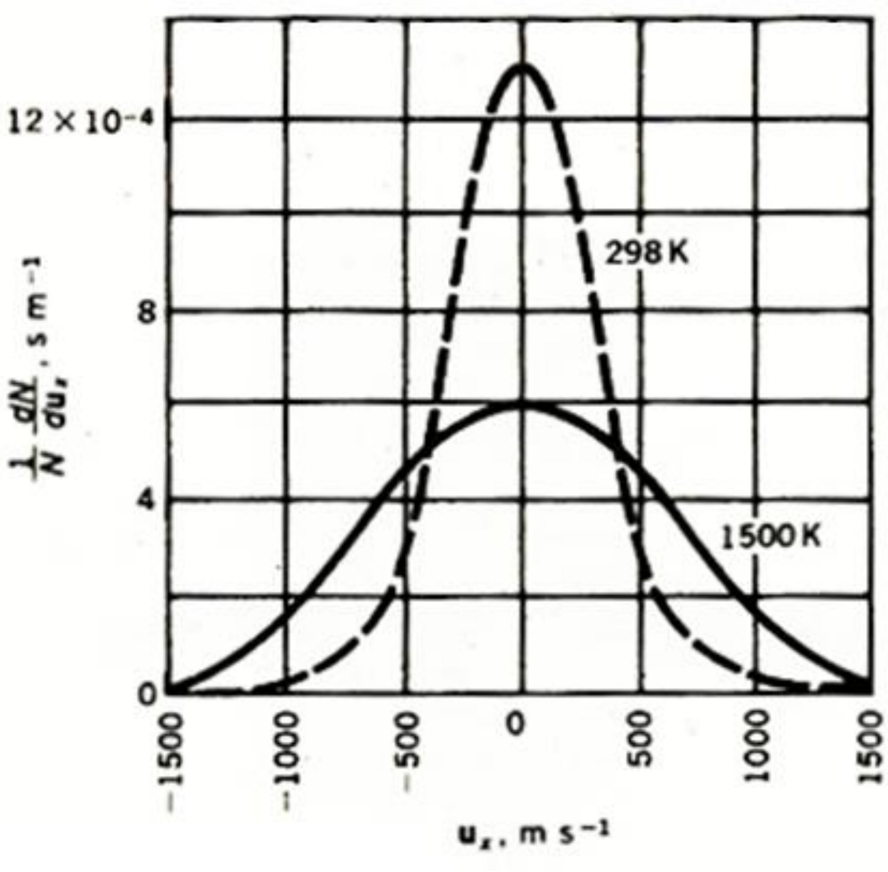
The relation between the Boltzmann constant and the universal gas constant is given by this equation: $R = N_A k$ where R is the ideal gas constant (sometimes called the universal gas constant) and N_A is the Avogadro constant (k is the Boltzmann constant of course).

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

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

- 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 ms^{-1}

Using equation (5)

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

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

= 8.065 x 10^{-4} 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

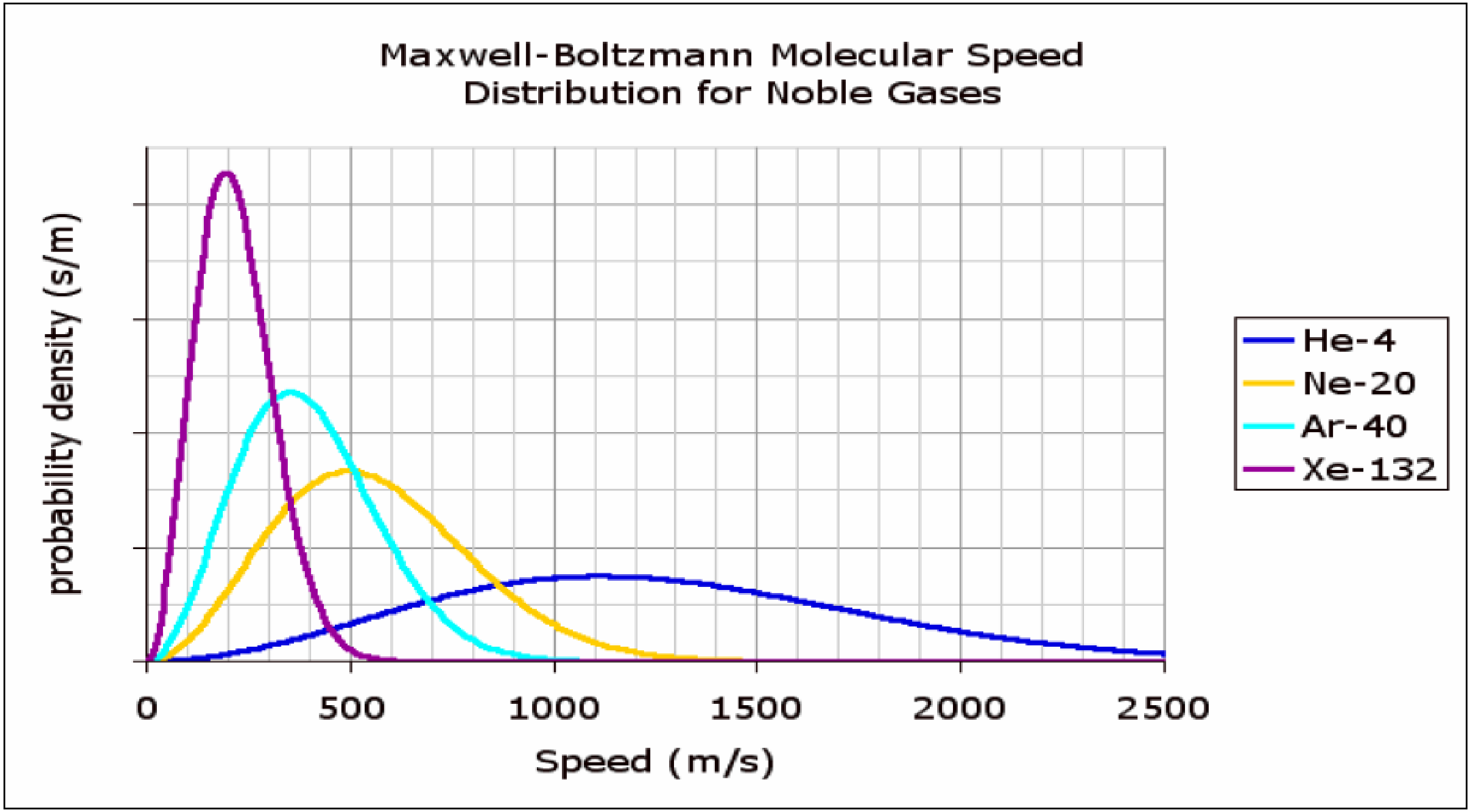
$$F(u)du = 4\pi u^2 \left(\frac{m}{2\pi kT}\right)^{3/2} \exp\left(\frac{-mu^2}{2kT}\right) du$$

- 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

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

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

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

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

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

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

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

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

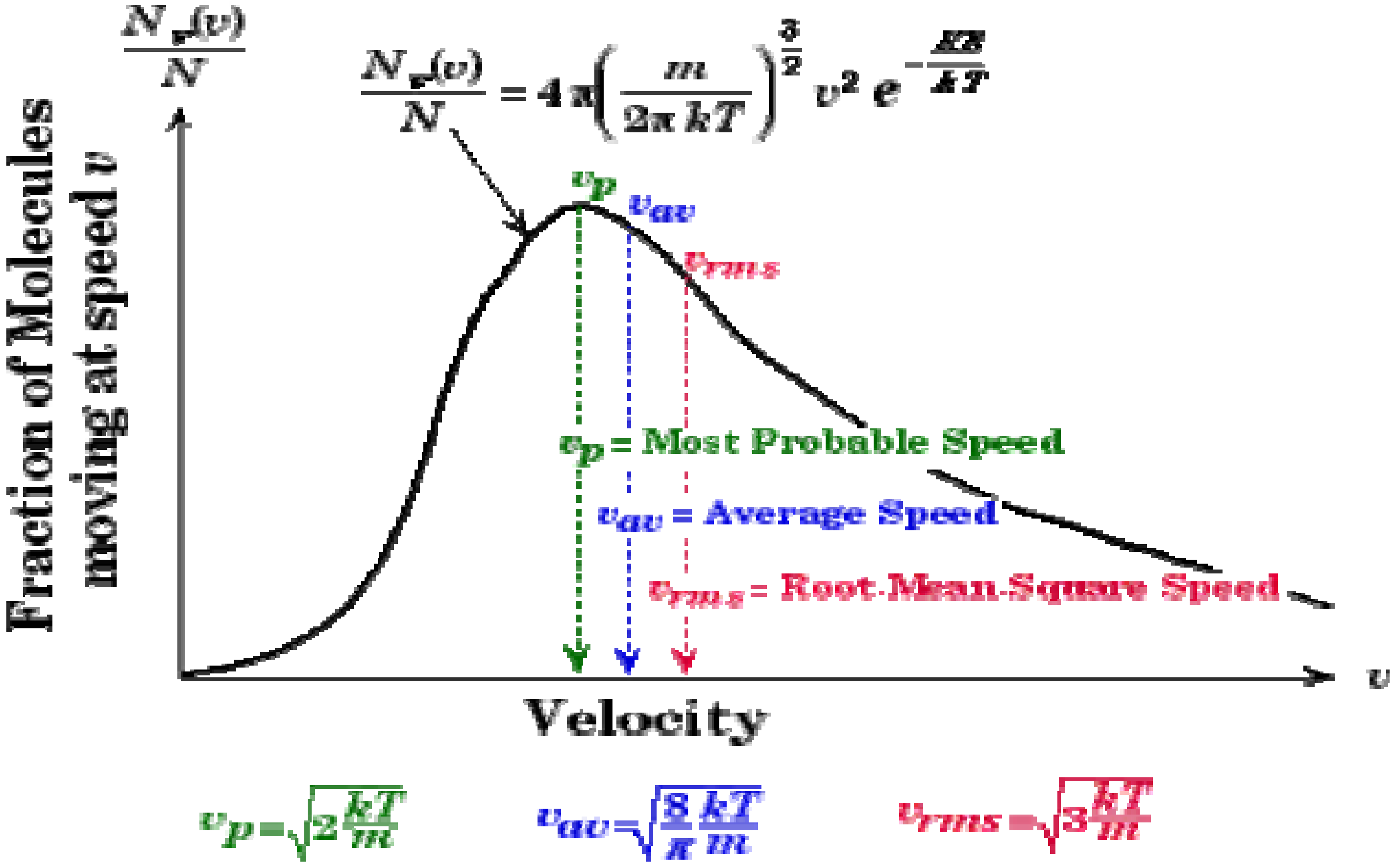
From these three calculations,

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

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

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

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



$$\frac{N_v(v)}{N} = 4\pi\left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} v^2 e^{-\frac{KE}{kT}}$$

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

- ✓ 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	$(u^2)^{1/2}/\mathrm{m\ s^{-1}}$	$(u)/\mathrm{m\ s^{-1}}$	$u_p/\mathrm{m\ s^{-1}}$
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.

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

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

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

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.

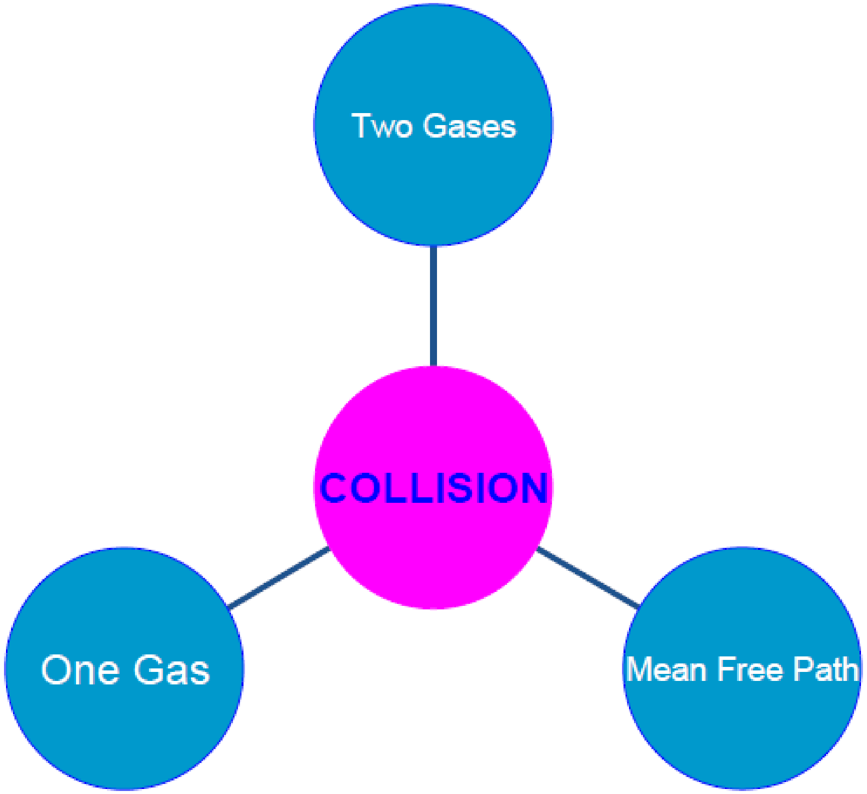
Exercise

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

Kinetic Molecular Theory

Part 3

Collision properties of gas molecules



- Collision Frequency
  - Two gases $Z_{1(2)}$
  - One gas $Z_{1(1)}$

- Collision Density
  - Two gasesZ_{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 .

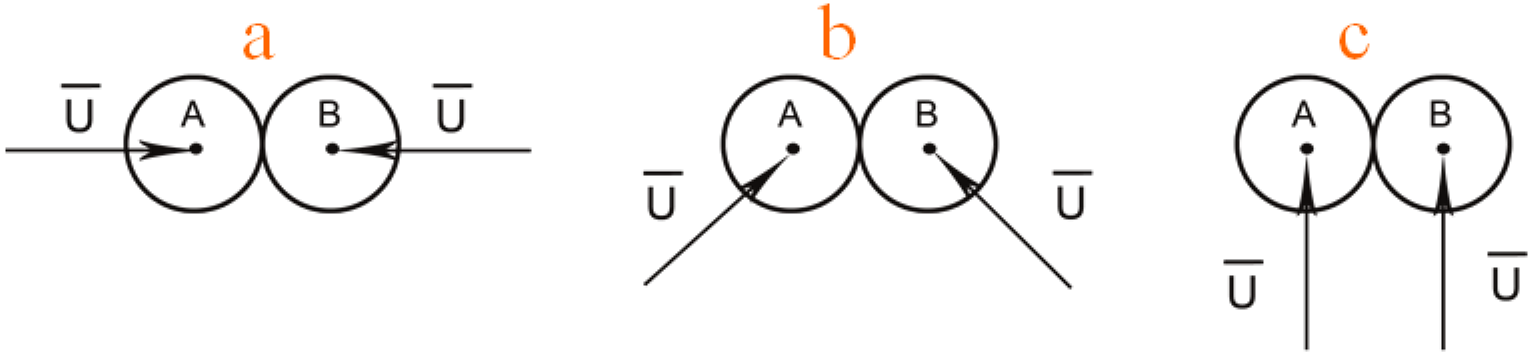
Reduced mass μ

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

- 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 velocity of each one and the angle of approach:



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

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

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

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).

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

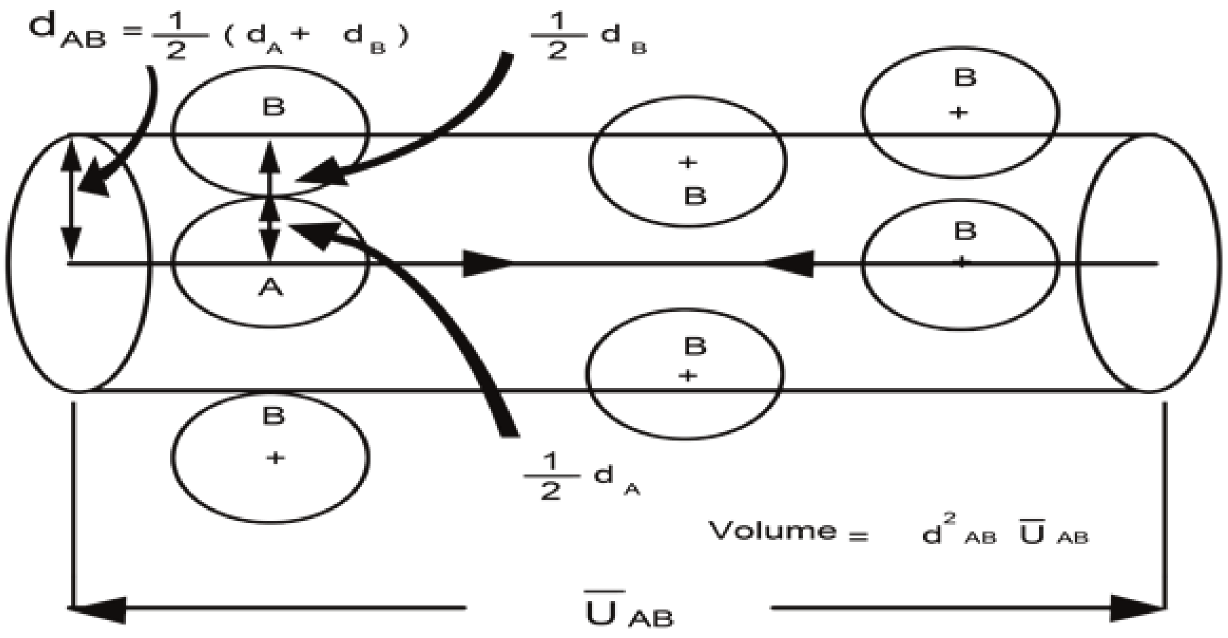
$$\bar{U}_A = \bar{U}_B$$

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

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

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

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



- 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 $\mathbf{u}_{\mathbf{AB}}$ should be used in calculating the rate of collisions $\mathbf{z}_{\mathbf{A(B)}}$ of a molecule of type A with molecules of type B. Thus,

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

or

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

- where $\mathbf{z}_{\mathbf{A(B)}}$ 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:

$$m_1 = \frac{2.016 \text{ x}10^{-3} \text{ kg mol}^{-1}}{6.022 \text{ x}10^{23} \text{ mol}^{-1}} = 3.348 \text{ x}10^{-27} \text{ kg}$$

$$m_2 = \frac{32.00 \text{ x}10^{-3} \text{ kg mol}^{-1}}{6.022 \text{ x}10^{23} \text{ mol}^{-1}} = 5.314 \text{ x}10^{-26} \text{ kg}$$

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

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

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

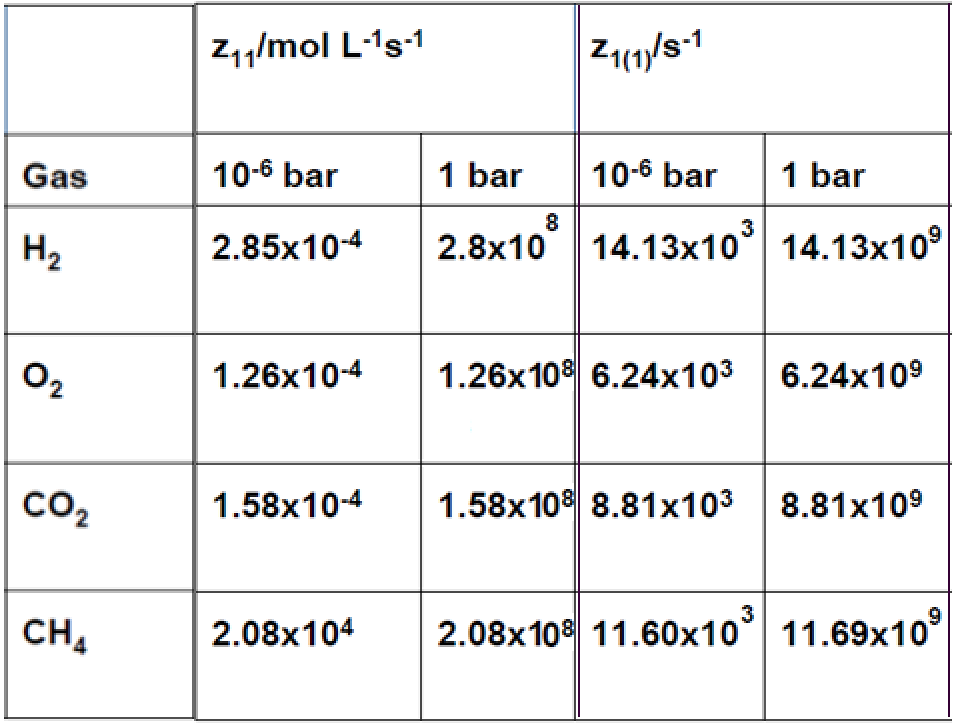
$$Z_{12} = \pi . d^2 . \bar{u}_{12} \rho_1 . \rho_2$$

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

$$Z = \pi d_{NH_3}^2 U_{A(A)} \rho_{NH_3}$$

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

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

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

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

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

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

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

$$Z_{A(A)} = 9.49 x 10^9 s^{-1}$$

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

$$Z_{AA} = Z_{AA}.\rho_{NH_3} = \frac{1}{2} Z_{A(A)} . \frac{P}{kT} = \frac{1}{2} x 9.49 x 10^9 s^{-1} x \left(\frac{100 x 10^3 pa}{1.381 \times 10^{-23} \mathrm{J.K}^{-1} \times (298 \mathrm{K})}\right)$$

$$Z_{AA} = 1.15 x 10^{15} s^{-1} . mol . m^{-3}$$

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 ^{o}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?

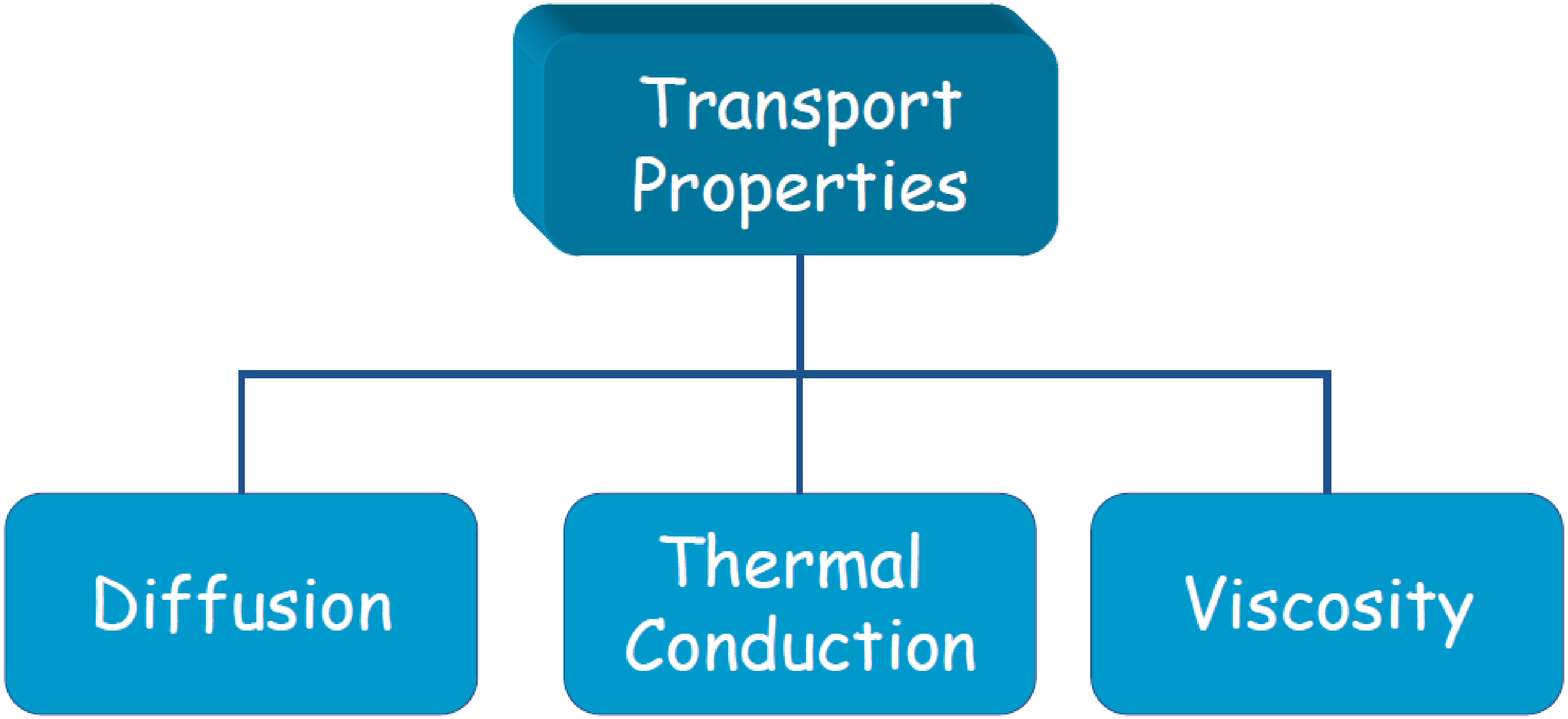
(b)

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:

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

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},

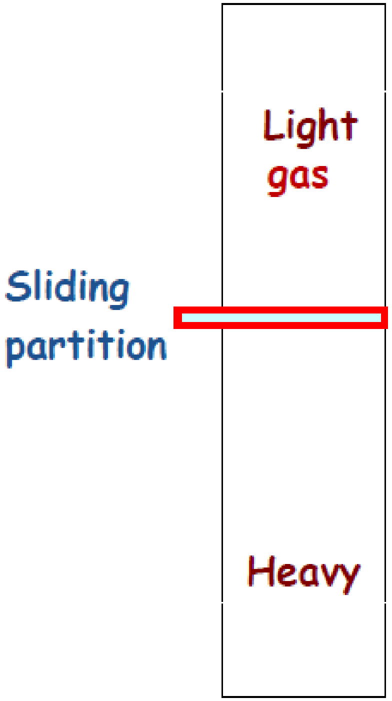
* dc_i/dz has the units of mol m^{-3}

* 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 dCi/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)

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

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

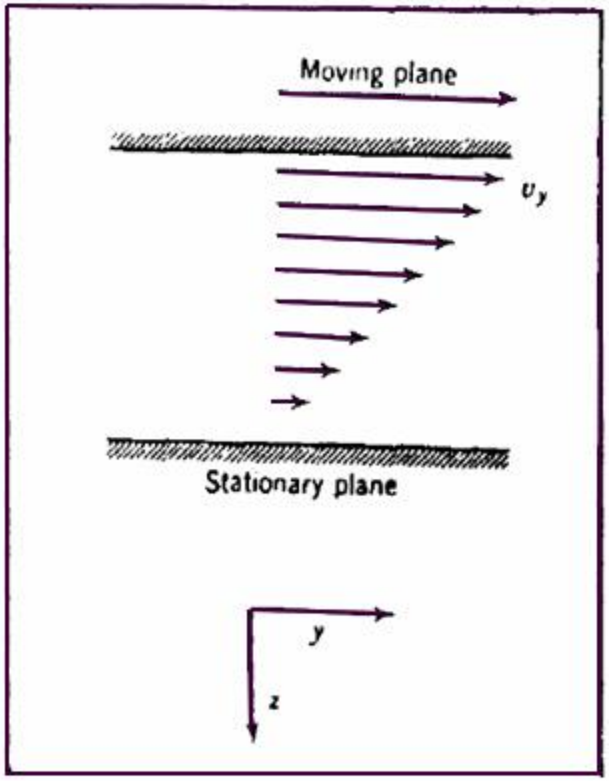
- K is the thermal conductivity.
- q_z has the units of J m^{-2} s^{-1} and
- d_T/d_z has the units of K m^{-1},
- K_T has the units of J m^{-1} s^{-1} K^{-1}.
- The negative sign indicates that if d_T/d_z is positive, the flow of heat is in the negative z direction, which is the direction toward lower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



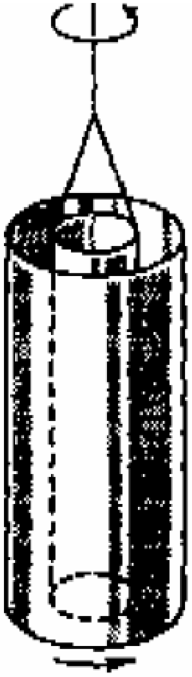
Rate of change of velocity with respect to distance measured perpendicular to the direction of flow is represented by

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

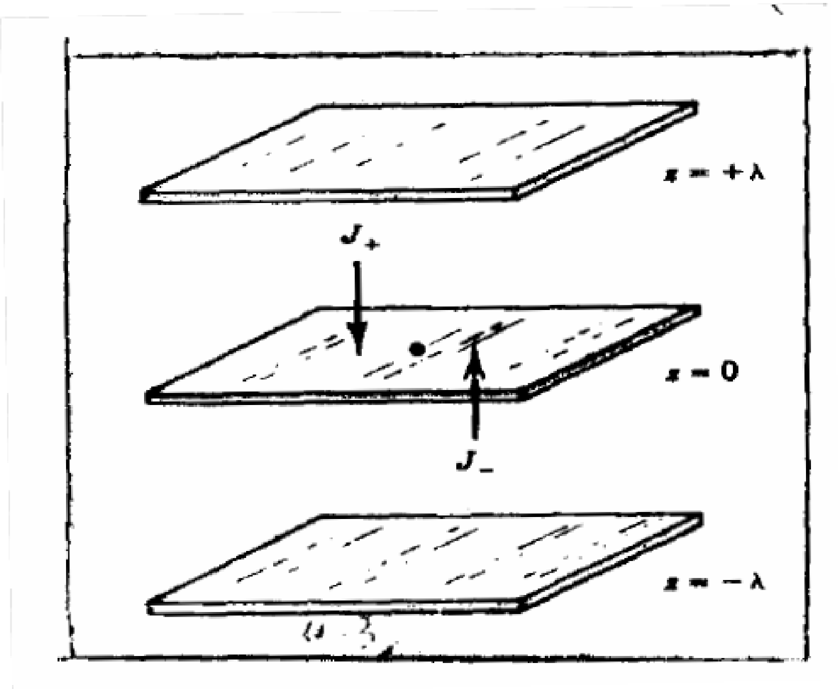
Calculation of Transport Coefficients

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 $\mathbf{x} = \pm\lambda$, 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.

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

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

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

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

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 JK^{-1} mol^{-1}.

Substituting data into Eq. (4.11) gives

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

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

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:

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

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

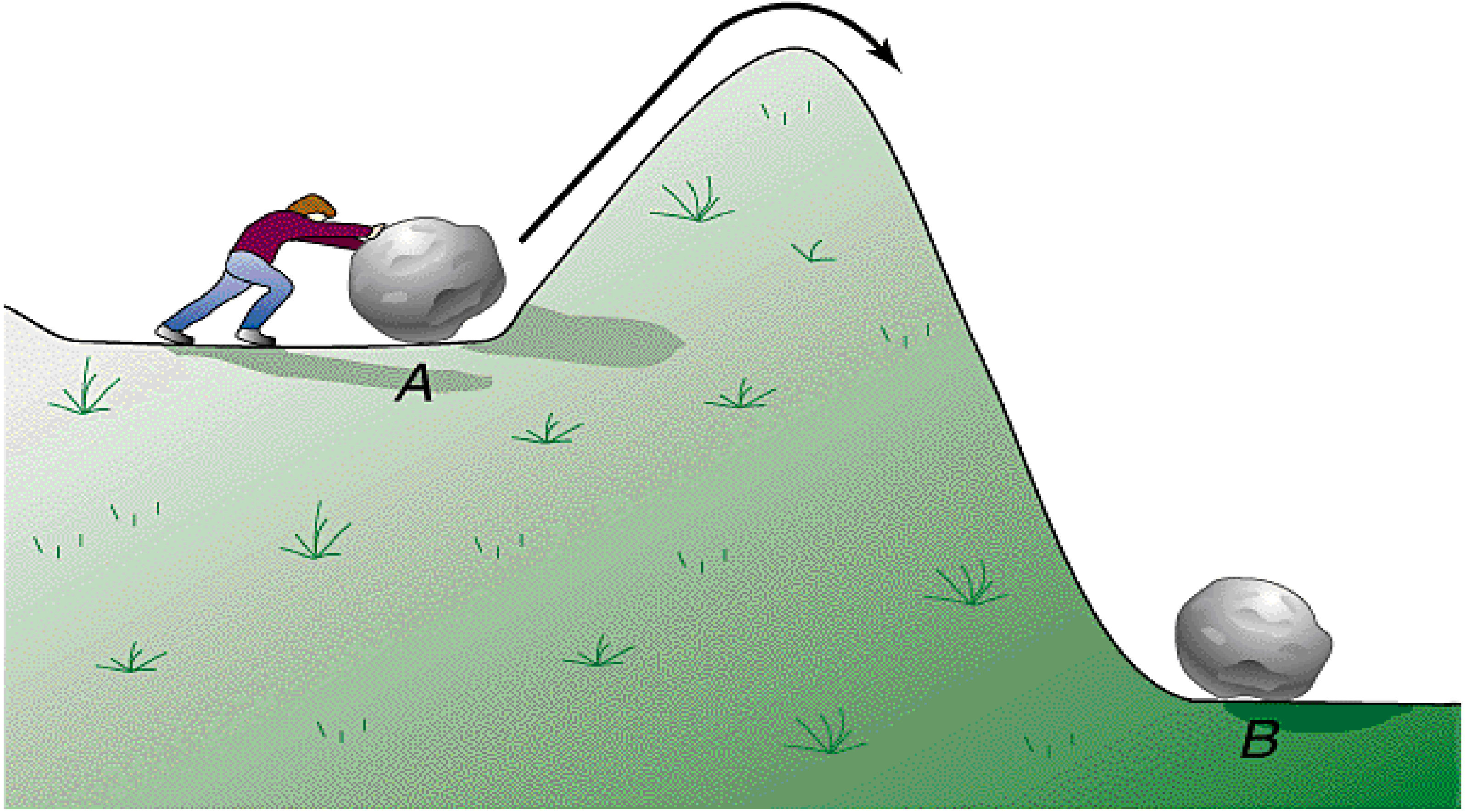
$$\eta = \frac{5\pi}{16}\left(\frac{kT}{\pi m}\right)^{1/2}\frac{m}{\pi d^2}$$

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

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

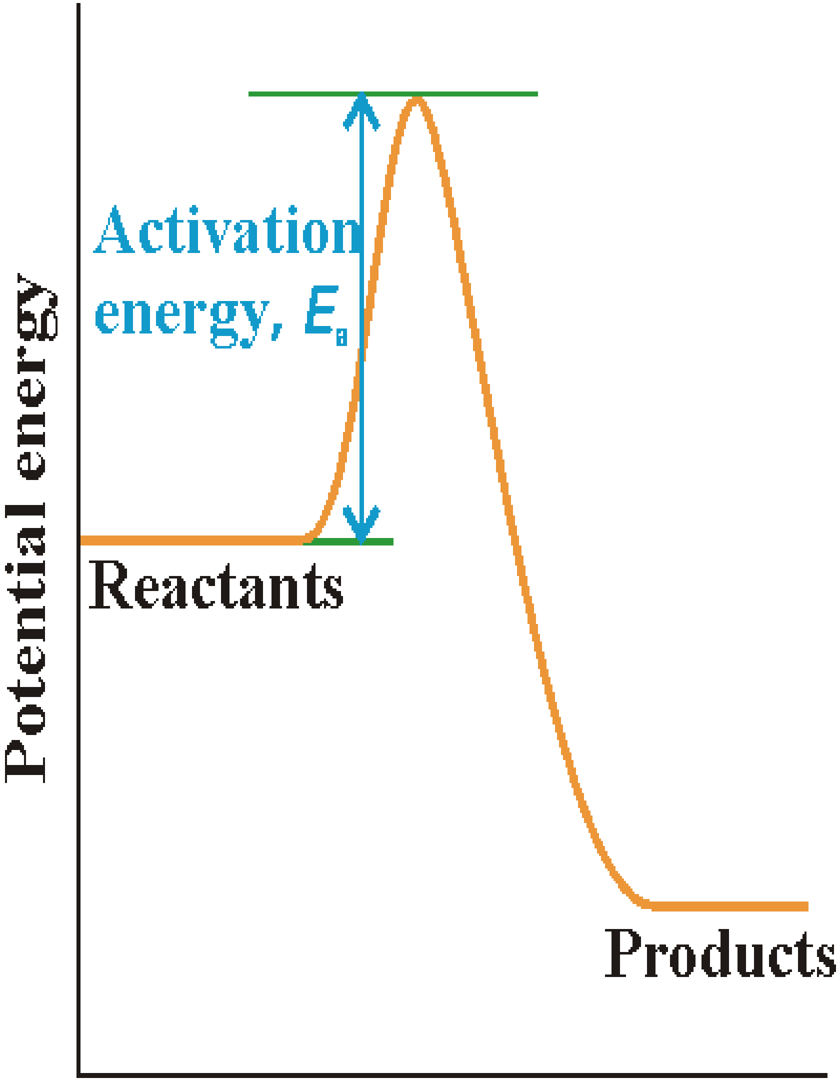
Kinetic Chemistry 1

Activation Energy

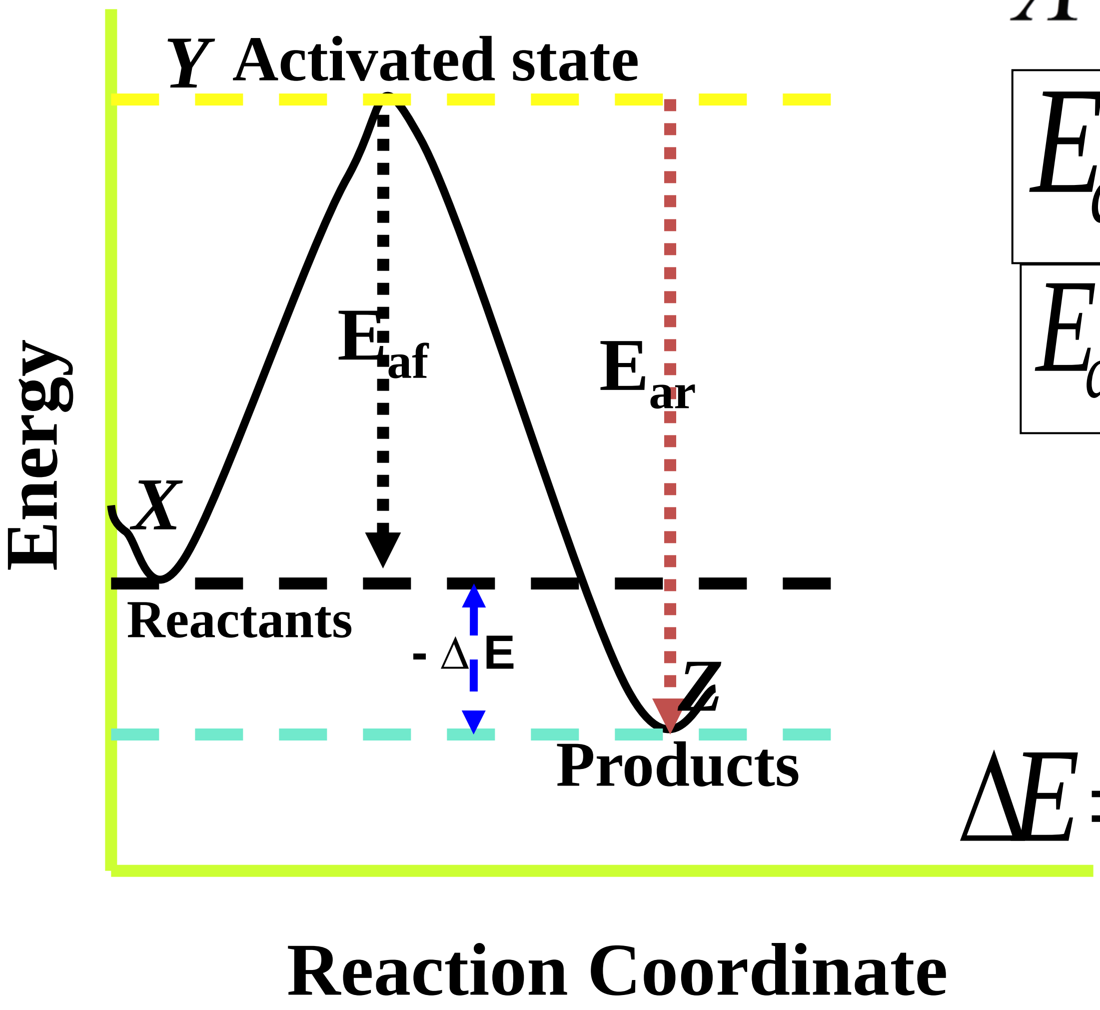


Activated Complex

- 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

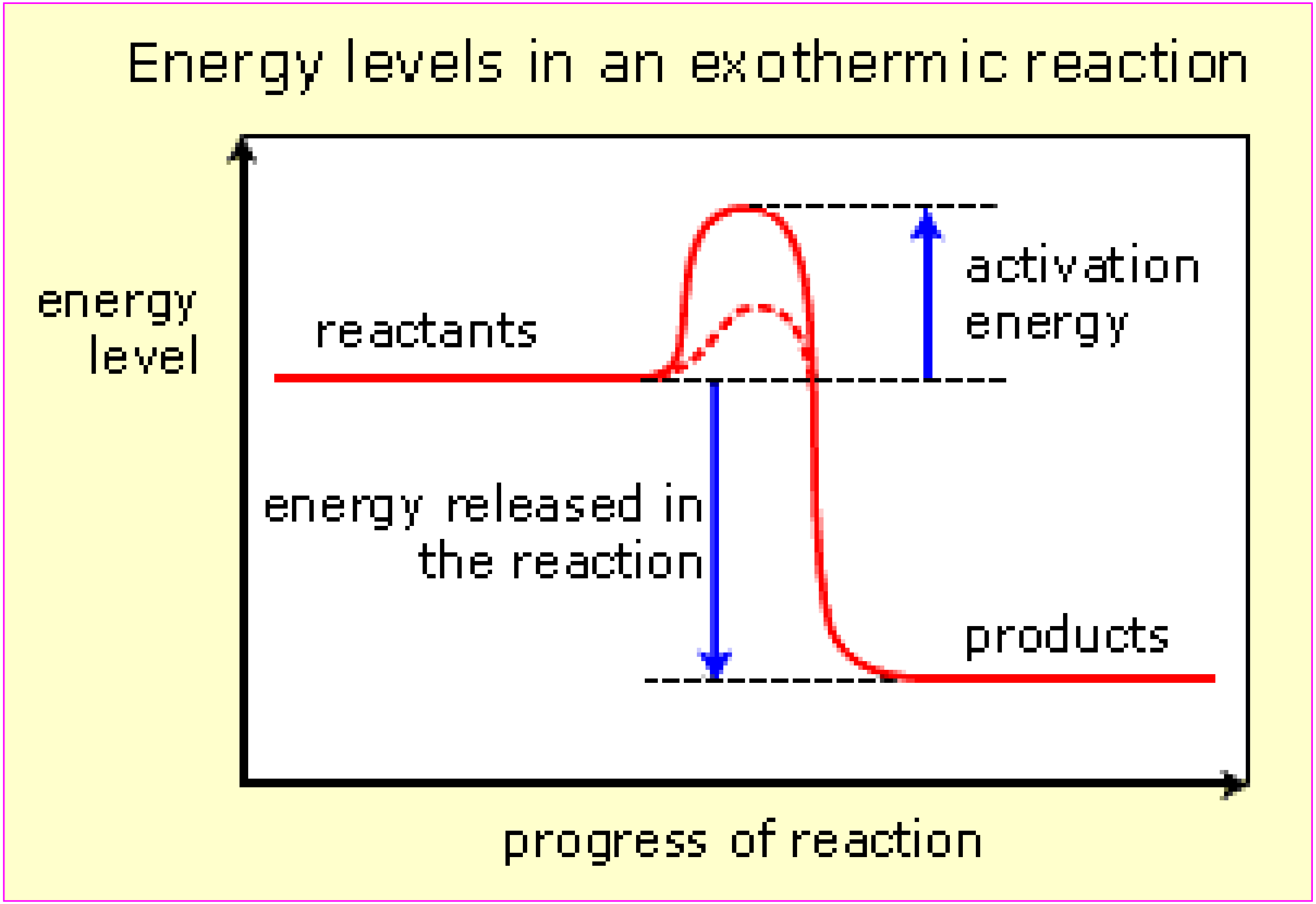
$$E_X \rangle E_Z$$

Exothermic reaction

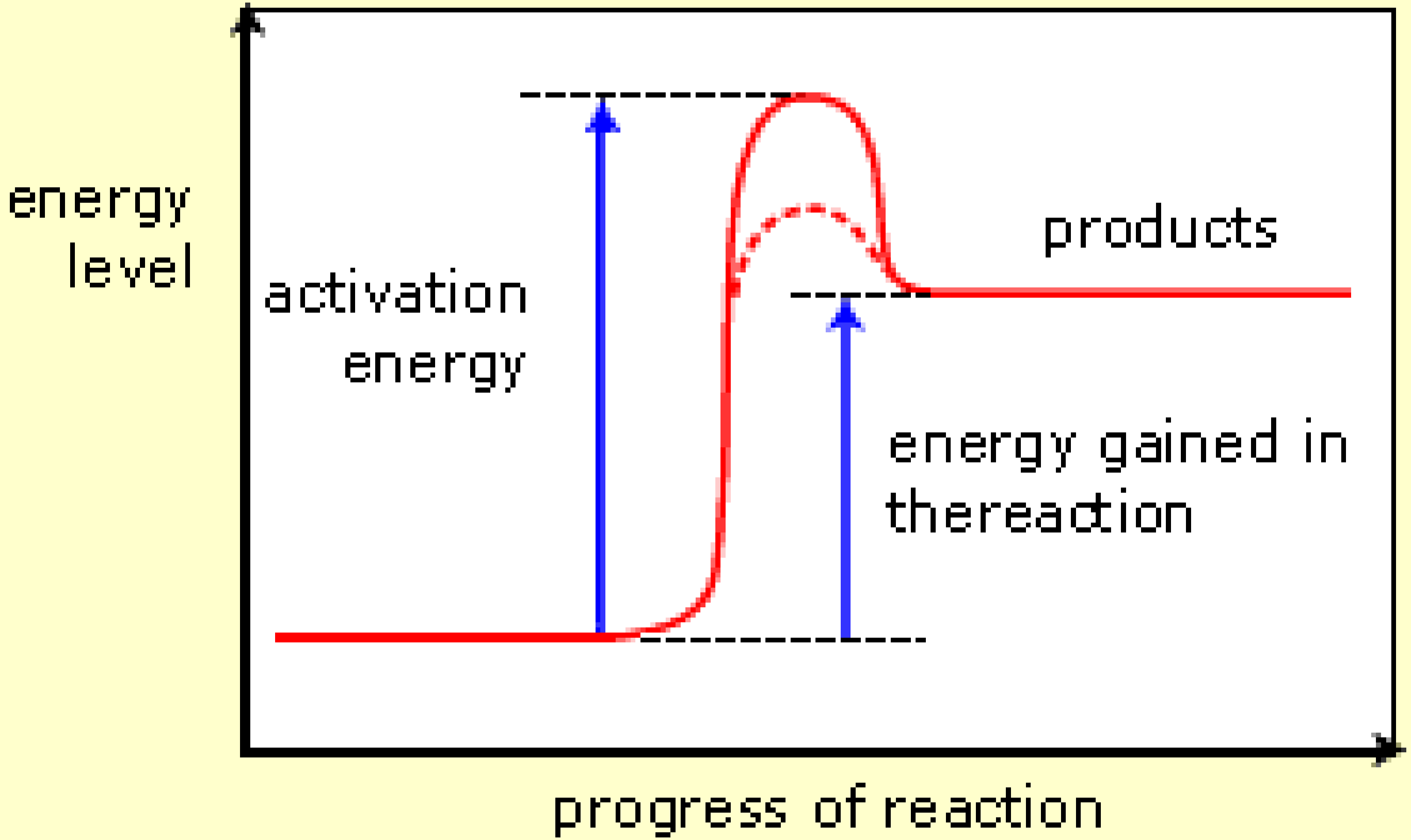
3- what is the meaning of the negative sign of ΔH

$$E_z \rangle E_x$$

Endothermic reaction

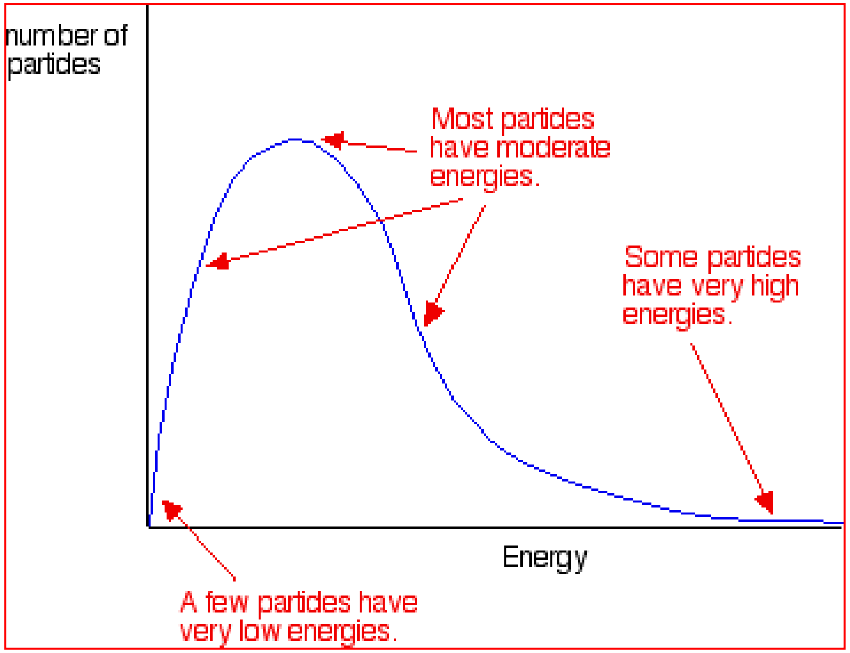

Energy levels in an exothermic reaction
energy level
reactants
activation energy
energy released in the reaction
products
progress of reaction

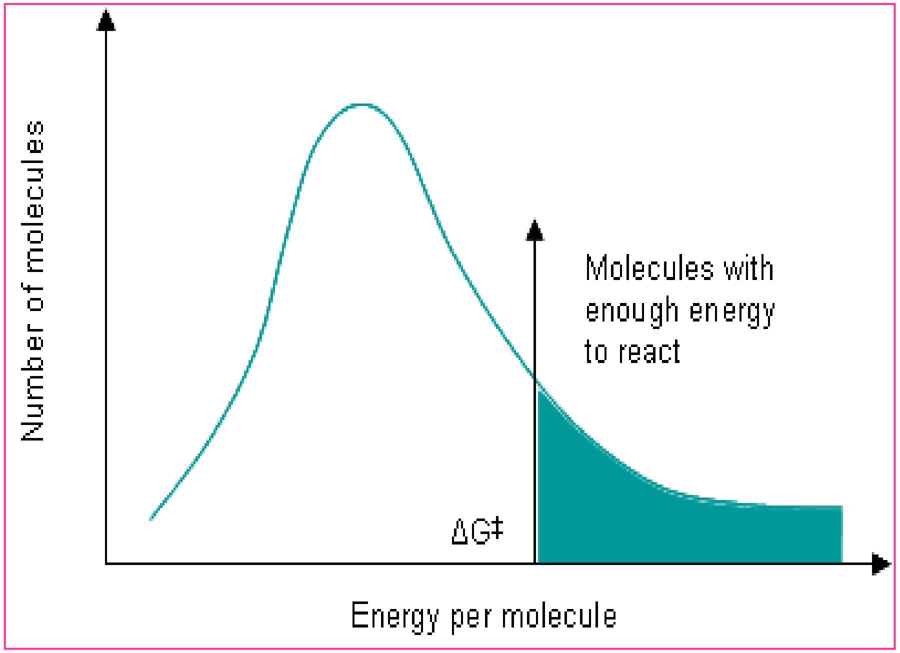
Energy levels in an endothermic reaction

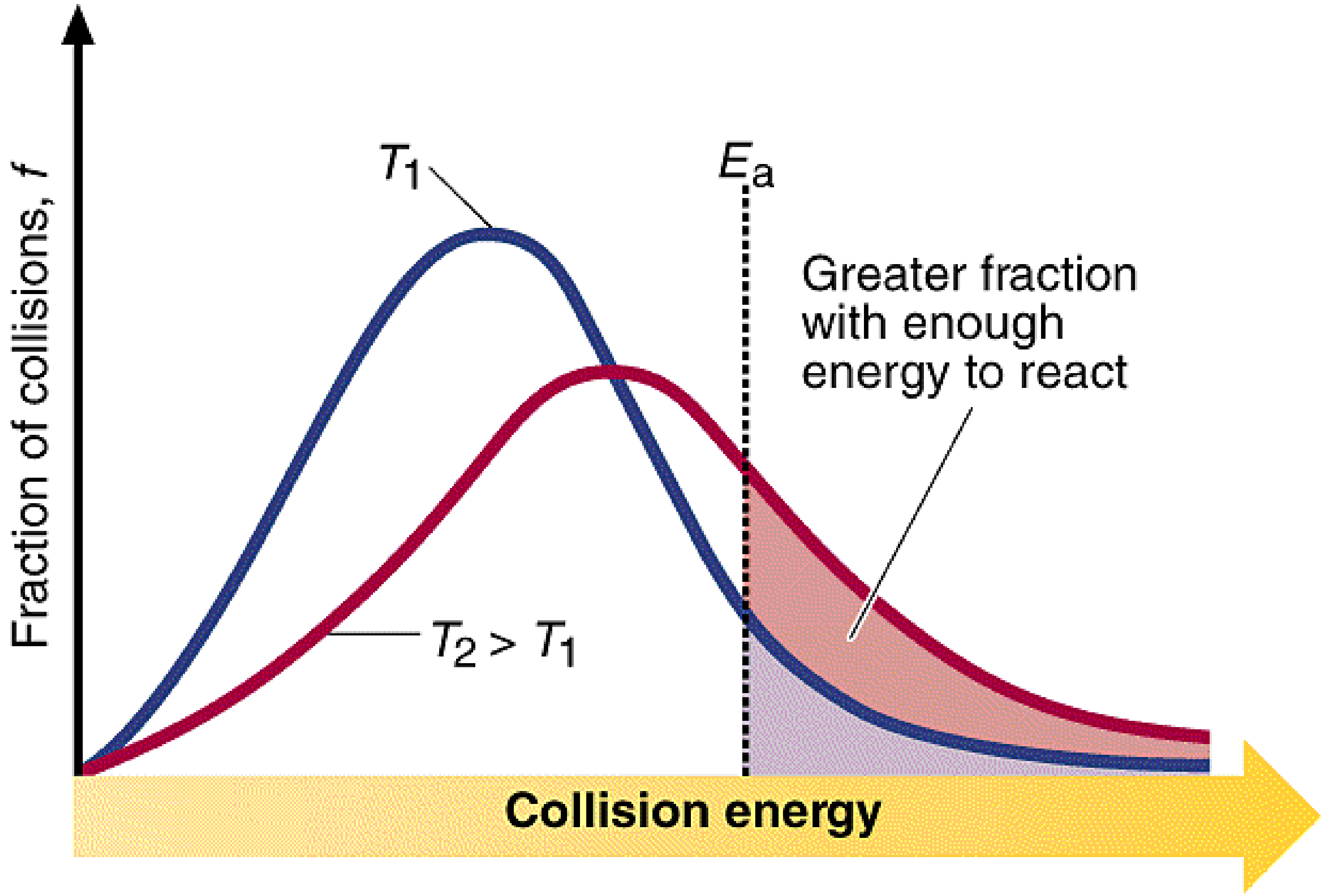


Dependence of the rate of the reaction on temperature

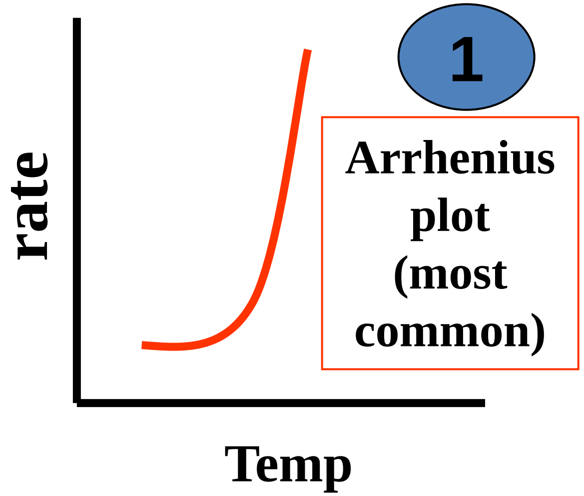
Maxwell and Boltzmann distribution and activation energy



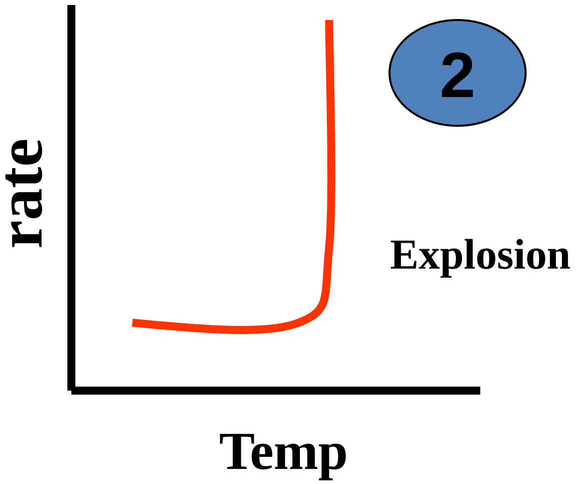



Fraction of collisions, f
T1
Ea
Greater fraction with enough energy to react
T2 > T1
Collision energy

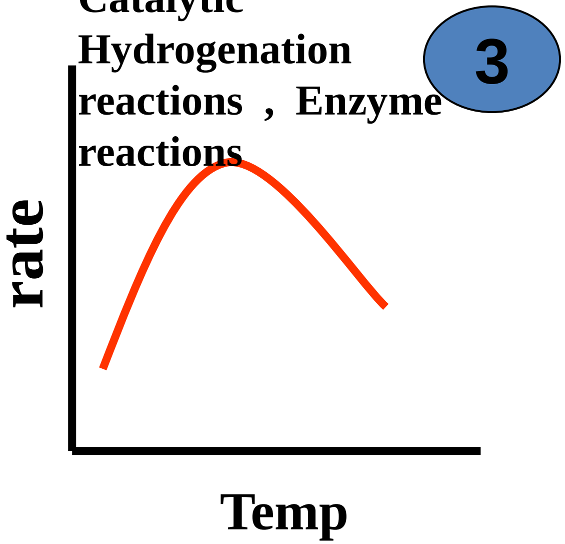
Relation between reaction rate and temperature



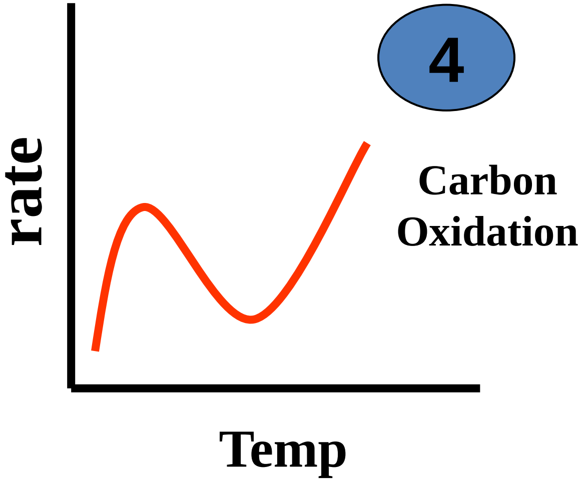
Arrhenius plot (most common)



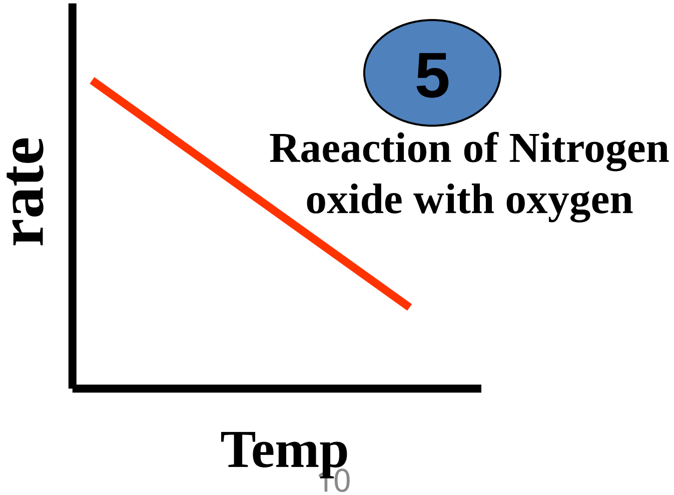
Explosion



Catalytic Hydrogenation reactions , Enzyme reactions



Carbon Oxidation



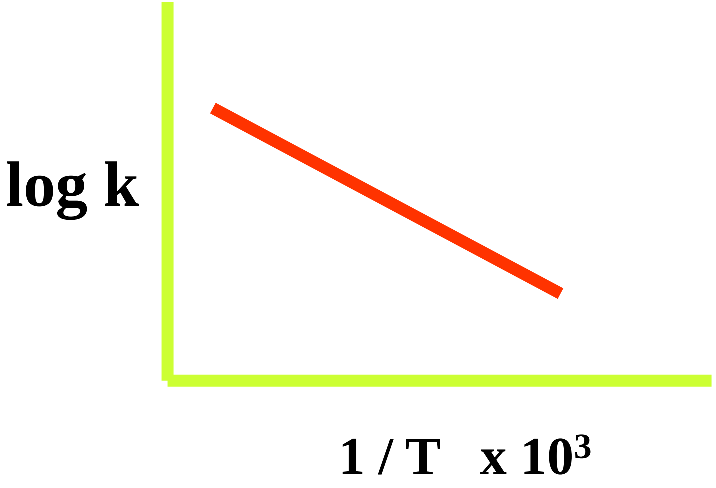
Raeaction of Nitrogen oxide with oxygen

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

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

$A' =$ contant ①

$B =$ constant



……

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

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

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

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

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

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

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

Arrhenius equation

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

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

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

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

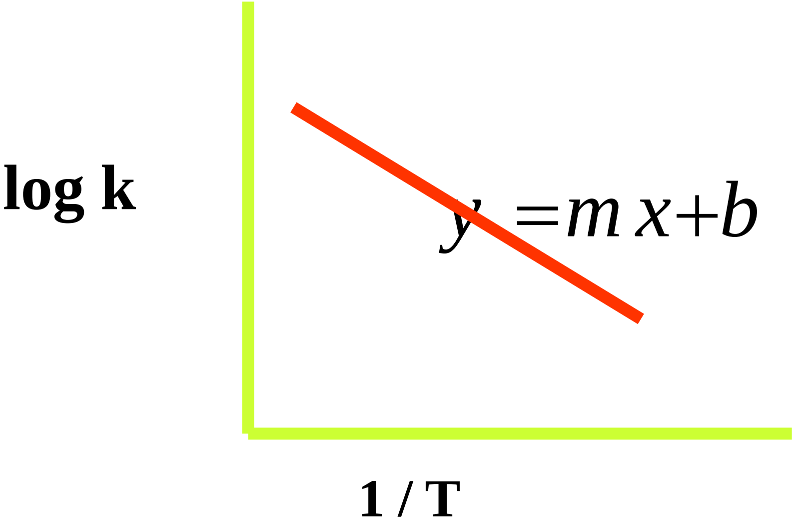
$$\ln k = -\frac{E_a}{RT} + \ln A$$

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

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

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

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



Slope=-E_a/2.303R

Equation 7 can be written as follows

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

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

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

$$\updownarrow \qquad \updownarrow \qquad \updownarrow \qquad \updownarrow$$

$$y = mx + b$$

If the reaction is carried out at two different tepmeratures

$$\log k_1 = -\frac{E_a}{2.303RT_1} + \log A \qquad ⑩$$

$$\log k_2 = -\frac{E_a}{2.303RT_2} + \log A \qquad ⑪$$

By subtraction of equation 10 from 11

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

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

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

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

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

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

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

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

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

Kinetic Chemistry 2

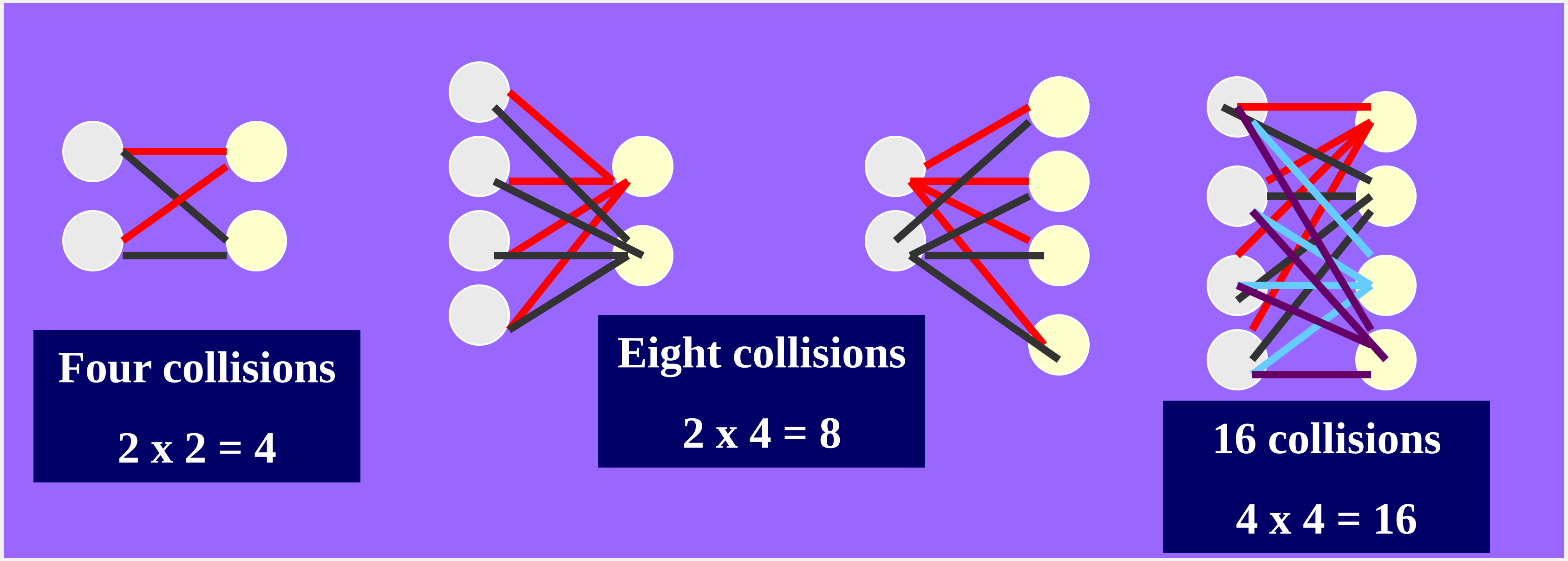
1-Collision Theory

2- Transition State Theory

1- Collision Theory

The theory deals with reactants molecules as solid balls

$$A + B \rightarrow Product$$



Four collisions

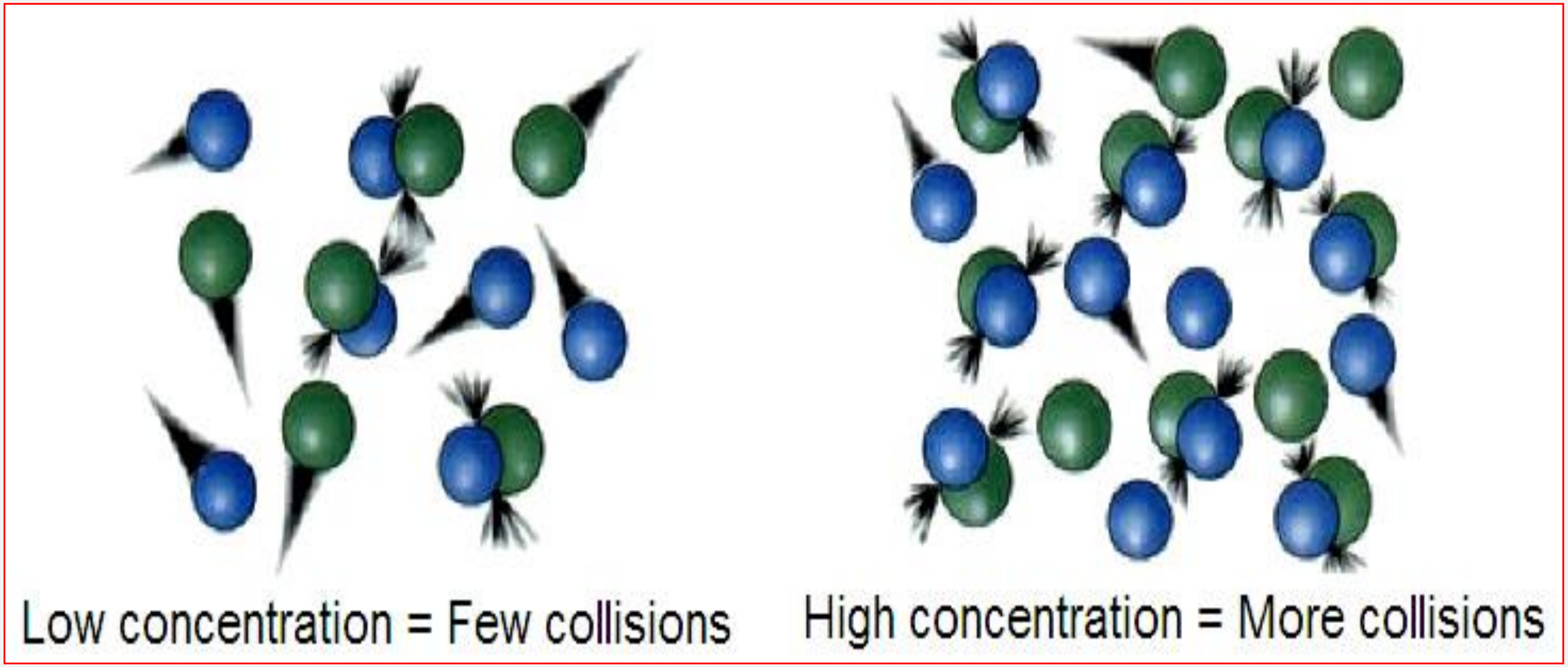
2 x 2 = 4

Eight collisions

2 x 4 = 8

16 collisions

4 x 4 = 16



what is the concentration?

concentration the number of reactants molecules in unit volume

Results

1- number of collisions is related to the number of molecules in unit volume i.e. concentration

2- Number of collisions equals the multiplication of the concentration of reactant A with that of Reactant B

3- Rate of Reaction $\propto$ number of collisions / s

$$Rate = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_A C_B \tag{①}$$

Discussion

Why some collisions are effective and result in the reaction to proceed while other collisions are ineffective and result in the reaction will not proceed to the formation of products?

Answer: there are two factors;

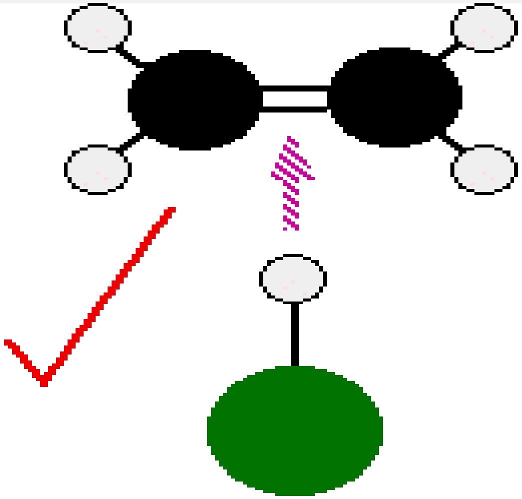
Example

The following reaction result in the formation of chloroethane.

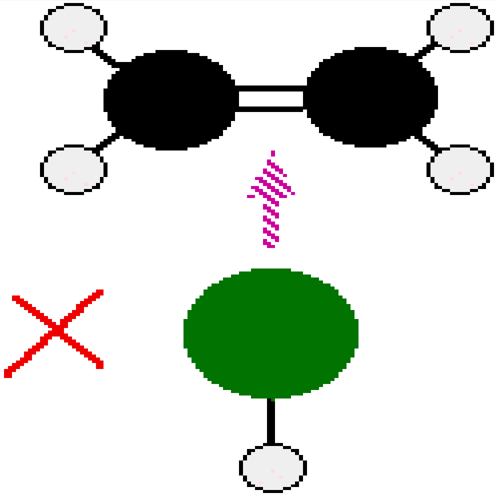
$$CH_2 = CH_2 + HCl \rightarrow CH_3CH_2Cl$$

The reaction can only happen if the hydrogen end of the H-Cl bond approaches the carbon-carbon double bond.

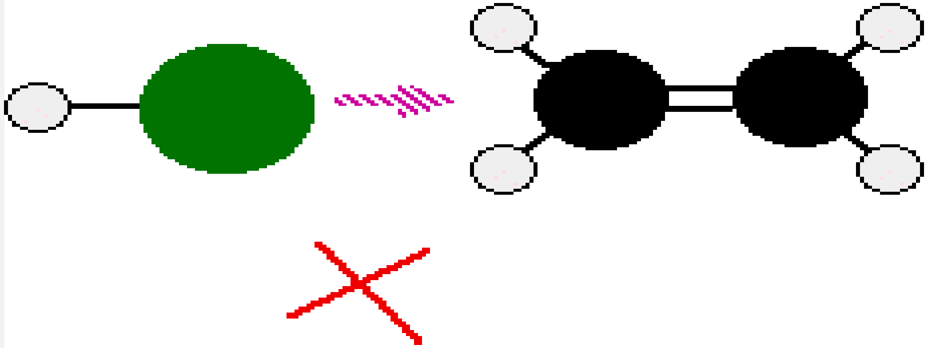
Any other collision between the two molecules doesn't work.



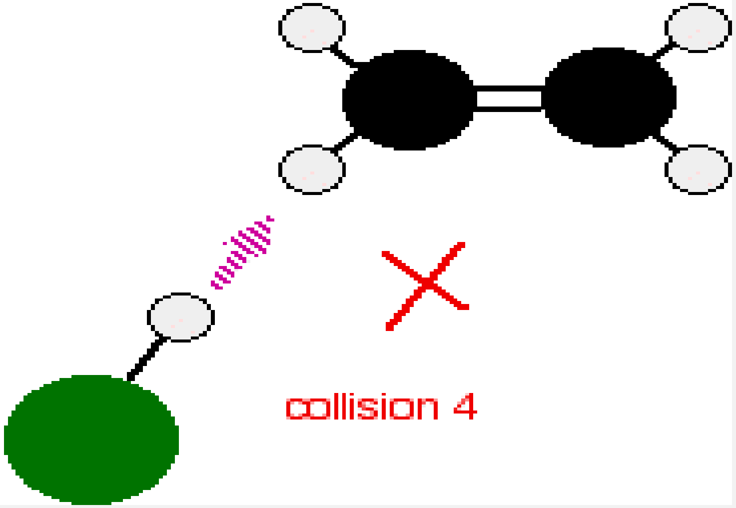
collision 1



collision 2

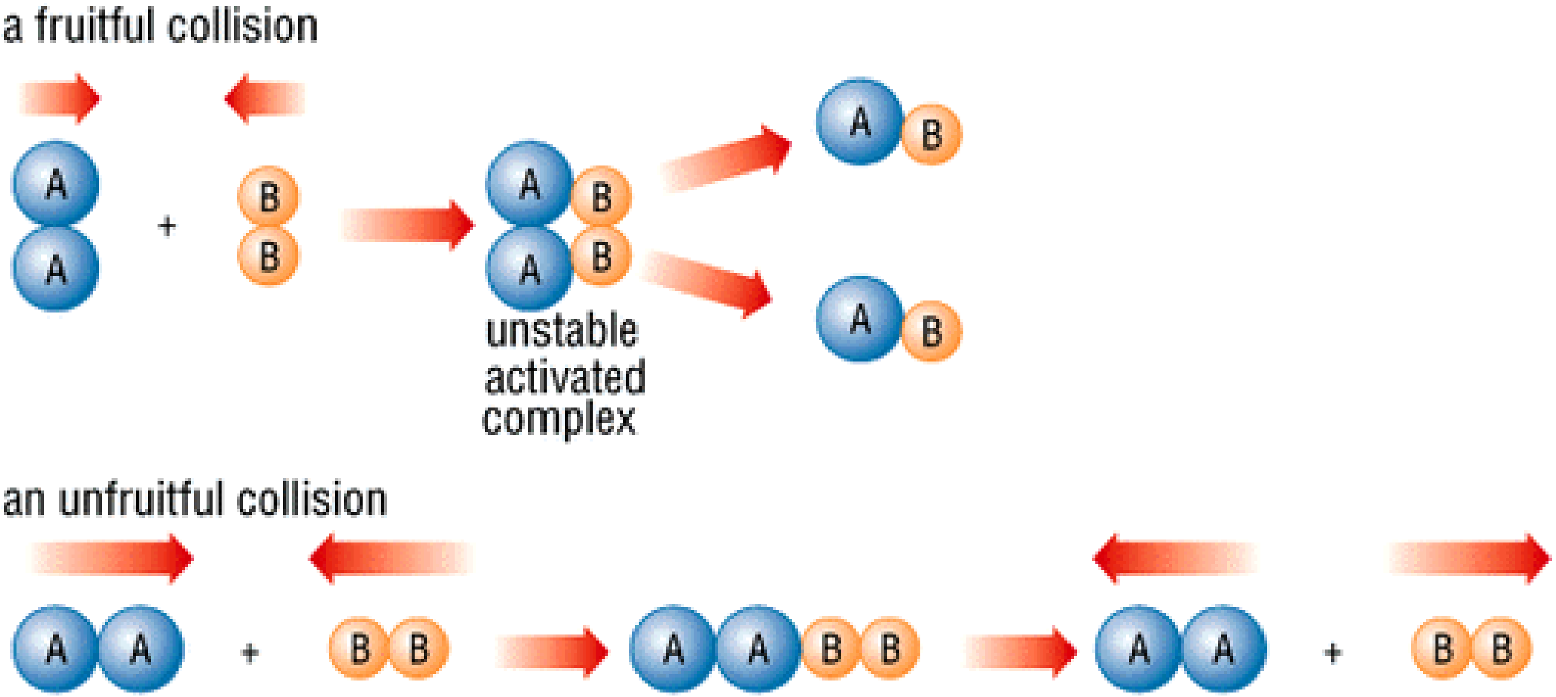


collision 3



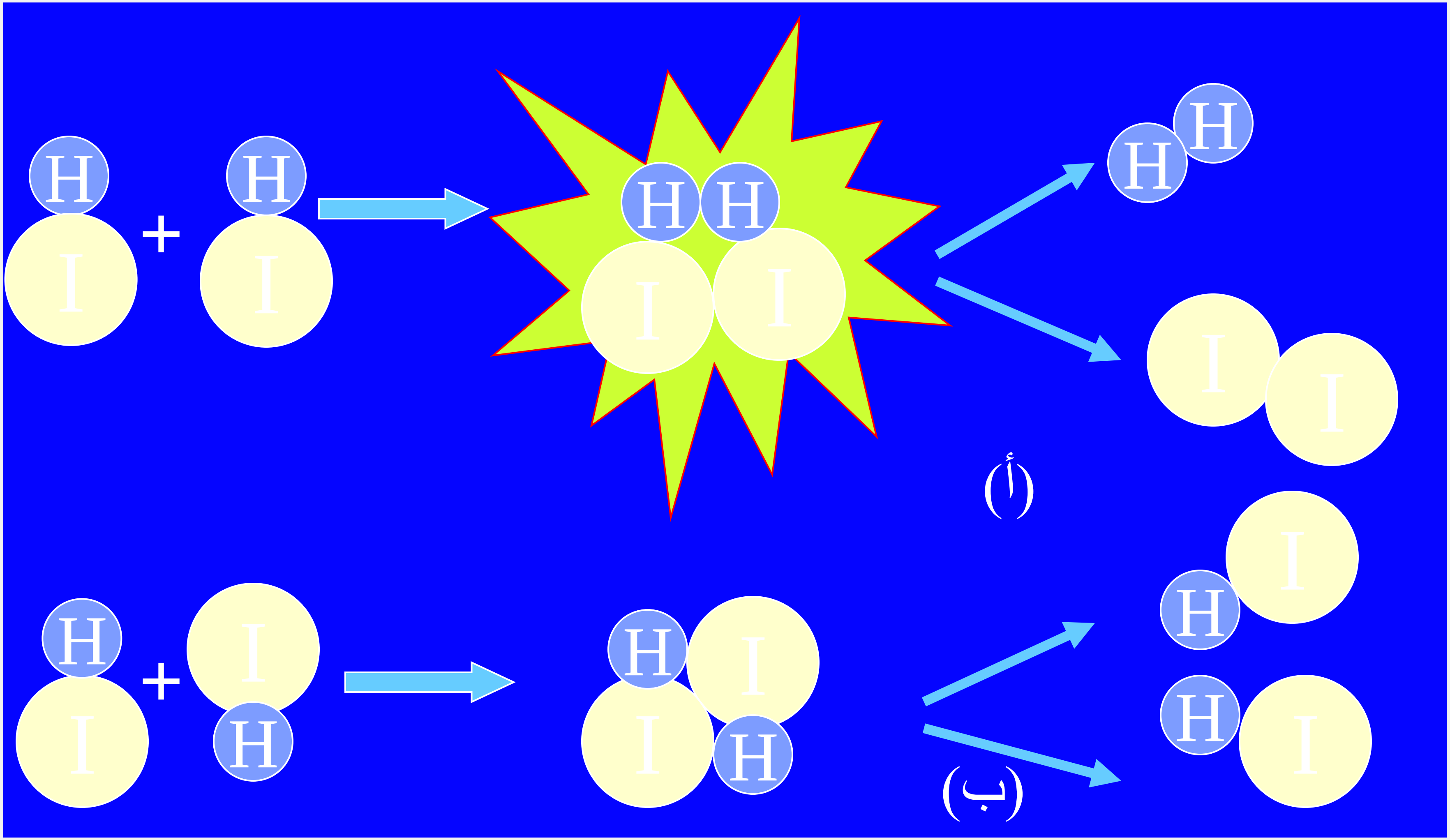
collision 4

Example


a fruitful collision
A
A
+
B
B
A
B
A
B
unstable activated complex
A
B
A
B
an unfruitful collision
A
A
+
B
B
A
A
B
B
A
A
+
B
B

Example

$$2HI \longrightarrow H_2 + I_2$$



1st factor : For a reaction to occur particles must collide with enough energy. The collided molecules must has energy sufficient for the destruct the bonds in the molecules and the formation of new bonds. This energy is equals to or exceeds the activation energy. Not all collisions are successful, because not all particles have the activation energy. The activation energy is the minimum energy required for a reaction to occur

2nd factor: the collided particles must be in suitable position at the time of collision.

Theoretical treatment

$$A + B \rightarrow \text{Product}$$

$$Rate = -\frac{dN_A}{dt} = -\frac{dN_B}{dt} = PFZ_{AB} \qquad (2)$$

F =is the part of collisions that the molecules has energy equals to or exceeds the activation energy

P = is the part of collisions where the molecules are in suitable positions to react

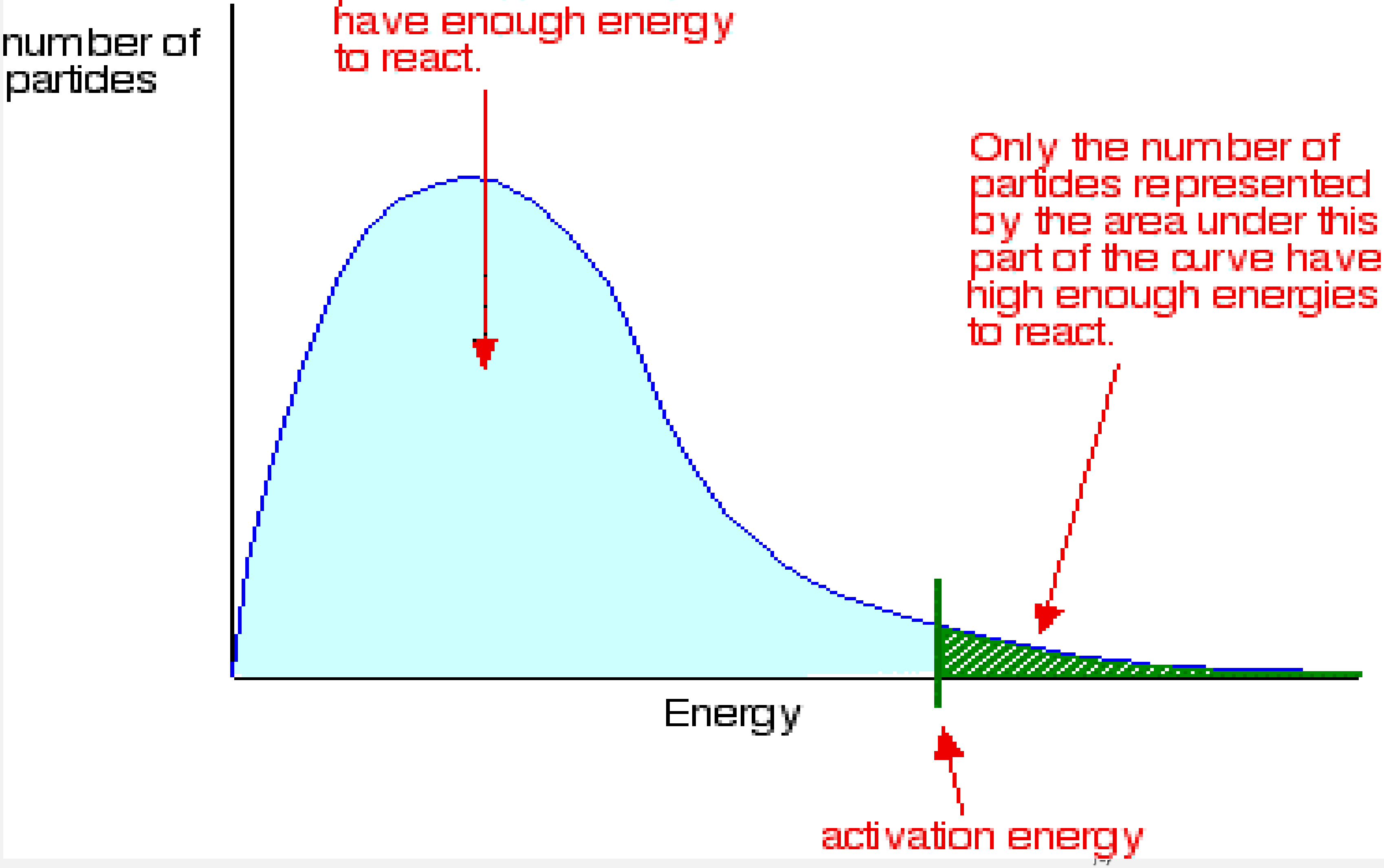
Z_{AB} = total number of collisions

$$F = \frac{Number\ activated\ molecules}{Total\ Number\ of\ molecules} = \frac{N(E)}{N}$$

How to get the value of F?

From Maxwell equation for the distribution of kinetic energy

$$F = \frac{N(E)}{N} = \exp(-E_a/RT) \quad (3)$$



The number of particles represented by the area under this part of the curve don't have enough energy to react.

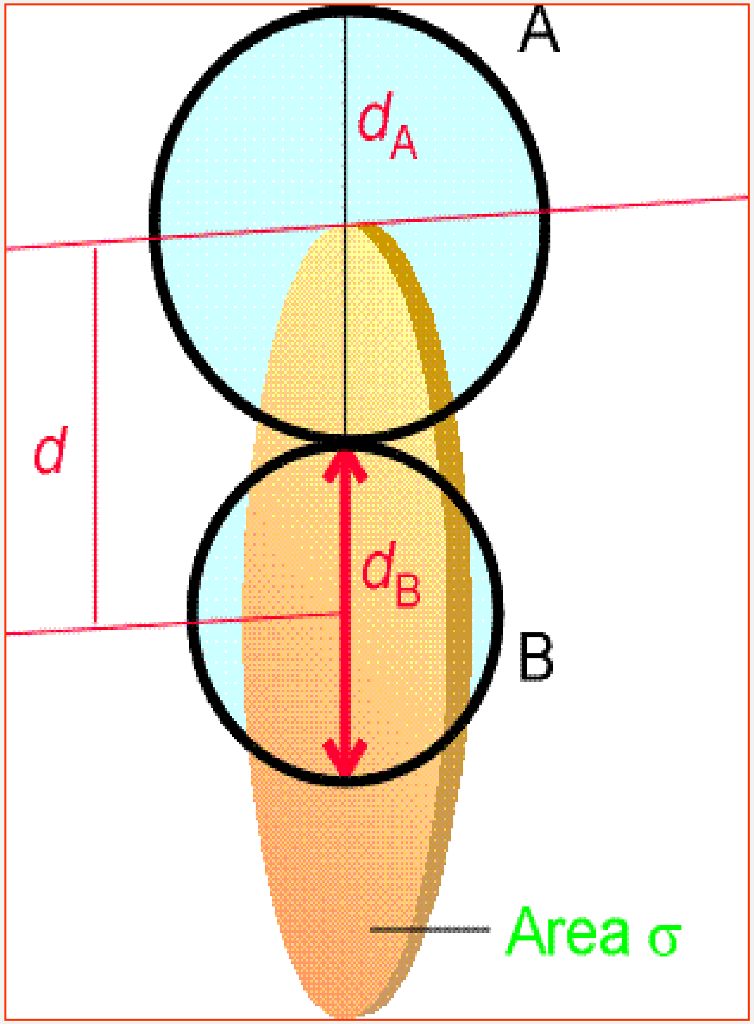
Only the number of particles represented by the area under this part of the curve have high enough energies to react.

activation energy

μ=mu

$$Z_{AB} = d_{AB}^2 \left(8\pi RT/\mu\right)^{1/2} N_A N_B$$

4



d_{AB}: collision diameter

$$d_{AB} = \frac{1}{2}\left(d_A + d_B\right)$$

μ: Reduced mass

$$\mu = \frac{M_A M_B}{M_A + M_B}$$

M: Molecular Mass

By substitution from equations 3 and 4 in equation 2

$$Rate = -\frac{dN_A}{dt} = -\frac{dN_B}{dt} = PFZ_{AB} \qquad 2$$

$$F = \frac{N(E)}{N} = \exp(-E_a / RT) \qquad 3$$

$$Z_{AB} = d^2_{AB}(8\pi RT / \mu)^{1/2} N_A N_B \qquad 4$$

$$-\frac{dN_A}{dt} = -\frac{dN_B}{dt} = Pd^2_{AB}(8\pi RT / \mu)^{1/2} N_A N_B \exp(-E_a / RT) \qquad 5$$

number of A molecules= number of A moles x Avogadro number

$$L = 6.02 x 10^{23} mol^{-1}$$

$$N_A = LC_A \xrightarrow{in\ 1ml} N_A = \frac{L}{10^3} C_A \qquad (6)$$

and $$dN_A = \frac{L}{10^3} dC_A \qquad (7)$$

$$N_B = \frac{L}{10^3} C_B \qquad (8)$$

and $$dN_B = \frac{L}{10^3} dC_B \qquad (9)$$

By substitution from eqns. 6,7,8 and 9 in 5

$$-\frac{dC_A}{dt}\left(\cancel{\frac{L}{10^3}}\right) = -\frac{dC_B}{dt}\left(\cancel{\frac{L}{10^3}}\right) = Pd^2_{AB}\left(8\pi RT/\mu\right)^{1/2}\left(\cancel{\frac{L}{10^3}}C_A\right)\left(\frac{L}{10^3}C_B\right)\exp\left(-E_a/RT\right)$$

$$-\frac{dC_A}{dt} = -\frac{dC_B}{dt} = Pd^2_{AB}\left(8\pi RT/\mu\right)^{1/2}\left(C_A\right)\left(\frac{L}{10^3}C_B\right)\exp\left(-E_a/RT\right) \tag{10}$$

By comparison between equation 10 and 1

$$-\frac{dC_A}{dt} = -\frac{dC_B}{dt} = kC_AC_B \tag{1}$$

$$k\cancel{C_A}\cancel{C_B} = Pd^2_{AB}\left(8\pi RT/\mu\right)^{1/2}\left(\cancel{C_A}\right)\left(\frac{L}{10^3}\cancel{C_B}\right)\exp\left(-E_a/RT\right)$$

$$k = Pd_{AB}^{2}\left(8\pi RT/\mu\right)^{1/2}\left(\frac{L}{10^{3}}\right)\exp\left(-E_{a}/RT\right) \tag{11}$$

On comparison of equation 11 and Arrhenius eqn.

$$k = A\exp\left(-E_{a}/RT\right)$$

$$A\,\cancel{\exp\left(-E_{a}/RT\right)} = Pd_{AB}^{2}\left(8\pi RT/\mu\right)^{1/2}\left(\frac{L}{10^{3}}\right)\cancel{\exp\left(-E_{a}/RT\right)}$$

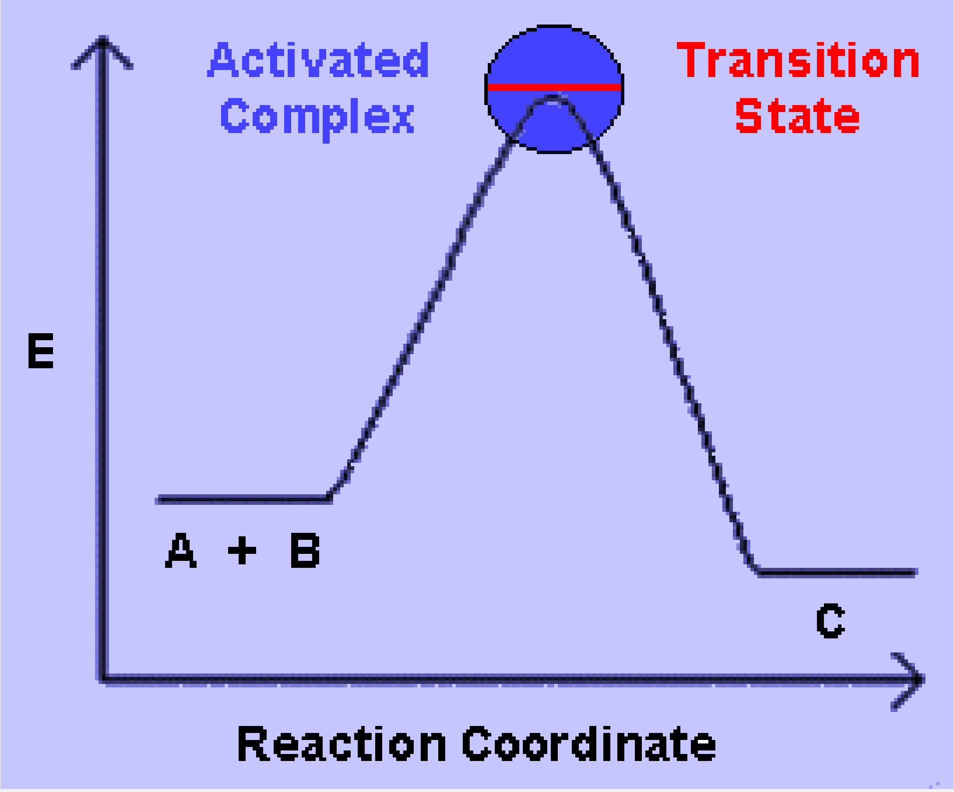
$$A = Pd_{AB}^{2}\left(8\pi RT/\mu\right)^{1/2}\left(\frac{L}{10^{3}}\right) \tag{12}$$

The values of k and A can be determined approximately without probability constant

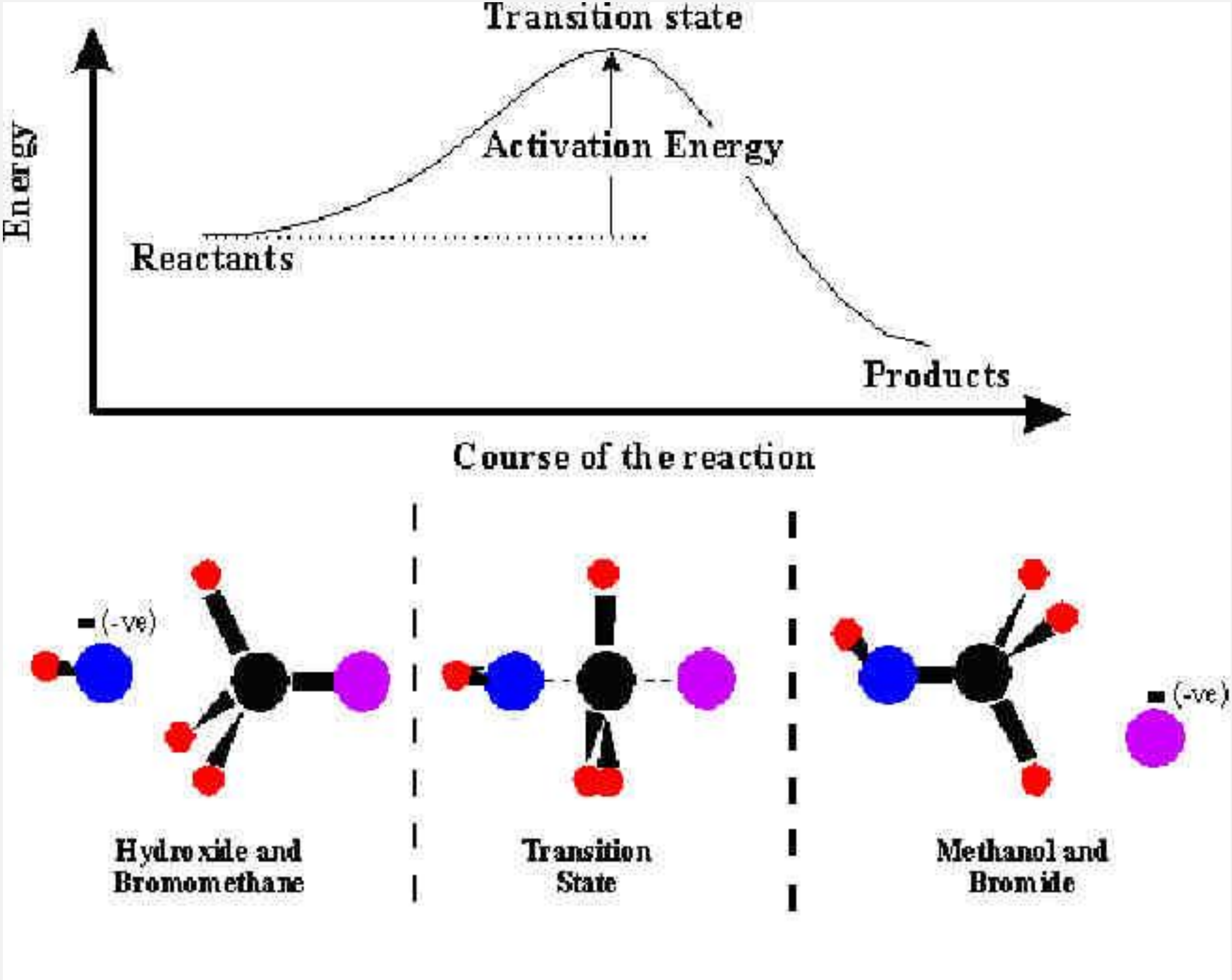
$$k = d_{AB}^2 \left(8\pi RT/\mu\right)^{1/2} \left(\frac{L}{10^3}\right) \exp\left(-E_a/RT\right) \tag{13}$$

$$A = d_{AB}^2 \left(8\pi RT/\mu\right)^{1/2} \left(\frac{L}{10^3}\right) \tag{14}$$

2- Transition State Theory



**Henry Eyring
1981-1901**


Transition state
Energy
Activation Energy
Reactants
Products
Course of the reaction
(-ve)
(-ve)
Hydroxide and Bromomethane
Transition State
Methanol and Bromide

افتراضات النظرية

1- ان تكوين النواتج لا يحدث مباشرة نتيجة لتصادم المتفاعلات

2- لابد ان تمر الجزيئات المتصادمة بحالة انتقالية او حالة نشطة يتكون عندها مركب نشط غير ثابت يسمى بالمعقد المنشط

3- اقترح ان يكون تركيب هذا المعقد وسطا بين المواد المتفاعلة والناتجة وفي حالة توازن مع المواد المتفاعلة

4- طاقة هذا المعقد اكبر من طاقة المواد المتفاعلة والناتجة

5- قيمة طاقة هذا المعقد مطابقة لقيمة قمة منحنى الطاقة

6- هذا المعقد كينونته مؤقتة ويتفكك بسرعة معينة ليعطي النواتج

$$Reactants \leftrightarrow ActivatedState \rightarrow Produc$$

المعالجة النظرية

تعتمد سرعة التفاعل على عاملين اساسين :

اـ تركيز المعقد المنشط

بـ السرعة التي يتفكك بها المعقد المنشط الى مواد ناتجة

اذا كان لدينا تفاعل بسيط ثنائي الجزيئية

$$A+B \xrightarrow{k} Product$$

ماهو قانون سرعة التفاعل؟

① $$Rate = k[A][B]$$

حسب نظرية التصادم

$$A+B \leftrightarrow (AB^*) \xrightarrow{k^*} Product$$

اذاَ قانون سرعة التفاعل

② $$Rate = k^*[AB^*]$$

يعتمد تفكك المعقد المنشط على شدة الاهتزاز الذي يخضع له هذا المركب

كلما كان عدد الذبذبات في الثانية كبيرا وسعة الذبذبة كبيرة زاد احتمال تفككه

$$k^{*} \approx \nu^{*} \qquad (3)$$

→ التردد أي عدد الذبذبات في الثانية

$$\text{Rate} = \nu^{*}\left[AB^{*}\right] \qquad (4)$$

طاقة التذبذب المصاحبة للتردد $\Delta\varepsilon$ تساوي

$$\Delta\varepsilon = h\nu^{*} = KT \qquad (5)$$

K= ثابت بلتزمان

Boltzmann constant

$K=1.38\times10^{-23}$ J K^{-1}

h= ثابت بلانك

Planck constant

$h=6.626\times10^{-34}$ J·s

اذا التردد يساوي

$$\nu^{*} = \frac{KT}{h}$$

ولكن

$$K = \frac{R}{L}$$

$$\therefore \nu^{*} = \frac{RT}{Lh} \qquad (6)$$

بالتعويض من معادلة 6 في 4

$$\text{Rate} = \frac{RT}{Lh}\left[AB^{*}\right] \qquad (7)$$

Kinetic Chemistry 3

Complex Reactions

It is a collection of elementary reactions

The mechanism of the reaction is a collection of elementary processes (elementary steps or elementary reactions) that describes how the total reaction occurs

Example

Conversion of Ozone to Oxygen

$$2O_3(g) \rightarrow 3O_2(g)$$

The mechanism of the reaction occurs via the following elementary steps

Elementary reaction $O_3 \xrightarrow{k_1} O_2 + O$

Elementary reaction $O + O_2 \xrightarrow{k_2} O_3$

Elementary reaction $O + O_3 \xrightarrow{k_3} 2O_2$

Molecularity of the reaction

It is the sum of the number of (molecules, ions or atoms) involved in the reaction

From the mechanism of conversion of Ozone into Oxygen:

Unimolecular reaction $\boxed{O_3 \xrightarrow{k_1} O_2 + O}$

Bimolecular reaction $\boxed{O + O_2 \xrightarrow{k_2} O_3}$

Bimolecular reaction $\boxed{O + O_3 \xrightarrow{k_3} 2O_2}$

Rate Law of Elementary Reactions

N.P. we cannot predict the law of reaction rate from the reaction equation but can get it experimentally

from the reaction mechanism, the rate law is:

$$r_1 = -\frac{d[O_3]}{dt} = \frac{d[O_2]}{dt} = \frac{d[O]}{dt} = k_1[O_3] \qquad O_3 \xrightarrow{k_1} O_2 + O$$

For first step

……

$$r_2 = -\frac{d[O]}{dt} = -\frac{d[O_2]}{dt} = \frac{d[O_3]}{dt} = k_2[O][O_2] \qquad O + O_2 \xrightarrow{k_2} O_3$$

For second step

……

$$r_3 = -\frac{d[O]}{dt} = -\frac{d[O_3]}{dt} = \frac{1}{2}\frac{d[O_2]}{dt} = k_3[O][O_3] \qquad O + O_3 \xrightarrow{k_3} 2O_2$$

For third step

……

In this treatment we deal with the primary reactions as molecularity equals to order

$$r_1 = -\frac{d[O_3]}{dt} = \frac{d[O_2]}{dt} = \frac{d[O]}{dt} = k_1[O_3]$$

$$\mathbf{r_2 = -\frac{d[O]}{dt} = -\frac{d[O_2]}{dt} = \frac{d[O_3]}{dt} = k_2[O][O_2]}$$

$$\mathbf{r_3 = -\frac{d[O]}{dt} = -\frac{d[O_3]}{dt} = \frac{1}{2}\frac{d[O_2]}{dt} = k_3[O][O_3]}$$

……

The rat of a reaction is sum of all different reactions rates $\boldsymbol{r=r_1+r_2+r_3}$ taking into consideration: 1. the compound is reactant or product 2. Stoichiometric numbers

……

The rate of consumption of Ozone

$$-\frac{d[O_3]}{dt} = \quad k_1[O_3] \quad -k_2[O][O_2] \quad +k_3[O][O_3]$$

……

$$\frac{d[O_2]}{dt} = k_1[O_3] - k_2[O][O_2] + 2k_3[O][O_3]$$

……

The rate of production of O atom

$$\frac{d[O]}{dt} = k_1[O_3] - k_2[O][O_2] - k_3[O][O_3]$$

Examble

Elementary reaction in a chain reaction is:

$$2\overset{\bullet}{C}H_3 \xrightarrow{k} C_2H_6$$

The rate law is:

$$-\frac{1}{2}\frac{d\left[\overset{\bullet}{C}H_3\right]}{dt}=k\left[\overset{\bullet}{C}H_3\right]^2 \quad\longrightarrow\quad -\frac{d\left[\overset{\bullet}{C}H_3\right]}{dt}=2k\left[\overset{\bullet}{C}H_3\right]^2$$

In general, if we have the hypothetic reaction

$$aA+bB+\ldots\ldots\ldots\rightarrow qQ+rR+\ldots\ldots\ldots$$

The rate law is:

$$\boxed{r=-\frac{1}{a}\frac{d[A]}{dt}=-\frac{1}{b}\frac{d[B]}{dt}=\frac{1}{q}\frac{d[Q]}{dt}=\frac{1}{r}\frac{d[R]}{dt}=k[A]^a[B]^b}$$

Types of complex reactions

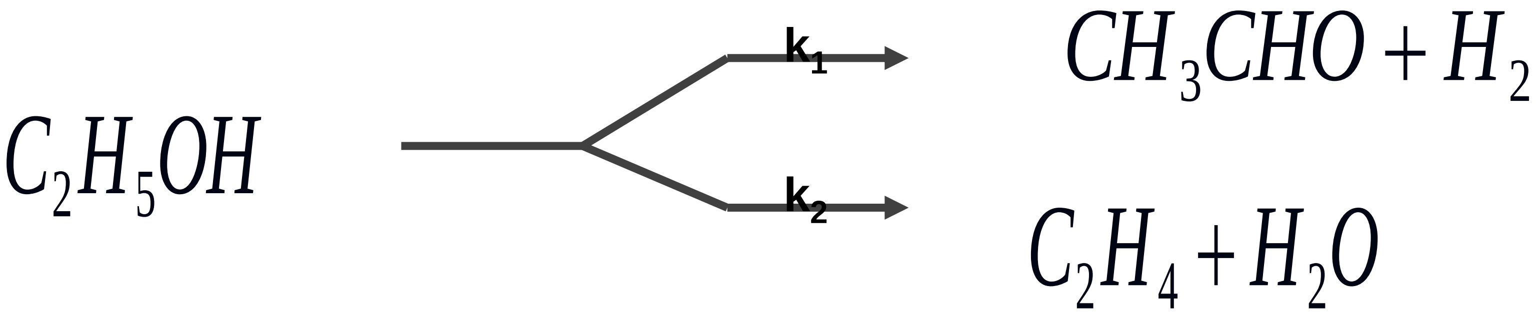
Chain reactions	**Consecutive reactions**	**Reversible reactions**	**Parallel Reactions**

Parallel Reactions

1. It is most common in organic chemistry
2. It forms different product compounds through one chemical reaction at he same time
3. The reaction that results in the formation of the main product is called main reaction
4. The reaction that results in the formation of less common product is called side reaction

Example

Dehydrogenation and dehydration of alcohol



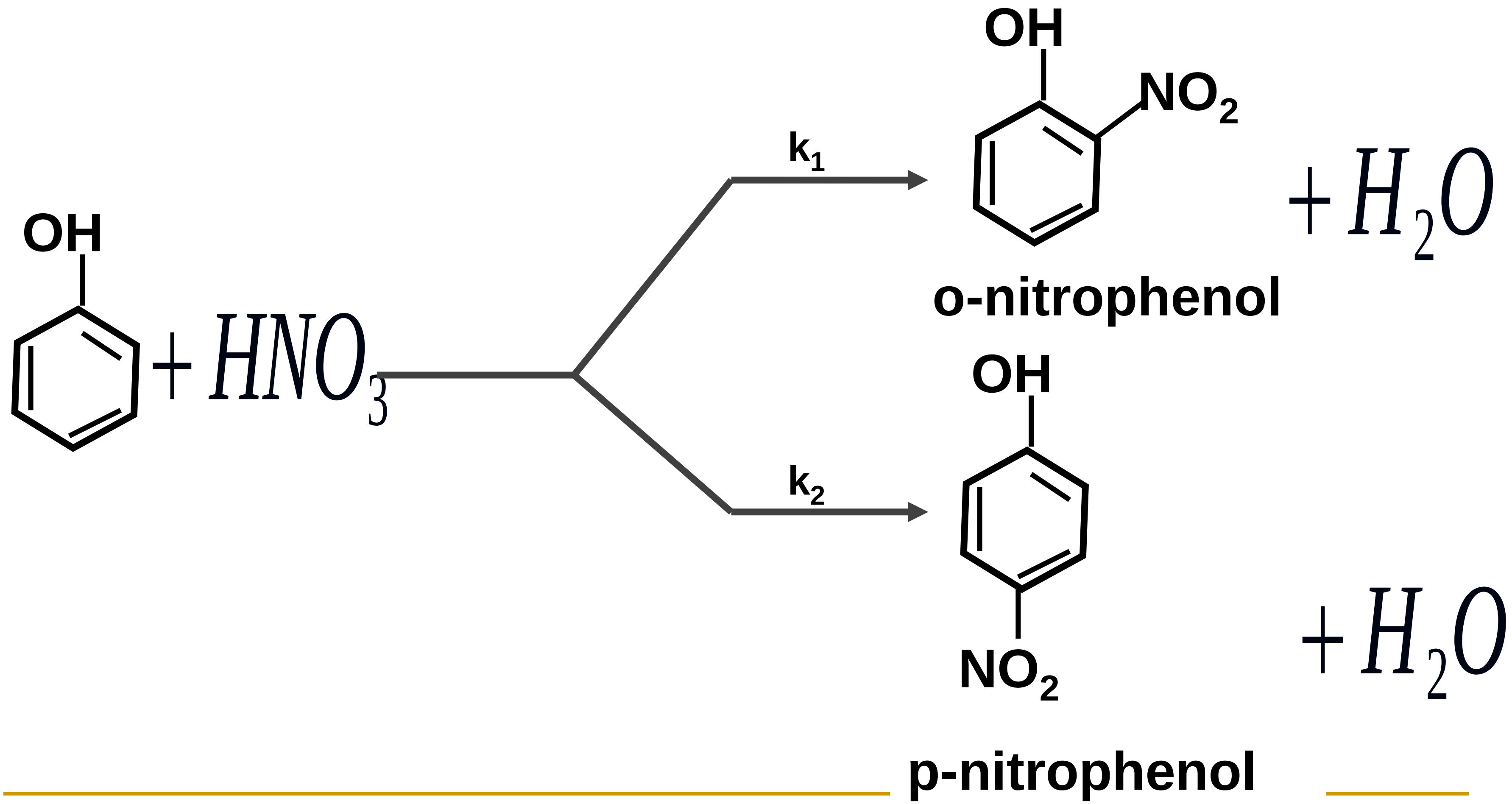
C_2H_5OH

$\xrightarrow{k_1}$ $CH_3CHO + H_2$

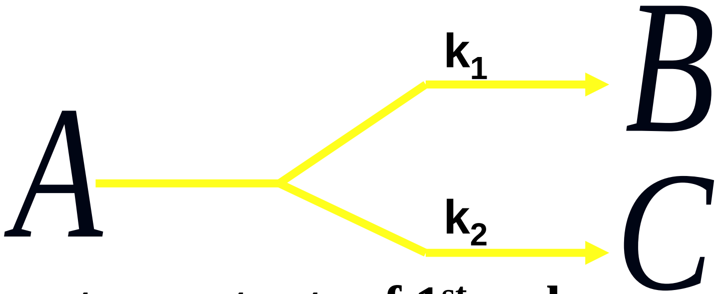
$\xrightarrow{k_2}$ $C_2H_4 + H_2O$

Examble

Nitration of phenol to ortho- and para-nitro phenol



We will discuss simple case for a parallel reaction of 1st order reaction



where k_1 and k_2 are rate constants of 1st order reactions

Elementary Reaction	$A \xrightarrow{k_1} B$	$A \xrightarrow{k_2} C$
Reaction rate	$r_1 = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1[A]$	$r_2 = -\frac{d[A]}{dt} = \frac{d[C]}{dt} = k_2[A]$
Rate of consumption of A	$-\frac{d[A]}{dt} = r_1 + r_2 = k_1[A] + k_2[A] = (k_1 + k_2)[A]$ ①	
Rate of formation of B	$\frac{d[B]}{dt} = r_1 = k_1[A]$ ②	
Rate of formation of C	$\frac{d[C]}{dt} = r_2 = k_2[A]$ ③	

First of all we will find the equation that relates the change in [A] with time

$$-\frac{d[A]}{dt} = (k_1 + k_2)[A]$$ ①

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = (k_1 + k_2)\int_0^t dt$$

$$[A]= \quad -\ln[A]\Big|_{[A]_0}^{[A]} = (k_1 + k_2)t\Big|_0^t$$

$$\ln[A] - \ln[A]_0 = -(k_1 + k_2)t$$

$$\ln\frac{[A]}{[A]_0} = -(k_1 + k_2)t$$

$$\cancel{e}^{\cancel{\ln}\frac{[A]}{[A]_0}} = e^{-(k_1 + k_2)t}$$

$$\frac{[A]}{[A]_0} = e^{-(k_1 + k_2)t} \quad \longrightarrow$$

④

Second: we will find the equation that relates the change in [B] with time.

By substitution from eqn.4 into eqn.2:

$$\frac{d[B]}{dt} = k_1[A] \quad (2)$$

$$[A] = [A]_0 e^{-(k_1+k_2)t} \quad (4)$$

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-(k_1+k_2)t}$$

$$\int_0^{[B]} d[B] = k_1[A]_0 \int_0^t e^{-(k_1+k_2)t} dt$$

$$[B]\Big|_0^{[B]} = -\frac{k_1[A]_0}{(k_1+k_2)} e^{-(k_1+k_2)t}\Big|_0^t$$

$$[B] = -\frac{k_1[A]_0}{(k_1+k_2)}\left(e^{-(k_1+k_2)t} - e^0\right)$$

$$[B] = -\frac{k_1[A]_0}{(k_1+k_2)}\left(e^{-(k_1+k_2)t} - 1\right)$$

$$\boxed{[B] = \frac{k_1[A]_0}{(k_1+k_2)}\left(1 - e^{-(k_1+k_2)t}\right)} \tag{5}$$

Third: we will find the equation that relates the change in [C] with time.

$$\boxed{[C] = \frac{k_2[A]_0}{(k_1+k_2)}\left(1 - e^{-(k_1+k_2)t}\right)} \tag{6}$$

From eqns. 5 and 6:

$$\frac{[B]}{[C]} = \frac{k_1}{k_2}$$

:There are two cases

if $k_1 \rangle\rangle k_2$

$$[B] = \frac{k_1 [A]_0}{(k_1 + k_2)} \left(1 - e^{-(k_1 + k_2)t}\right)$$

⑤

$$[B] = \frac{\cancel{k_1} [A]_0}{\cancel{k_1}} \left(1 - e^{-k_1 t}\right)$$

$$[B] = [A]_0 \left(1 - e^{-k_1 t}\right)$$

If $k_2 \rangle\rangle k_1$

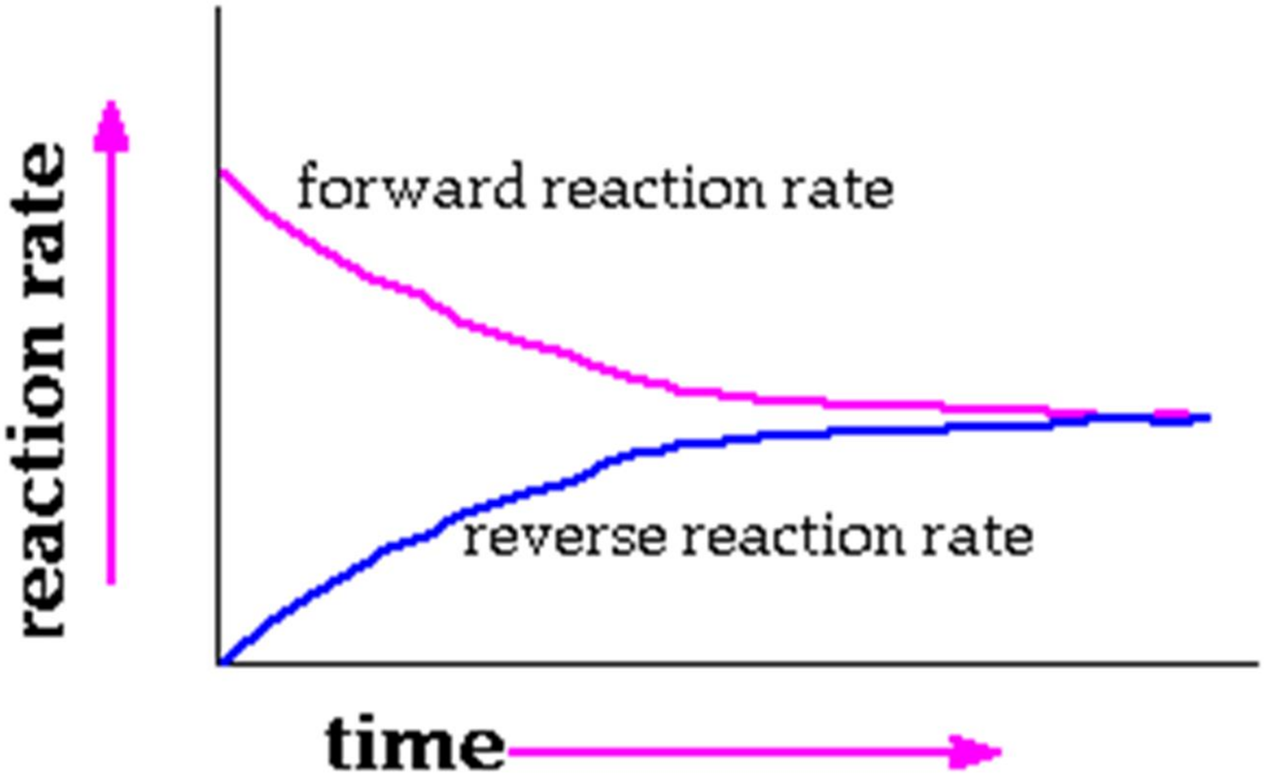
$$[C] = \frac{k_2 \lfloor A \rfloor_0}{(k_1 + k_2)} \left(1 - e^{-(k_1+k_2)t}\right)$$ ⑥

$$[C] = \frac{\cancel{k_2} \lfloor A \rfloor_0}{\cancel{k_2}} \left(1 - e^{-k_2 t}\right)$$

$$\lfloor C \rfloor = \lfloor A \rfloor_0 \left(1 - e^{-k_2 t}\right)$$

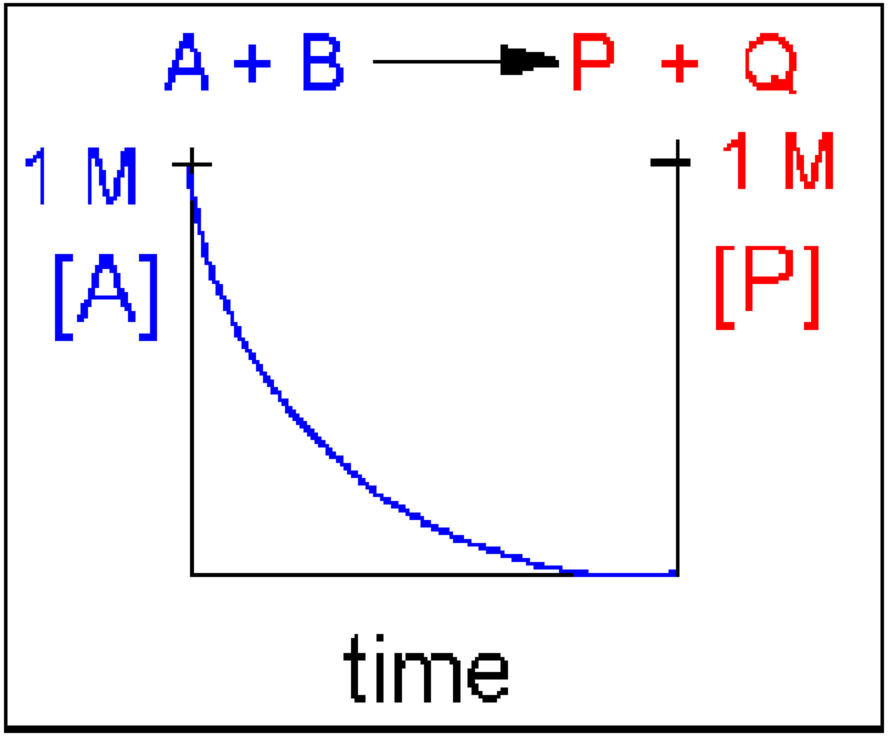
Kinetic Chemistry 4

Reversible Reactions

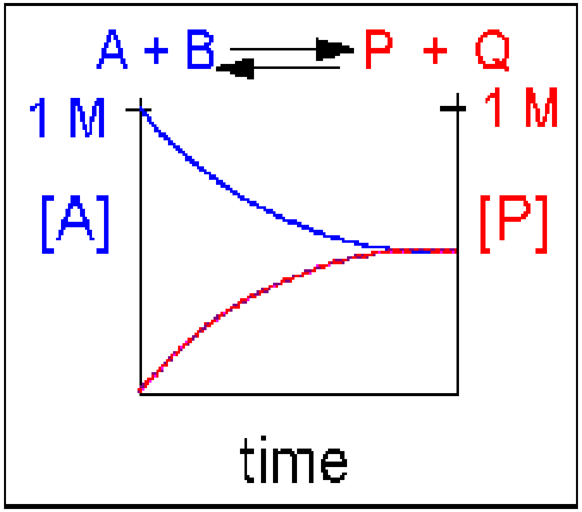


Irreversible Reaction

Irreversible reaction in which the reverse reaction occurs to a **negligible extent**. In this reaction, the reverse reaction occurs to such a small extent that we can neglect it.

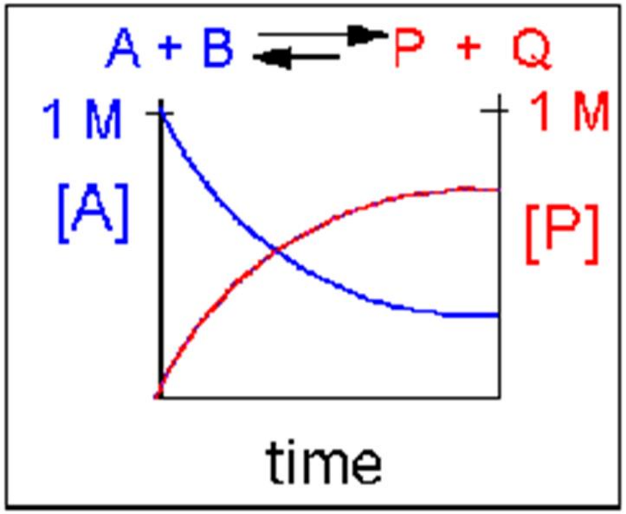


Reversible Reaction



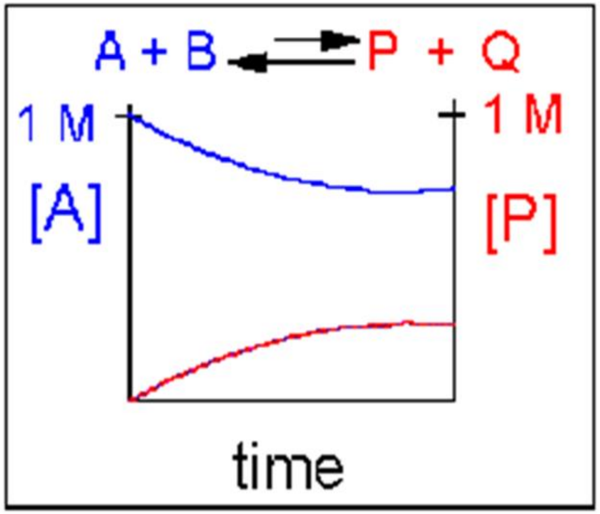
Reversible Reaction in which **forward** and **reverse** reactions are **equally favored**.

Because the reactants and products are equally favored, their concentration will be equal at equilibrium.



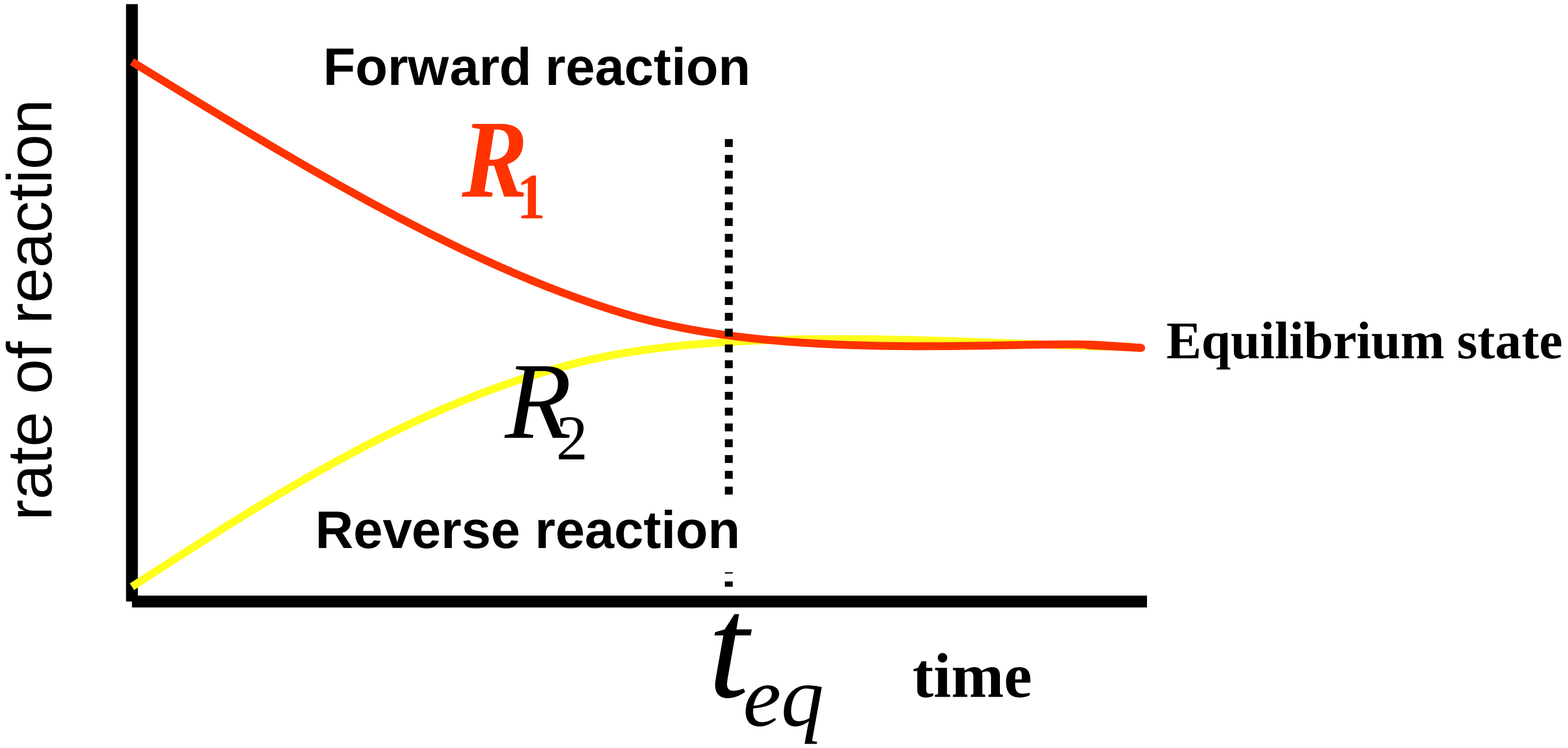
Reversible reaction in which the **forward** reaction is favored.

Again [A] decreases and [P] increases, but in this case, some A remains since the reaction is reversible.



Reversible Reaction in which the reverse reaction is favored.

An example of this kind of reaction, is the reaction of acetic acid (a weak acid) with water.


Forward reaction
R_1
R_2
Reverse reaction
Equilibrium state
rate of reaction
t_{eq}
time

Two cases

$$A \xleftrightarrow[k_{-1}]{k_1} B$$

Case 2

If the experiment is started using impure A, of concentration a_0

Case 1

If the experiment is started using pure A , of concentration a_0

Case 1 If the experiment is started using pure A , of concentration a_0

Time	A	B
0	a	0
t	$a - x$	x
عند الاتزان	$a - x_e$	x_e

$X_e \longrightarrow$ equilibrium

Determination of X_e

Via following up the concentration of the product compound with time till reaches a constant value with time

Determination of $(a-X_e)$

Via following up the concentration of the reactant compound with time till reaches a constant value.

$$A \xrightarrow{k_1} B$$

Forward reaction

$$B \xrightarrow{k_{-1}} A$$

Reversible reaction

Reaction mechanism

$$A \xrightarrow{k_1} B$$

……

The rate law

$$r_1 = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1[A] = k_1(a-x)$$

First step

……

$$r_2 = \frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_{-1}[B] = k_{-1}x$$

Second step

……

$$\frac{d[B]}{dt} = \frac{dx}{dt} = r_1 + r_2 \longrightarrow \frac{d[B]}{dt} = \frac{dx}{dt} = \mathbf{k_1(a-x) - k_{-1}x}$$

$$\int_0^x \frac{1}{a-bx}\,dx =$$

$$= \frac{1}{-b}\ln(a-bx)$$

$$\frac{dx}{dt} = k_1(a-x) - k_{-1}x$$

$$\frac{dx}{dt} = k_1 a - k_1 x - k_{-1}x$$

$$\frac{dx}{dt} = k_1 a - (k_1 + k_{-1})x$$ ①

$$\int_0^x \frac{dx}{k_1 a - (k_1 + k_{-1})x} = \int_0^t dt$$

$$-\frac{1}{(k_1 + k_{-1})}\ln\left[k_1 a - (k_1 + k_{-1})x\right]_0^x = t\Big|_0^t$$

$$-\frac{1}{(k_1+k_{-1})}\ln\left[k_1a-(k_1+k_{-1})x\right]_0^x = t\Big|_0^t$$

$$-\frac{1}{(k_1+k_{-1})}\left\{\ln\left[k_1a-(k_1+k_{-1})x\right]-\ln k_1a\right\}=t$$

$$-\frac{1}{(k_1+k_{-1})}\ln\frac{k_1a-(k_1+k_{-1})x}{k_1a}=t$$

$$\frac{1}{(k_1+k_{-1})}\ln\frac{k_1a}{k_1a-(k_1+k_{-1})x}=t$$

$$\ln\frac{k_1a}{k_1a-(k_1+k_{-1})x}=(k_1+k_{-1})\,t$$ ②

At equilibrium

$$R_1 = R_2$$

the rate of the reaction at equilibrium equals zero

$$\frac{d(A+B)}{dt} = 0$$

the concentration of the product B at equilibrium equals Xe instead of X

From eqn.1

$$\frac{dx}{dt} = \mathbf{R_1 + R_2 = k_1a - (k_1 + k_{-1})x_e = 0}$$

$$k_1a = (k_1 + k_{-1})x_e$$ ③

from eqns. 2 and 3

By substitution of k1a from eqn. 3 into eqn.2

$$k_1a=(k_1+k_{-1})x_e \quad ③ \qquad \ln\frac{k_1a}{k_1a-(k_1+k_{-1})x}=(k_1+k_{-1})\,t \quad ②$$

$$\ln\frac{\cancel{(k_1+k_{-1})}x_e}{\cancel{(k_1+k_{-1})}x_e-\cancel{(k_1+k_{-1})}x}=(k_1+k_{-1})\,t$$

$$\ln\frac{x_e}{x_e-x}=(k_1+k_{-1})\,t \quad ④$$

What the slope for equation 4 ? k_1+k_{-1}

What is the absolute value of each constant?

Cannot calculated from the slope of eqn. 4

As follows

By substitution of k_1+k_{-1} from eqn. 3 into eqn. 4

$$k_1 a = (k_1 + k_{-1}) x_e \quad ③ \qquad \frac{k_1 a}{x_e} = (k_1 + k_{-1})$$

$$\ln \frac{x_e}{x_e - x} = (k_1 + k_{-1})\, t \quad ④$$

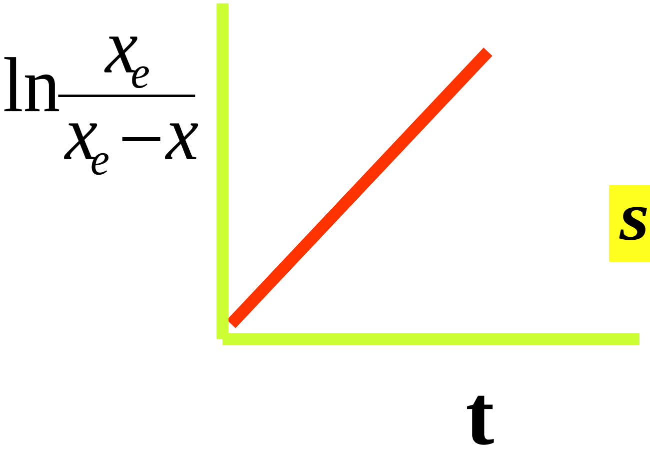
$$\ln \frac{x_e}{x_e - x} = \frac{k_1 a}{x_e} t \quad ⑤$$

The slope of eqn. 5 is $\frac{k_1 a}{x_e}$

where the absolute values of k_1 and k_{-1} can be calculated as follows

$$\ln\frac{x_e}{x_e - x} = (k_1 + k_{-1})\,t \quad ④$$

$$\ln\frac{x_e}{x_e - x} = \frac{k_1 a}{x_e}\,t \quad ⑤$$



$$slope = \frac{k_1 a}{x_e}$$

$$slope = (k_1 + k_{-1})$$

Case 2

If the experiment is started using impure A, of concentration a containing some of component B as impurities of concentration b

Time	A	B
0	a	b
t	$a - x$	$b + x$
عند الاتزان	$a - x_e$	$b + x_e$

$$A \xrightarrow{k_1} B$$ **Forward reaction**

$$B \xrightarrow{k_{-1}} A$$ **Reversible reaction**

Reaction mechanism $$A \xrightarrow{k_1} B$$

The rate law

$$r_1 = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1[A] = k_1(a-x)$$

First step

$$r_2 = \frac{d[A]}{dt} = -\frac{d[B]}{dt} = k_{-1}[B] = k_{-1}(b+x)$$

Second step

$$\frac{d[B]}{dt} = \frac{dx}{dt} = r_1 - r_2 \longrightarrow \frac{d[B]}{dt} = \frac{dx}{dt} = \boldsymbol{k_1(a-x) - k_{-1}(b+x)}$$

$$\frac{dx}{dt} = k_1(a - x) - k_{-1}(b + x)$$

$$\frac{dx}{dt} = k_1 a - k_1 x - k_{-1} b - k_{-1} x$$

$$\frac{dx}{dt} = k_1 a - k_{-1} b - (k_1 + k_{-1})x \qquad \textcircled{1}$$

$$\int_0^x \frac{dx}{k_1 a - k_{-1} b - (k_1 + k_{-1})x} = \int_0^t dt$$

$$-\frac{1}{(k_1 + k_{-1})} \ln\left[k_1 a - k_{-1} b - (k_1 + k_{-1})x\right] \Big|_0^x = t \Big|_0^t$$

$$-\frac{1}{\left(k_1+k_{-1}\right)}\ln\left[k_1a-k_{-1}b-\left(k_1+k_{-1}\right)x\right]\Big|_0^x=t\Big|_0^t$$

$$-\frac{1}{\left(k_1+k_{-1}\right)}\left\{\ln\left[k_1a-k_{-1}b-\left(k_1+k_{-1}\right)x\right]-\ln\left(k_1a-k_{-1}b\right)\right\}=t$$

$$-\frac{1}{\left(k_1+k_{-1}\right)}\ln\frac{k_1a-k_{-1}b-\left(k_1+k_{-1}\right)x}{k_1a-k_{-1}b}=t$$

$$\frac{1}{\left(k_1+k_{-1}\right)}\ln\frac{k_1a-k_{-1}b}{k_1a-k_{-1}b-\left(k_1+k_{-1}\right)x}=t$$

$$\ln\frac{k_1a-k_{-1}b}{k_1a-k_{-1}b-\left(k_1+k_{-1}\right)x}=\left(k_1+k_{-1}\right)t$$ ②

At equilibrium

$$R_1 = R_2$$

The net rate of the reaction equals zero

The concentration of B is X_e instead of X

From eqn. 1

$$\frac{dx}{dt} = R_1 + R_2 = k_1 a - k_{-1} b - (k_1 + k_{-1}) x_e = 0$$

$$k_1 a - k_{-1} b = (k_1 + k_{-1}) x_e \qquad ③$$

From eqns. 2 and 3

$$\boxed{k_1 a - k_{-1} b} = (k_1 + k_{-1}) x_e \quad ③$$

$$\ln \frac{k_1 a - k_{-1} b}{k_1 a - k_{-1} b - (k_1 + k_{-1}) x} = (k_1 + k_{-1})\, t \quad ②$$

$$\ln \frac{\cancel{(k_1 + k_{-1})} x_e}{\cancel{(k_1 + k_{-1})} x_e - \cancel{(k_1 + k_{-1})} x} = (k_1 + k_{-1})\, t$$

$$\ln \frac{x_e}{x_e - x} = (k_1 + k_{-1})\, t \quad ④$$

The slope is $k_1 + k_{-1}$

ثم

by substitution from eqn. 3 into eqn. 4 for k_1+k_{-1}

$$k_1a-k_{-1}b=(k_1+k_{-1})x_e \quad ③ \qquad \frac{k_1a-k_{-1}b}{x_e}=(k_1+k_{-1})$$

$$\ln\frac{x_e}{x_e-x}=(k_1+k_{-1})\,t \quad ④$$

$$\ln\frac{x_e}{x_e-x}=\frac{k_1a-k_{-1}b}{x_e}\,t \quad ⑤$$

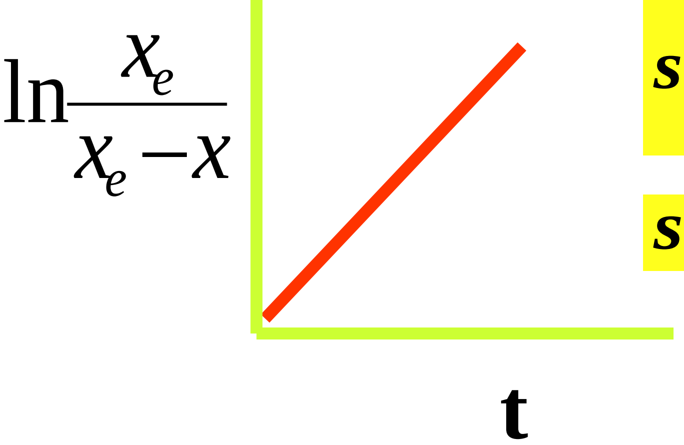
The slope of eqn. 5 is $\dfrac{k_1a-k_{-1}b}{x_e}$

then

$$\ln\frac{x_e}{x_e-x}=\left(k_1+k_{-1}\right)t$$ ④

$$\ln\frac{x_e}{x_e-x}=\frac{k_1a-k_{-1}b}{x_e}t$$ ⑤

One plot only



$$slope=\frac{k_1a-k_{-1}b}{x_e}$$

$$slope=\left(k_1+k_{-1}\right)$$

Kinetic Chemistry 5

Consecutive Reactions

$$A + B \xrightarrow{k_1} C \xrightarrow{k_2} D$$

$$A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B \xrightarrow{k_2} C$$

In this kind of reactions the product compound 1in the first reaction is converted in a second reaction to another product compound 2

Example

Thermal decomposition of Acetone

$$CH_3COCH_3 \rightarrow H_2C=C=O+CH_4$$

$$H_2C=C=O \rightarrow \frac{1}{2}C_2H_4+CC$$

Example

Decomposition of sodium hypochlorite

$$2NaClO \rightarrow NaCl+NaClO_2$$

$$NaClO_2+NaClO \rightarrow NaCl+NaClO_3$$

we will consider a simple case where the consecutive reactions are 1st order and are not reversible reactions

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C$$

Where k_1 and k_2 are rate constants for the 1st order reactions 1 and 2

Elementary reaction	$A \xrightarrow{k_1} B$	$B \xrightarrow{k_2} C$
Reaction rate	$r_1 = -\frac{d[A]}{dt} = \frac{d[B]}{dt} = k_1[A]$	$r_2 = -\frac{d[B]}{dt} = \frac{d[C]}{dt} = k_2[B]$
Rate of Disappearance of component A	$-\frac{d[A]}{dt} = r_1$	①
Rate of formation of component B	$\frac{d[B]}{dt} = r_1 + r_2$	②
Rate of formation of component C	$\frac{d[C]}{dt} = r_2$	③

We will consider the reaction starts with the reactant A is present only

Time	A	B	C
0	$[A]_0 = [A]_0$	$[B]_0 = 0$	$[C]_0 = 0$
t	$[A]_t = [A]$	$[B]_t = [B]$	$[C]_t = [C]$

Fist, we will find an equation that relates the change of [A] concentration with time. By integration of eqn. 1:

$$-\frac{d[A]}{dt} = k_1[A]$$ ①

$$-\int_{[A]_0}^{[A]} \frac{d[A]}{[A]} = k_1 \int_0^t dt$$

$$-\ln[A]\Big|_{[A]_0}^{[A]} = k_1 t\Big|_0^t$$

$$\ln[A] - \ln[A]_0 = -k_1 t$$

$$\ln\frac{[A]}{[A]_0} = -k_1 t$$

$$\cancel{e}^{\cancel{\ln}\frac{[A]}{[A]_0}} = e^{-k_1 t}$$

$$\longrightarrow \quad \therefore [A] = [A]_0 e^{-k_1 t}$$ ④

Second we will find an eqn. that relates the change in [B] concentration with time. By substitution for [A] from eqn. 4 into eqn. 2:

$$\frac{d[B]}{dt} = k_1[A] - k_2[B]$$ ②

$$[A] = [A]_0 e^{-k_1 t}$$ ④

$$\frac{d[B]}{dt} = k_1[A]_0 e^{-k_1 t} - k_2[B]$$ ⑤

$$\frac{d[B]}{dt} e^{k_2 t} = k_1[A]_0 e^{-k_1 t} e^{k_2 t} - k_2[B] e^{k_2 t}$$

On arrangement of the last eqn.

$$e^{k_2 t} \frac{d[B]}{dt} + [B]\, k_2 e^{k_2 t} = k_1[A]_0 e^{(k_2 - k_1)t}$$

$$e^{k_2 t}\frac{d}{dt}[B] + [B]k_2 e^{k_2 t} = k_1[A]_0 e^{(k_2-k_1)t}$$

(مشتقة الأولى × الثانية) + (مشتقة الثانية × الأولى)

= الاشتقاق (الأولى × الثانية)

$$\frac{d}{dt}\left(e^{k_2 t}[B]\right) = k_1[A]_0 e^{(k_2-k_1)t}$$

$$e^{k_2 t}d[B] = k_1[A]_0 e^{(k_2-k_1)t}dt$$

$$e^{k_2 t}\int_0^{[B]} d[B] = k_1[A]_0\int_0^{t} e^{(k_2-k_1)t}dt$$

$$e^{k_2 t}\int_0^{[B]} d[B] = k_1[A]_0 \int_O^t e^{(k_2-k_1)t}\,dt$$

$$e^{k_2 t}[B]_0^{[B]} = \frac{k_1[A]_0}{(k_2-k_1)} e^{(k_2-k_1)t}\Big|_0^t$$

$$e^{k_2 t}([B]-0) = \frac{k_1[A]_0}{(k_2-k_1)}\left(e^{(k_2-k_1)t} - e^0\right)$$

$$e^{k_2 t}[B] = \frac{k_1[A]_0}{(k_2-k_1)}\left(e^{(k_2-k_1)t} - 1\right)$$

$$e^{k_2t}[B]=\frac{k_1[A]_0}{(k_2-k_1)}\left(e^{(k_2-k_1)t}-1\right)$$

وبضرب المعادلة السابقة في الحد e^{-k_2t}

$$\cancel{e^{-k_2t}}\,\cancel{e^{k_2t}}[B]=\frac{k_1[A]_0}{(k_2-k_1)}\left(\cancel{e^{-k_2t}}\,e^{(\cancel{k_2}-k_1)t}-e^{-k_2t}\right)$$

$$\boxed{\therefore [B]=\frac{k_1[A]_0}{(k_2-k_1)}\left(e^{-k_1t}-e^{-k_2t}\right)}$$ ⑥

Second we will find an eqn. that relates the change in [C] concentration with time. By substitution for [B] from eqn. 6 into eqn. 3:

$$\frac{d[C]}{dt} = k_2[B] \tag{3}$$

$$[B] = \frac{k_1[A]_0}{(k_2 - k_1)}\left(e^{-k_1 t} - e^{-k_2 t}\right) \tag{6}$$

$$\frac{d[C]}{dt} = k_2 \frac{k_1[A]_0}{(k_2 - k_1)}\left(e^{-k_1 t} - e^{-k_2 t}\right)$$

وبترتيب المعادلة السابقة وإجراء التكامل

$$\int_0^C d[C] = k_2 \frac{k_1[A]_0}{(k_2 - k_1)}\left(\int_0^t e^{-k_1 t} dt - \int_0^t e^{-k_2 t} dt\right)$$

$$[C]\Big|_0^{[C]} = k_2 \frac{k_1[A]_0}{(k_2 - k_1)}\left\{-\frac{1}{k_1} e^{-k_1 t}\Big|_0^t - \left(-\frac{1}{k_2} e^{-k_2 t}\Big|_0^t\right)\right\}$$

$$[C]\Big|_0^{[C]}=[A]_0\frac{k_1k_2}{(k_2-k_1)}\left\{-\frac{1}{k_1}e^{-k_1t}\Big|_0^t-\left(-\frac{1}{k_2}e^{-k_2t}\Big|_0^t\right)\right\}$$

$$[C]-0=[A]_0\frac{k_1k_2}{(k_2-k_1)}\left\{-\frac{1}{k_1}\left(e^{-k_1t}-e^0\right)+\left(\frac{1}{k_2}\left(e^{-k_2t}-e^0\right)\right)\right\}$$

$$[C]=[A]_0\frac{k_1k_2}{(k_2-k_1)}\left\{\frac{1}{k_1}\left(1-e^{-k_1t}\right)+\left(\frac{1}{k_2}\left(e^{-k_2t}-1\right)\right)\right\}$$

$$[C]=[A]_0\left\{\frac{\cancel{k_1}k_2}{(k_2-k_1)}\frac{1}{\cancel{k_1}}\left(1-e^{-k_1t}\right)+\left(\frac{k_1\cancel{k_2}}{(k_2-k_1)}\frac{1}{\cancel{k_2}}\left(e^{-k_2t}-1\right)\right)\right\}$$

$$[C]=[A]_0\left\{\frac{k_2}{(k_2-k_1)}\left(1-e^{-k_1t}\right)+\left(\frac{k_1}{(k_2-k_1)}\left(e^{-k_2t}-1\right)\right)\right\}$$

$$[C]=[A]_0\left\{\frac{k_2}{(k_2-k_1)}-\frac{k_2}{(k_2-k_1)}e^{-k_1t}+\frac{k_1}{(k_2-k_1)}e^{-k_2t}-\frac{k_1}{(k_2-k_1)}\right\}$$

$$\frac{k_2}{(k_2-k_1)}-\frac{k_1}{(k_2-k_1)}=\frac{k_2-k_1}{(k_2-k_1)}=1$$

$$\therefore [C]=[A]_0\left\{1-\frac{k_2}{(k_2-k_1)}e^{-k_1t}+\frac{k_1}{(k_2-k_1)}e^{-k_2t}\right\}$$

Results

1- the concentration of component A decreases while that of product C increases with time

2- the concentration of component [B] depends on the ratio of the rate constants k_1 and k_2.

$$[B]=\frac{k_1[A]_0}{(k_2-k_1)}\left(e^{-k_1 t}-e^{-k_2 t}\right) \tag{6}$$

$$k_1 \rangle\rangle k_2$$

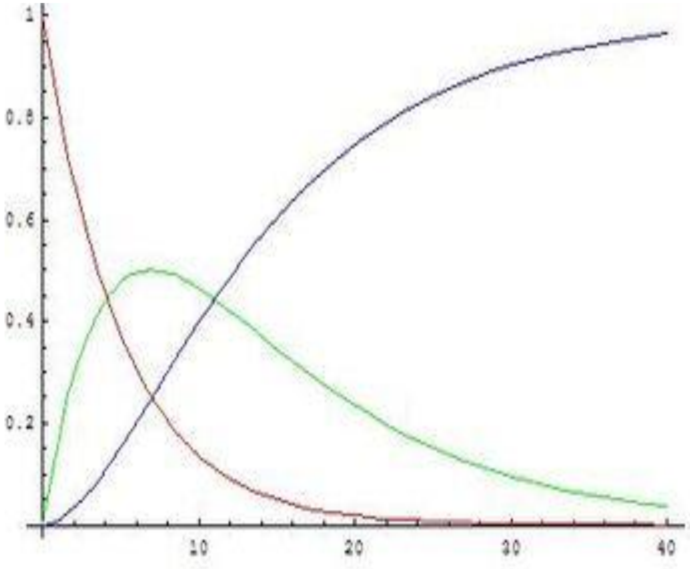
$$[B]=\cancel{-}\frac{\cancel{k_1}[A]_0}{\cancel{k_1}}\left(\cancel{-}e^{-k_2 t}\right)$$

$$k_1 \langle\langle k_2$$

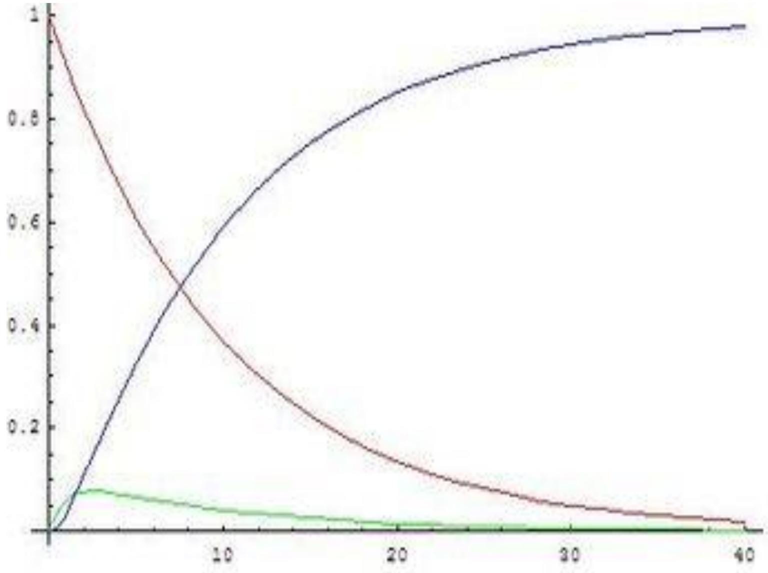
$$[B]=\frac{k_1}{k_2}[A]_0 e^{-k_1 t}$$

$k_1 \rangle\rangle k_2$

$k_1 \langle\langle k_2$



Concentration vs. time. Concentration of intermediate in green, product in blue and substrate in red
(k_2 / k1 = 0.5)

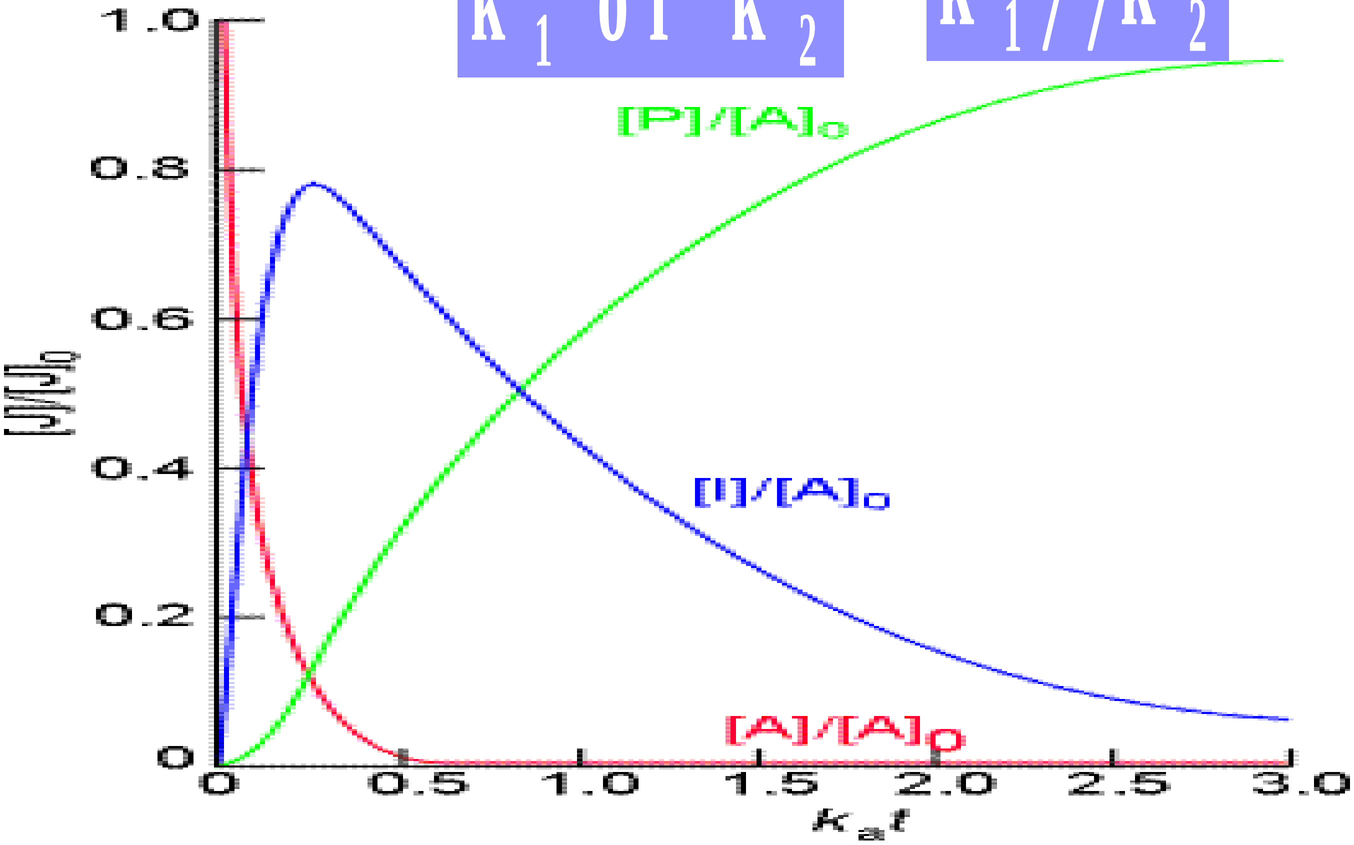


Concentration vs. time. Concentration of intermediate in green, product in blue and substrate in red
(k_2 / k_1 = 10)

ايهما اكبر

k_1 or k_2

$k_1 \rangle\rangle k_2$



The concentrations of A, I, and P in the consecutive reaction scheme A -> I -> P. The curves are plots with *ka* = 10*kb*

Example

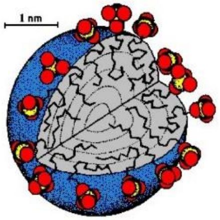
For consecutive reaction from first order, the $k_1=0.3\ s^{-1}$ and $k_2=0.2\ s^{-1}$, the time in seconds that the intermediate becomes at the highest concentration is:

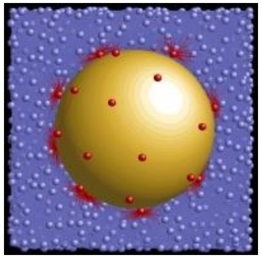
A. 1.176
B. 0.244
C. 0.405
D. 1.761
E. 4.05
F. 2.708

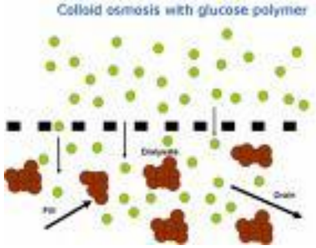
The percentage of intermediate in the same time is:

A. 92.21 %
B. 66.67 %
C. 3.375 %
D. 44.4 %
E. 2.25 %
F. 29.54 %

Introduction to Colloid & Surface Chemistry



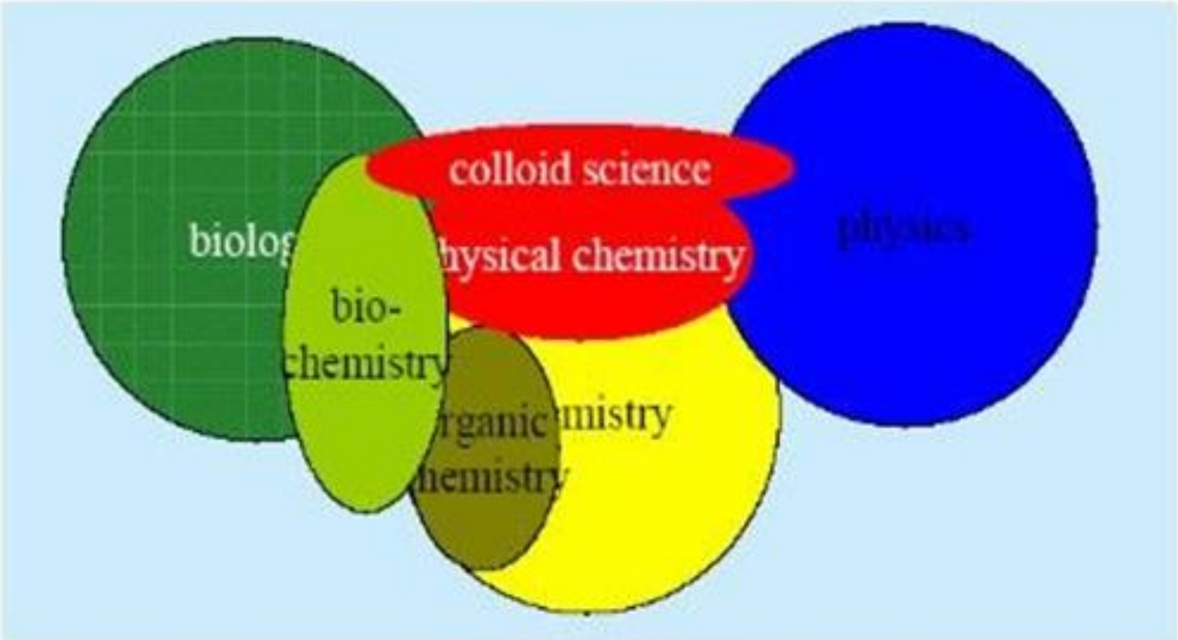




Part 1
Colloidal state

Colloid science is interdisciplinary

1. partly physical chemistry
   - it is not the chemical composition which is important
   - the state is independent of the composition
2. partly physics
   - the physical properties are of great importance
   - basic law of physics can be applied
3. partly biology
   - biological materials are colloids
   - the mechanisms of living systems are related to colloid- and interfacial chemistry



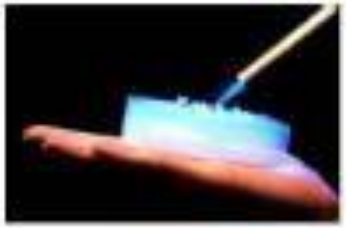
Examples of colloidal systems from daily life


Foams


Milk


Fog, smoke


Detergents


Aerogel


Blood


Paints


Cosmetics

Background (Old and new conceptions of colloids)

- In 1861, Thomas Graham divided soluble substances into two classes according to diffuse into water across a permeable membrane:
- He observed that crystalline substances such as sugar, urea, and sodium chloride passed through the membrane, while others like glue, gelatin and gum did not.

Thomas Graham

- He called the former **crystalloids** and the latter **colloids** (Greek, kolla = glue). Graham thought that the difference in the behavior of 'crystalloids' and 'colloids' was due to the particle size.

Crystalline

Crystalloids:

Diffuse rapidly across vegetable or animal membranes such as salt, sugar and urea.

amorphous

Colloids:

Exhibit little or no tendency to diffuse across vegetable or animal membranes such as gelatin, starch and gum.

Greek: *kola*= glue and *eiods*= like

Background (Old and new conceptions of colloids)

- According to Graham NaCl is crystalloid but it has been obtained in the colloidal state in benzene.
- Soap behaves as colloid in water and as crystalloid in alchohol

Later it was realized that (New conception):

►The difference in the rate of diffusion between crystalloids and colloids is due to the difference in the particle size

►Any substance, regardless of its nature, could be converted into a colloid by subdividing it into particles of colloidal size.

►We should speak of the colloidal state of matter as we speak of the gaseous, liquid or solid state of matter rather than to call a particular material as colloid or crystalloid

Nature of colloidal solutions (What are colloids)?

Sugar + water

True solution

1- 10 A^{o}

Sand + water

Suspension

>1000 A^{o}

Starch + water

Colloidal solution

10- 1000 A^{o}

Nature of colloidal solutions (What are colloids) ?

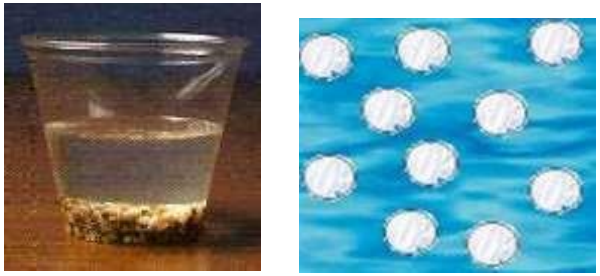
In **a true solution** as sugar or salt in water, the solute particles are dispersed in the solvent as single molecules with diameter less than 1 nm

Sugar + water (true solution(

< **1 nm**

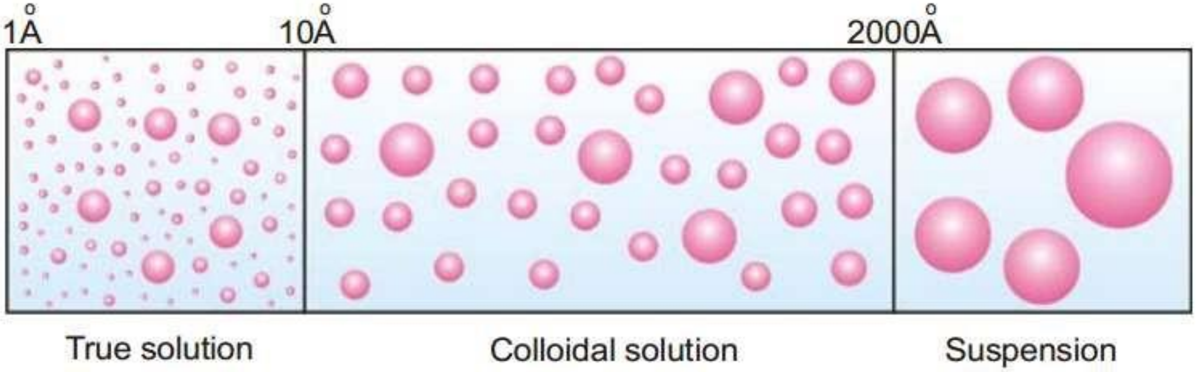
On the other hand, if **a suspension** as sand stirred into water, the dispersed particles are aggregates of millions of molecules. The diameter of these particles is of the order 1 000،Å or more

Sand + water (suspension(



<1 000Å

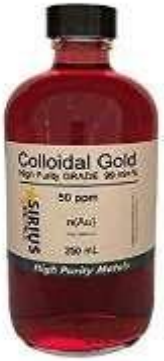
The colloidal solutions or colloidal dispersions are intermediate between true solutions and suspensions. In other words, the diameter of the dispersed particles in a colloidal dispersion is more than that of the solute particles in a true solution and smaller than that of a suspension.



Examples of colloidal solutions

Ink

Paint



Colloidal Gold

Nature of colloidal solutions (What are colloids) ?

True solution	**Suspension**	**Colloidal solution**
1- 10 A°	>1000 A°	10- 1000 A°
Transparent to light	Not transparent to light	Not transparent to light

Nature of colloidal solutions (What are colloids) ?

True solution	Suspension	Colloidal solution
1- 10 Aº	>1000 Aº	10- 1000 Aº
Transparent to light	Not transparent to light	Not transparent to light
Can not be seen by the naked eyes or even under a microscope	Can be seen by the naked eye	Can not be seen by the naked eye or with ordinary microscope

Nature of colloidal solutions (What are colloids) ?

True solution	Suspension	Colloidal solution
1- 10 Aº	>1000 Aº	10- 1000 Aº
Transparent to light	Not transparent to light	Not transparent to light
Can not be seen by the naked eyes or even under a microscope	Can be seen by the naked eye	Can not be seen by the naked eye or with ordinary microscope
Not influenced by the gravitational pull and remain suspended in the solvent all the time	They are influenced by the gravitational pull and settle down automatically on standing	Not influenced by the gravitational pull and remain suspended in the solvent all time

Nature of colloidal solutions (What are colloids) ?

True solution	Suspension	Colloidal solution
1- 10 A°	>1000 A°	10- 1000 A°
Transparent to light	Not transparent to light	Not transparent to light
Can not be seen by the naked eyes or even under a microscope	Can be seen by the naked eye	Can not be seen by the naked eye or with ordinary microscope
Not influenced by the gravitational pull and remain suspended in the solvent all the time	They are influenced by the gravitational pull and settle down automatically on standing	Not influenced by the gravitational pull and remain suspended in the solvent all time
Pass through an ordinary filter paper	Retained by an ordinary filter paper	Pass through an ordinary filter paper

Colloidal particles under microscope

Light microscope

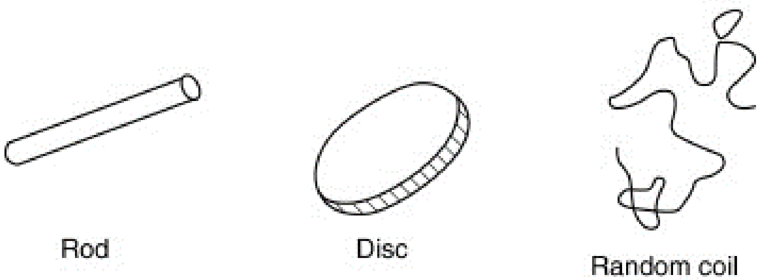
Ultra- microscope

Electron microscope

The colloidal particles are smaller than the wavelength of the visible light. Thus, they are unable to reflect light and hence cannot be seen by ordinary microscope

Note that

The colloidal particles are not necessarily corpuscular in shape. In fact, these may be rod-like, disc-like, thin films, or long filaments. For matter in the form of corpuscles, the diameter gives a measure of the particle size .



However, in other cases one of the dimensions (length, width and thickness) has to be in the colloidal range for the material to be classed as colloidal .

Thus in a broader context we can say:

“A system with at least one dimension (length, width, or thickness) of the dispersed particles in the range 10 Å to 1 000‹Å, is classed as a colloidal dispersion”

Classification of colloids

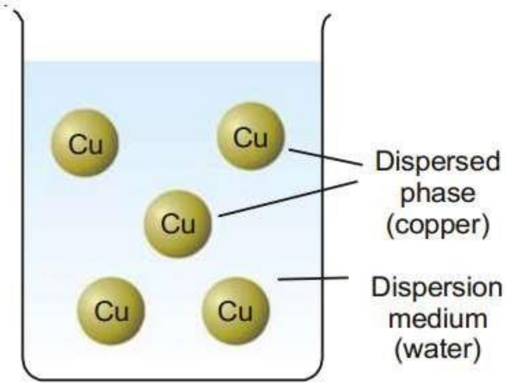
Classification is based on following criteria:

1. Physical state of dispersed phase and dispersion medium.
2. Nature of interaction between dispersed phase and dispersion medium.
3. Types of particles of the dispersed phase.

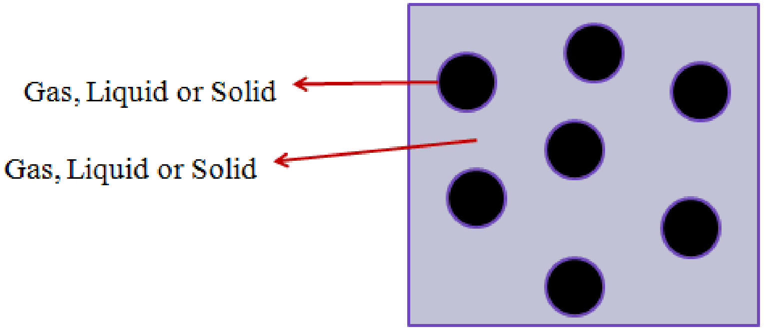
Classification based on physical state of dispersed phase and dispersion medium

Any colloidal system is made of two phases. The substance distributed as the colloidal particles is called the **Dispersed Phase** and the second continuous phase in which the colloidal particles are dispersed is called the **Dispersion Medium.**

For example, for a colloidal solution of copper in water, copper particles constitute the dispersed phase and water the dispersion medium.



Either the dispersed phase or the dispersion medium can be a gas, liquid or solid



A colloidal dispersion of one gas in another is not possible since the two gases would give a homogeneous molecular mixture. So that, there are **Eight** possible types of colloidal systems

Dispersed phase	Gas	Gas	Gas	Liquid	Liquid	Liquid	Solid	Solid	Solid
Dispersion medium	Gas	Liquid	Solid	Gas	Liquid	Solid	Gas	Liquid	Solid

1 Foam

Dispersed phase: Gas **Dispersion medium:** Liquid

Examples

Whipped cream

Shaving cream

Soda water

Soap Solution

2 Solid Foam

Dispersed phase: Gas **Dispersion medium:** Solid

Examples

Cork stoppers

Pumice stone

Foam rubber

Marshmallow

3 Aerosol

Dispersed phase: Liquid

Dispersion medium: Gas

Examples


Cloud


Aerosol spray


Mist


Fog

4 Emulsion

Dispersed phase: Liquid

Dispersion medium: Liquid

Examples


Milk

Hair cream


Mayonnaise


Emulsified water

5 Solid Emulsion (Gel)

Dispersed phase: Liquid

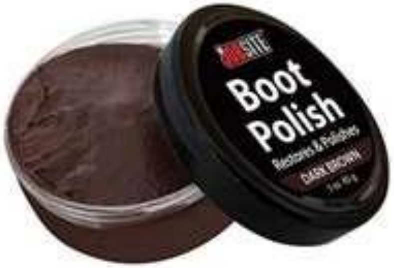
Dispersion medium: Solid

Examples

Butter

Cheese

Jelly



Boot Polish

6 Smoke

Dispersed phase: Solid

Dispersion medium: Gas

Examples

7 Sol (Colloidal Solutions)

Dispersed phase: Solid
Dispersion medium: Liquid

Examples

Ink

Paint

Colloidal Gold

8 Solid Sol

Dispersed phase: Solid

Dispersion medium: Solid

Examples

Colored Glass

Metal Alloys

Classification of colloids

Classification is based on following criteria:

1. Physical state of dispersed phase and dispersion medium.
2. Nature of interaction between dispersed phase and dispersion medium.
3. Types of particles of the dispersed phase.

Classification based on nature of interaction

Solid dispersed in liquid (Sols(

Lyophilic (solvent-loving) **and Lyophobic** (solvent-hating) **sols**

Lyophilic sols: are those in which the dispersed phase exhibits a definite affinity for the medium or the solvent.

The examples of Lyophilic sols are dispersions of starch, gum, and protein in water.

Lyophobic sols: are those in which the dispersed phase has no attraction for the medium or the solvent.

The examples of Lyophobic sols are dispersion of gold, iron (III) hydroxide and sulphur in water.

Solid dispersed in liquid (Sols(

Lyophilic (solvent-loving) **and Lyophobic** (solvent-hating) **sols**

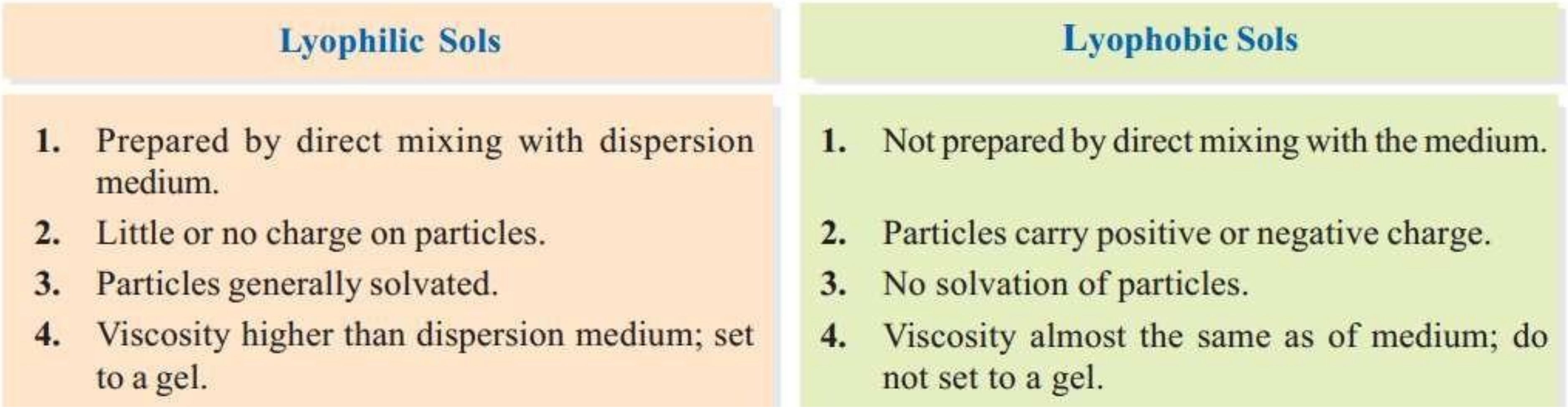
- The affinity or attraction of the sol particles for the medium, in a lyophilic sol, is due to hydrogen bonding with water .

- If the dispersed phase is a protein (as in egg) hydrogen bonding takes place between water molecules and the amino groups (–NH–, $–NH_2$) of the protein molecule.

- In a dispersion of starch in water, hydrogen bonding occurs between water molecules and the – OH groups of the starch molecule.

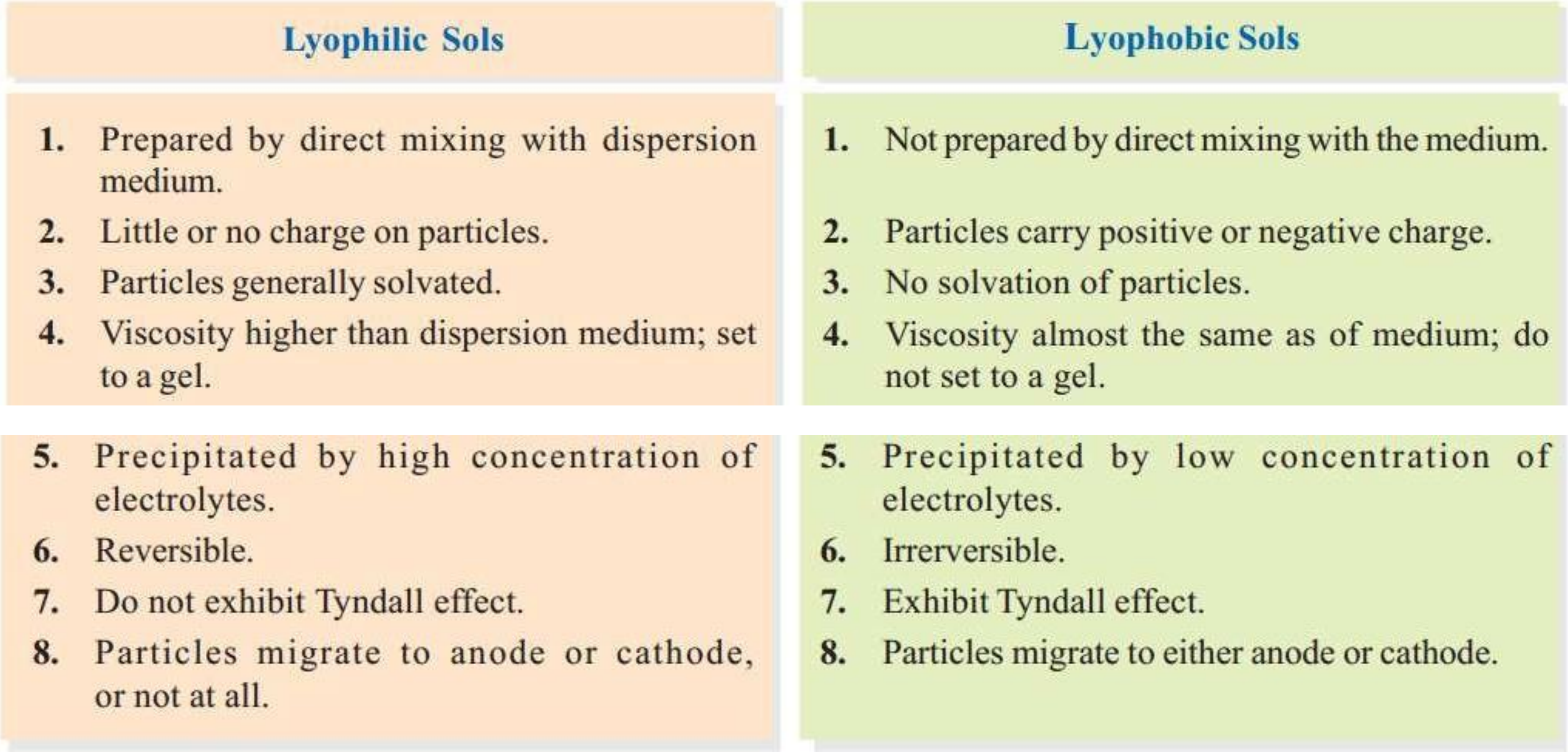
- There are no similar forces of attraction when sulphur or gold is dispersed in water.

Differences between lyophilic and lyophobic sols



Lyophilic Sols	Lyophobic Sols
1. Prepared by direct mixing with dispersion medium.	1. Not prepared by direct mixing with the medium.
2. Little or no charge on particles.	2. Particles carry positive or negative charge.
3. Particles generally solvated.	3. No solvation of particles.
4. Viscosity higher than dispersion medium; set to a gel.	4. Viscosity almost the same as of medium; do not set to a gel.

Differences between lyophilic and lyophobic sols



Lyophilic Sols	Lyophobic Sols
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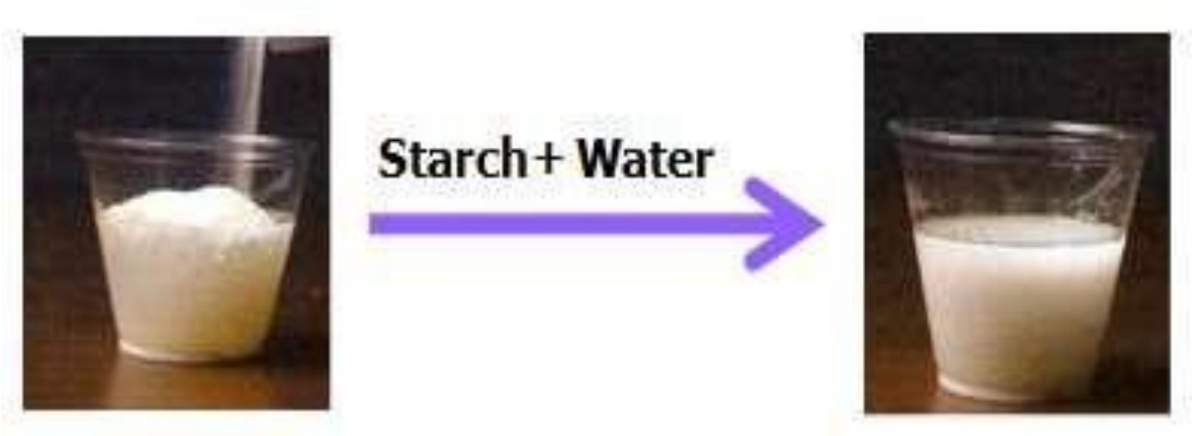
2. Little or no charge on particles.	2. Particles carry positive or negative charge.
3. Particles generally solvated.	3. No solvation of particles.
4. Viscosity higher than dispersion medium; set to a gel.	4. Viscosity almost the same as of medium; do not set to a gel.
5. Precipitated by high concentration of electrolytes.	5. Precipitated by low concentration of electrolytes.
6. Reversible.	6. Irrerversible.
7. Do not exhibit Tyndall effect.	7. Exhibit Tyndall effect.
8. Particles migrate to anode or cathode, or not at all.	8. Particles migrate to either anode or cathode.

Preparation of sols

Lyophilic sols may be prepared by simply warming the solid with the liquid dispersion medium e.g., starch with water.



Preparation of sols

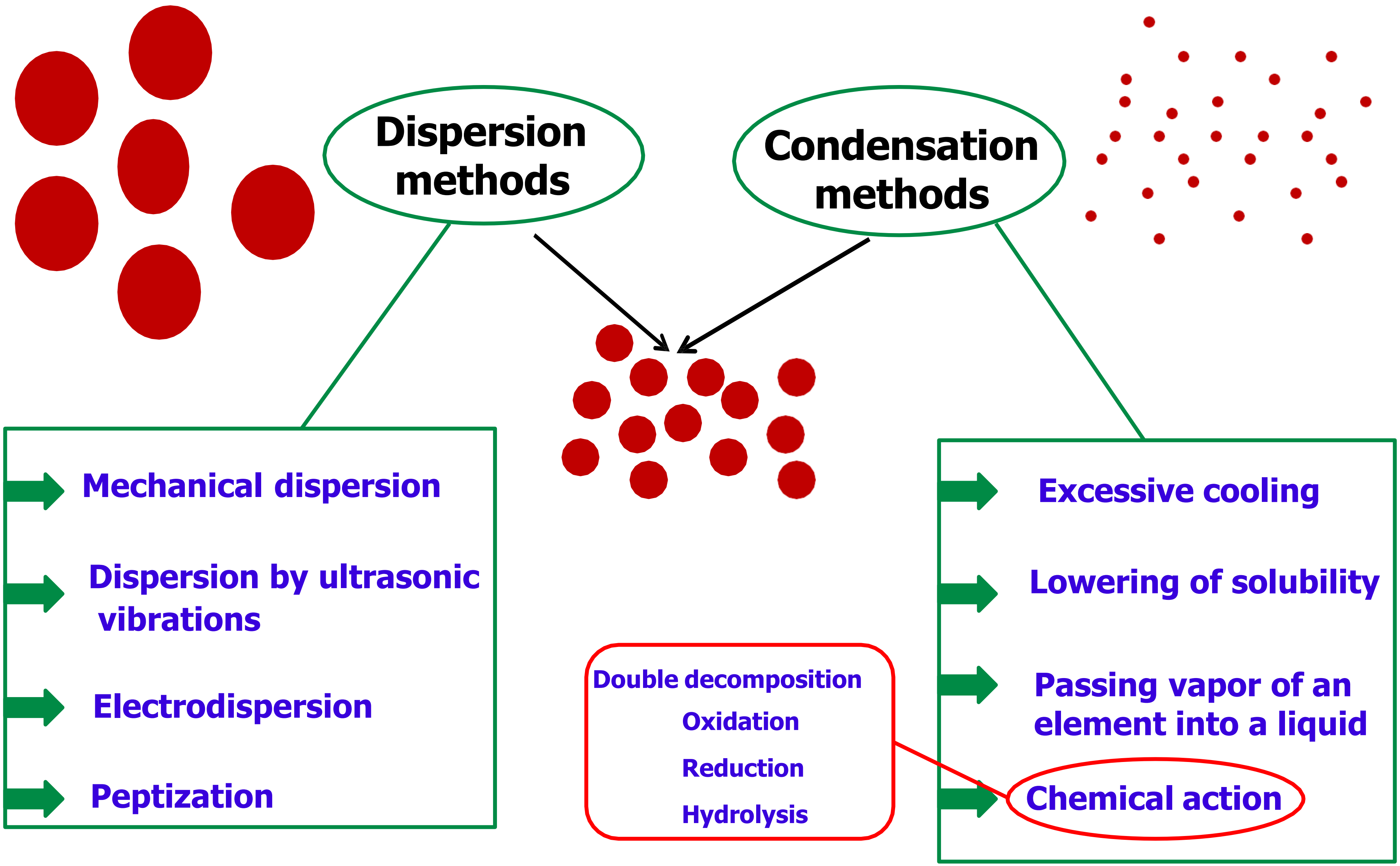
Lyophobic sols

Have to be prepared by special methods. These methods fall into two categories :

Dispersion Methods: in which larger macro-sized particles are broken down to colloidal size.

Aggregation (Condensation) Methods: in which colloidal size particles are built up by aggregating single ions or molecules of true solution

Preparation of colloidal solutions



Dispersion methods

- Mechanical dispersion
- Dispersion by ultrasonic vibrations
- Electrodispersion
- Peptization

Condensation methods

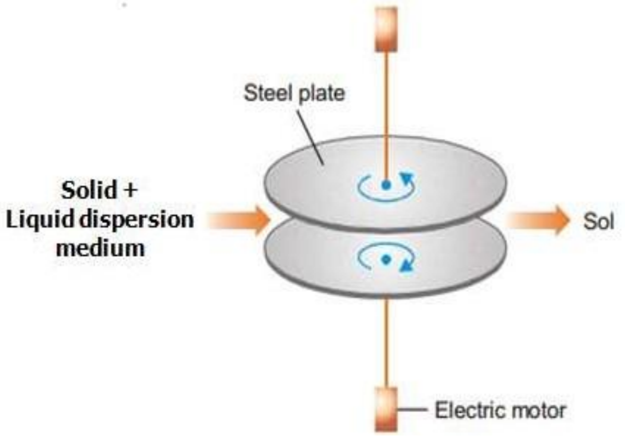
- Excessive cooling
- Lowering of solubility
- Passing vapor of an element into a liquid
- Chemical action

Double decomposition
Oxidation
Reduction
Hydrolysis

A- Dispersion Methods

-1Mechanical dispersion using colloid mill

- The solid along with the liquid dispersion medium is fed into a Colloid disk mill.
- The mill consists of two steel plates nearly touching each other and rotating in opposite directions with high speed.
- The solid particles are ground down to colloidal size and are then dispersed in the liquid to give the sol.
- Colloidal graphite and printing inks are made by this method.

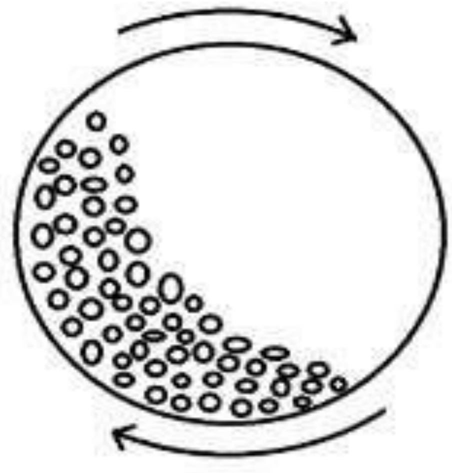


Disk mill

A- Dispersion Methods

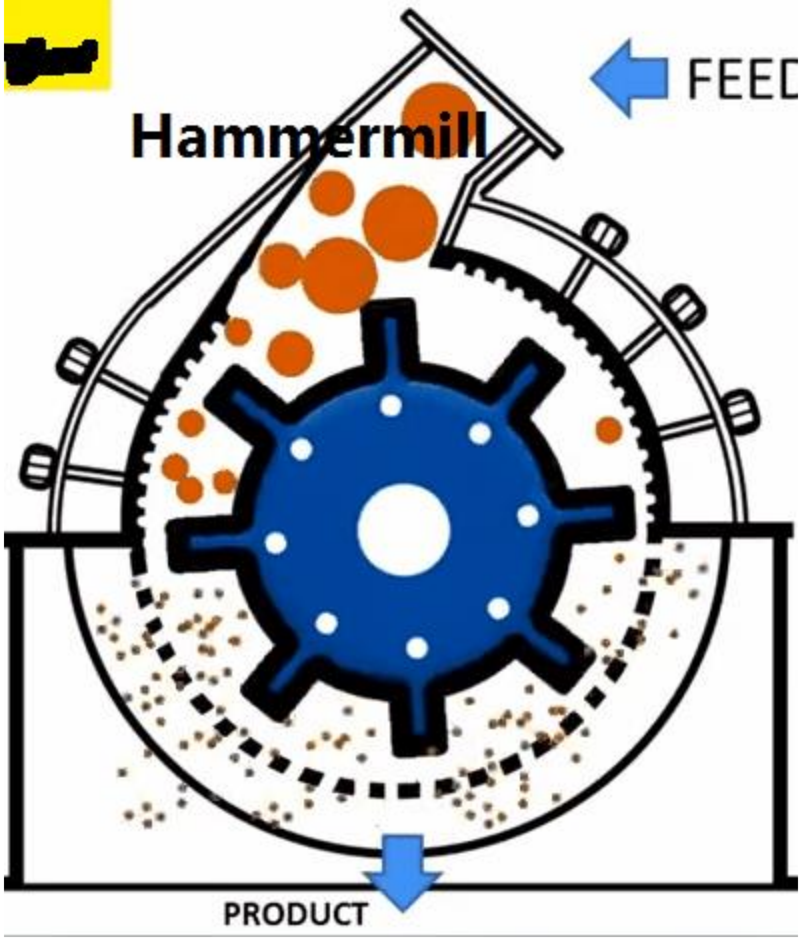
-1Mechanical dispersion using colloid mill

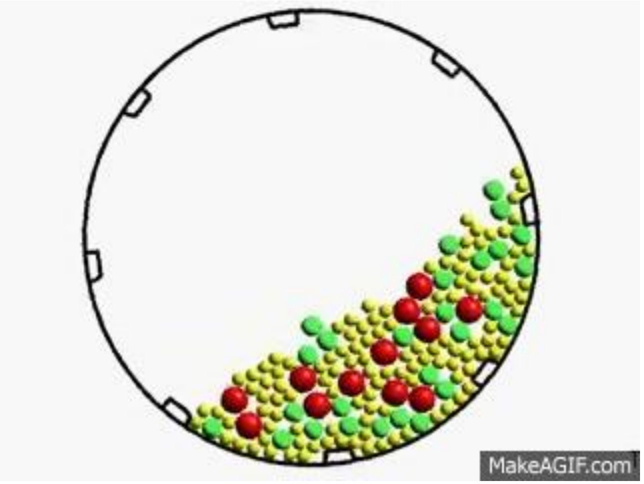
- A colloidal ball mill can also employed to obtain a colloidal solution from suspension .
- Due to the high speed rotation of the mill the coarse particles roll over one another to form fine particles of the colloidal size.



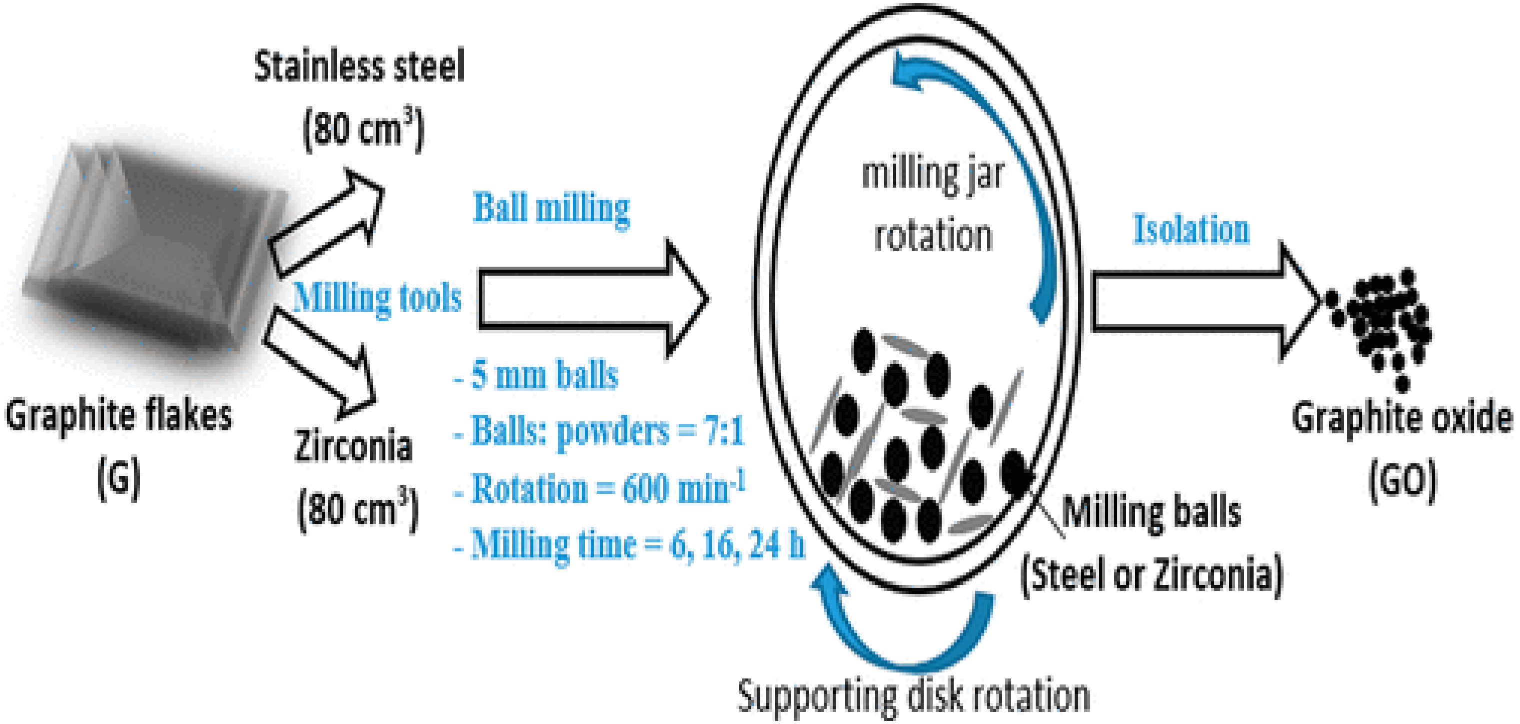
Ball mill

1- Mechanical dispersion using colloid mill





-1Mechanical dispersion using colloid mill



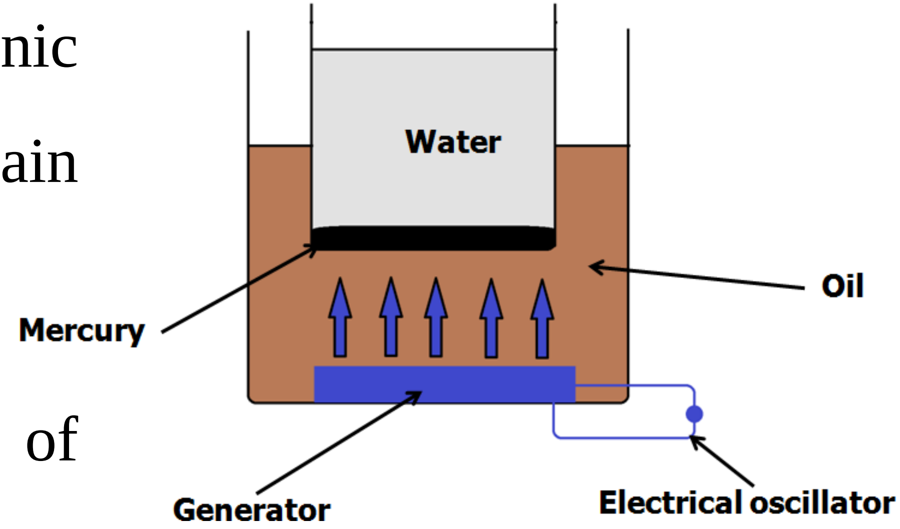
Ref: Sustainable Synthesis of High-Surface-Area Graphite Oxide via Dry Ball Milling, Alaa El Din Mahmoud, Achim Stolle, and Michael Stelter, *ACS Sustainable Chem. Eng.* 2018, 6, 5, 6358–6369.

-2Dispersion by ultrasonic vibrations

- In this case, the transformation of coarse particles to the colloidal size is carried out using the ultrasonic vibrations produced by a certain generator.

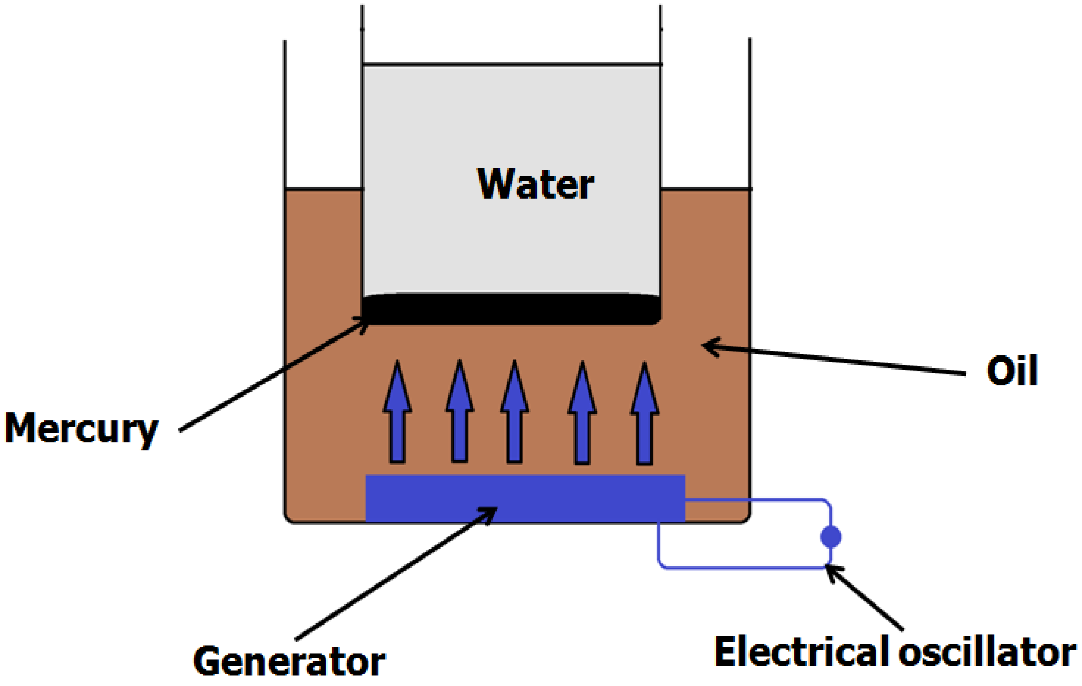
- The figure shows the formation of colloidal solution of mercury in water.

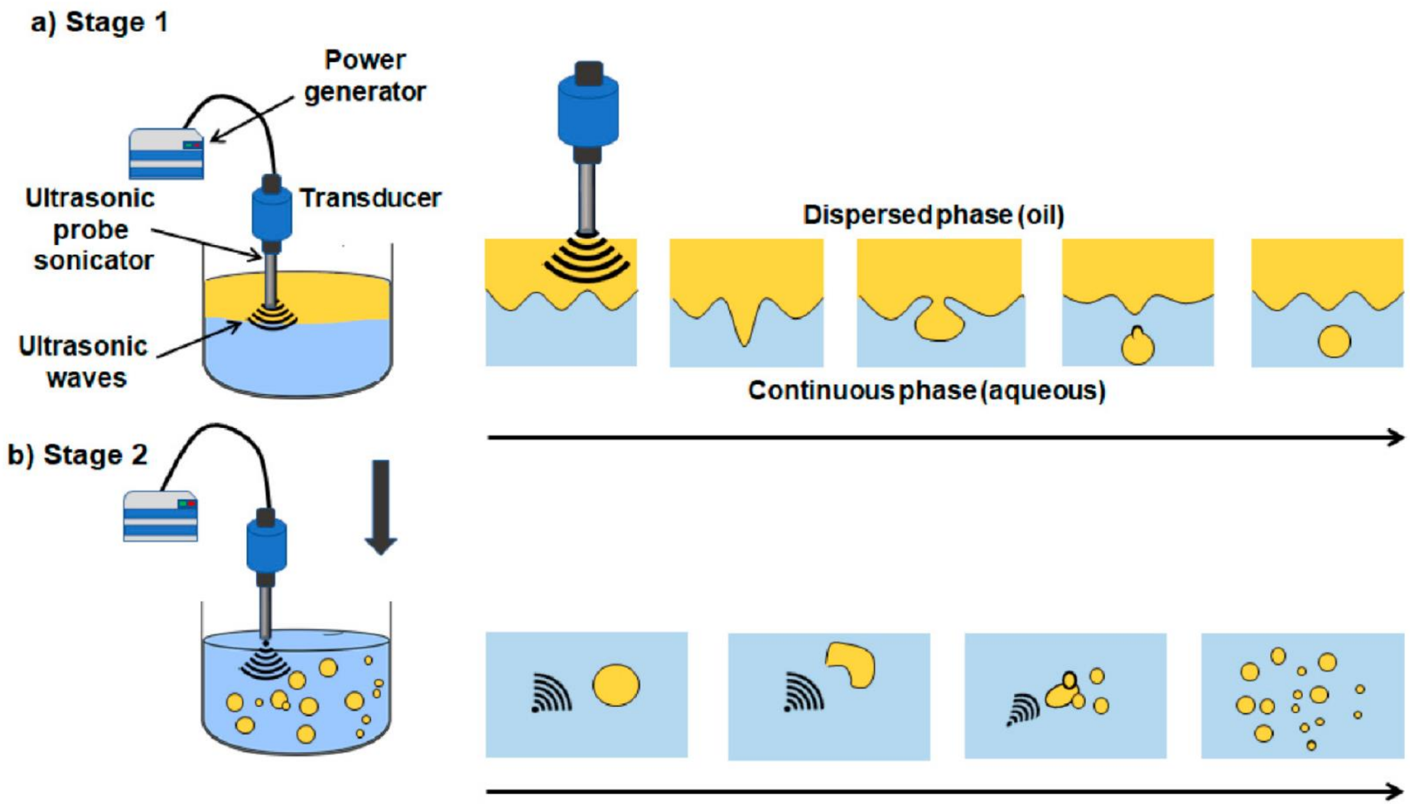
- Ultrasonic vibrations spread through the oil and hit the vessel having mercury under water .



-2Dispersion by ultrasonic vibrations

- The ultrasonic vibrations travels through the walls of the mercury container and produce clouds of mercury which form the mercury sol.





Schematic representation of ultrasonic emulsification.

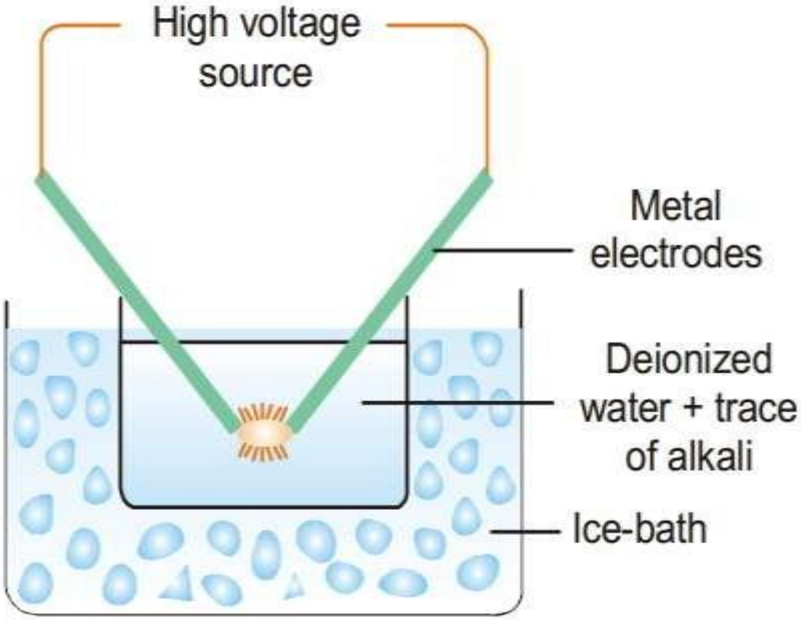
(a) The shear forces generated during acoustic cavitation near the interface between the aqueous phase and oil phase promote the eruption of large oil drops (dispersed phase) in the continuous aqueous phase.

(b) The oil droplets formed in the first stage are reduced to smaller droplets as a consequence of the shock waves generated during cavitation

(adapted from Perdih et al., 2019 and Plüisch and Wittemann, 2016).

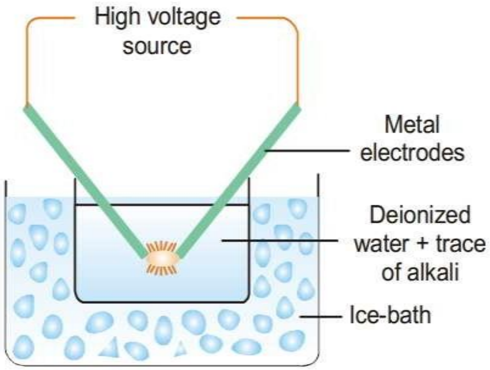
-3Bredig's Arc Method (electrical disintegration)

- It is used for preparing hydrosols of metals e.g., silver, gold and platinum .
- An arc is struck between the two metal electrodes held close together in de- ionized water with trace of alkali .
- The water is kept cold by immersing the container in ice/water bath.
- The intense heat of the spark across the electrodes vaporizes some of the metal and the vapor condenses under water.

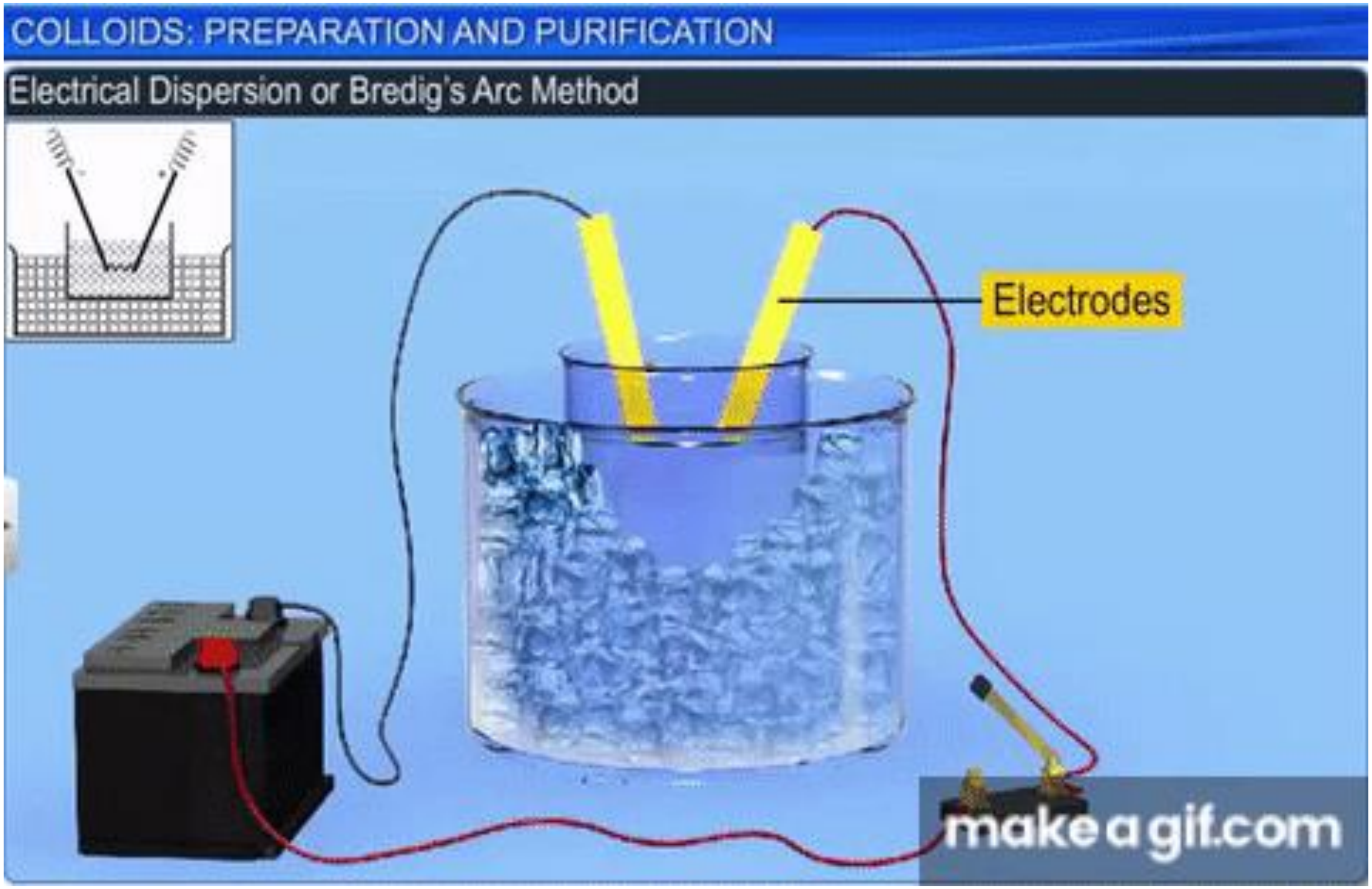


-3Bredig's Arc Method

- Thus the atoms of the metal present in the vapour aggregate to form colloidal particles in water .
- Since the metal has been ultimately converted into sol particles (via metal vapour), this method has been treated as of dispersion method also.
- Non-metal sols can be made by suspending coarse particles of the substance in the dispersion medium and striking an arc between iron electrodes.
- This method is not suitable when the dispersion medium is an organic liquid as considerable charring occurs.



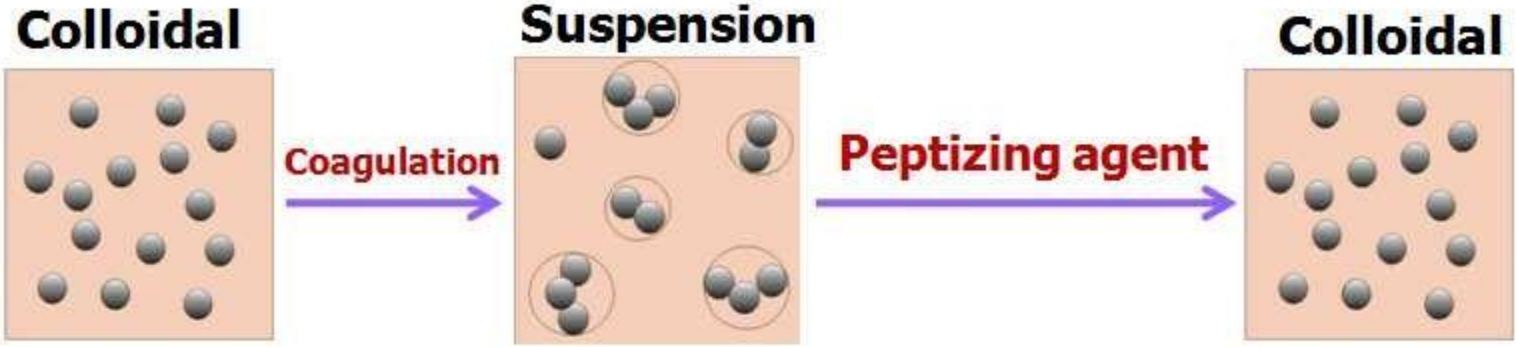
3- Bredig's Arc Method



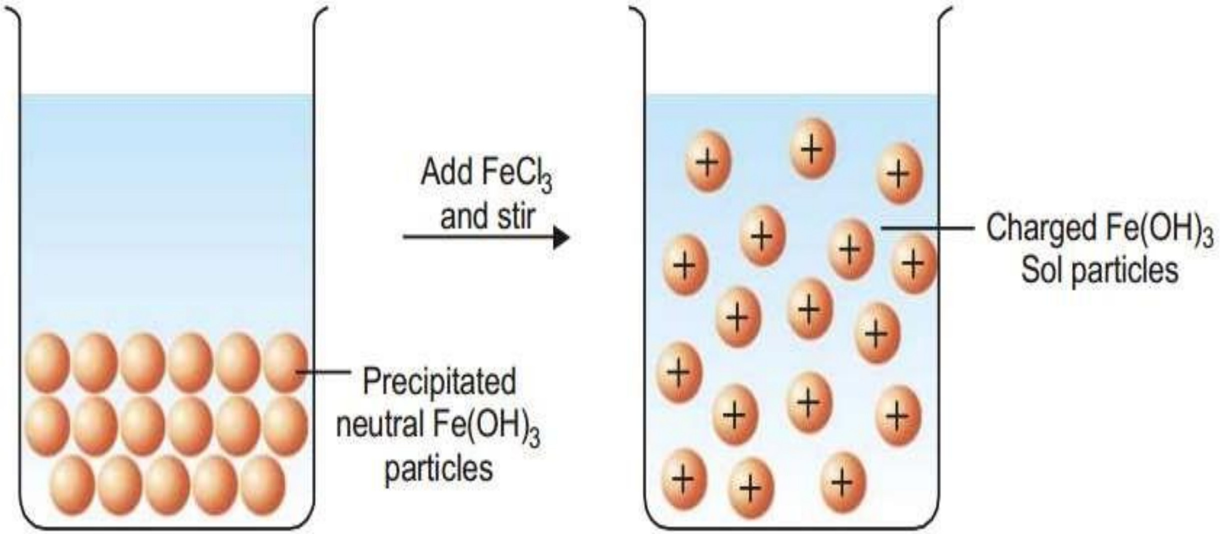
-4Peptization

- Some freshly precipitated ionic solids are dispersed into colloidal solution in water by the addition of small quantities of electrolytes, particularly those containing a common ion .

- The precipitate particles adsorbs the common ions to be electrically charged particles, then split from each other to form colloidal solution.



Sol of ferric hydroxide is obtained by stirring fresh precipitate of ferric hydroxide with a small amount of $FeCl_3$

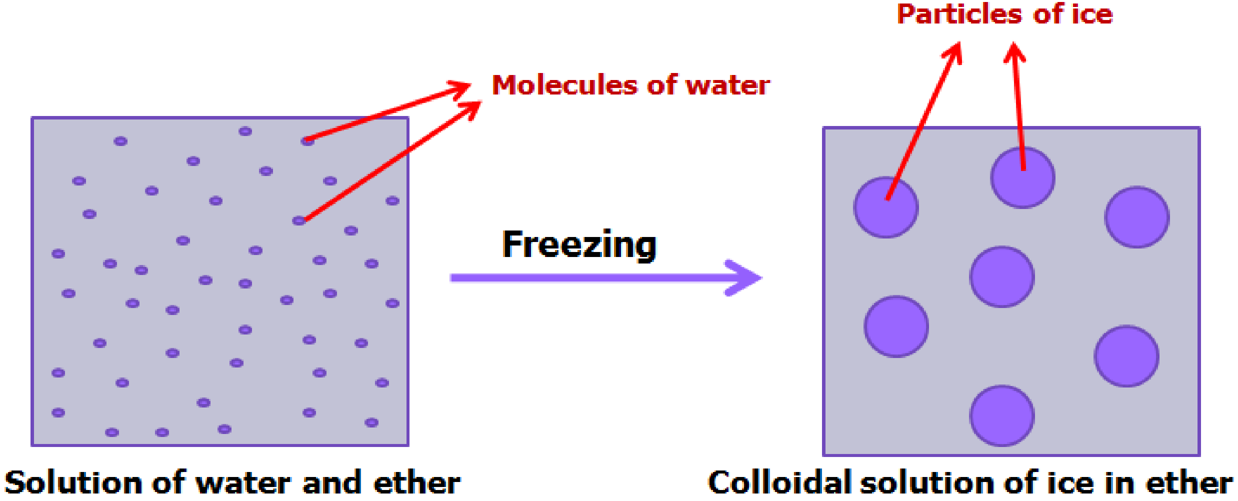


- The transformation of a precipitated material to colloidal solution by the action of an electrolyte in solution, is termed **peptization** which is the reverse of **coagulation** and the electrolyte used is called a peptizing agent.
- Another examples of preparation of sols by peptization is silver chloride, AgCl which can be converted into a sol by adding hydrochloric acid

B- Aggregation Methods

The more important aggregation methods are:

-1Extensive cooling

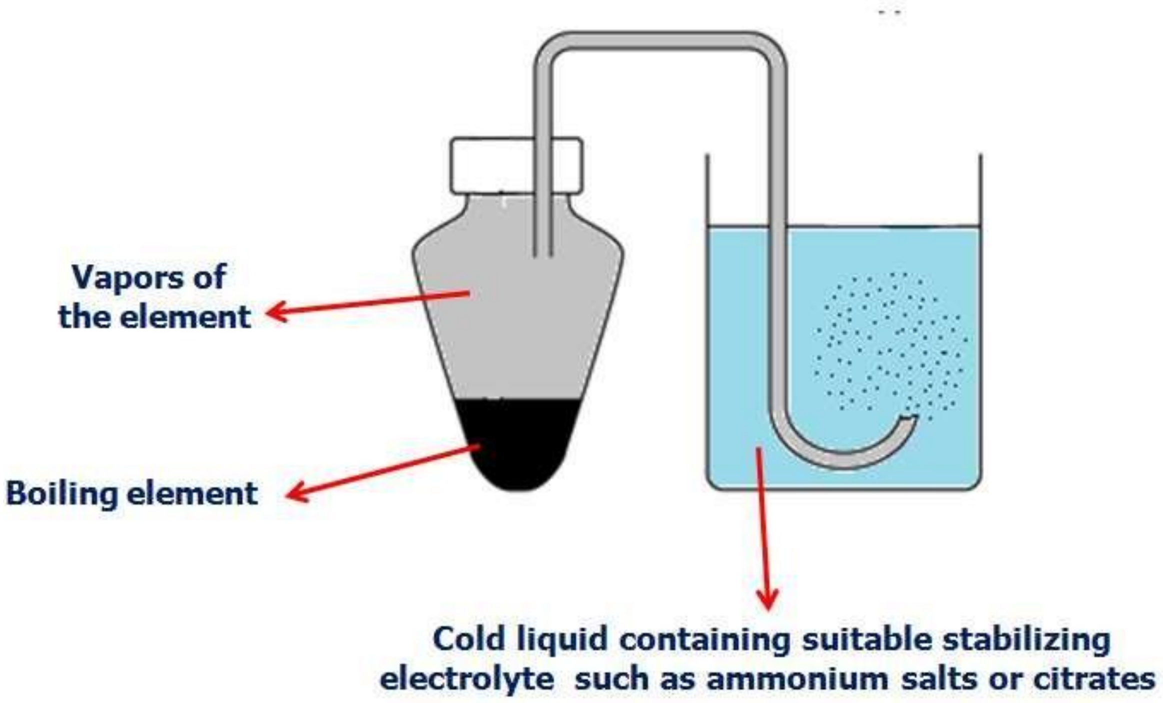


- The colloidal solution of ice in an organic solvent like ether is obtained by freezing a solution of water in the solvent .
- As a result of the sudden freezing of the solution, the molecules of water held together to form particles in the colloidal size dispersed in the organic solvent (ether(

-2Lowering of solubility by exchange of solvent

- Substances like **sulphur**, **phosphorous**, etc., which are more soluble in alcohol than in water give a hydrosol by pouring a small amount of their alcoholic solution in excess of water .
- By the transference from alcohol to water, the substance is transformed from the **molecular state (true solution)** to the **colloidal state** by the coagulation of molecules together to form particles in the colloidal range.
- Phenolphthalein indicator, for example, is soluble in alcohol and not in water, so that, it is supplied to laboratory as alcoholic solution. If water is added to this solution, a milky liquid of colloidal phenolphthalein in water is produced.

-3Passing vapor of an element into a liquid



- If the vapors of a boiling element are conducted into a cold liquid, condensation takes place. Sometimes, this condensation resulted in the formation of a stable sol .
- Mercury and sulphur sols can be prepared by this method.

-4Chemical action

a- Double decomposition

- An arsenic sulphide (As_2S_3) sol is prepared by passing a slow stream of hydrogen sulphide gas through a cold solution of arsenious oxide (As_2O .($_3$

$$\mathbf{As_2O_3 \quad + \quad 3\ H_2S \rightarrow As_2S_{3(yellow\ sol\ )} \quad + \ 3\ H_2O}$$

- This is continued till the yellow colour of the sol attains maximum intensity.

-4Chemical action

b- Reduction

Silver sols and gold sols can be obtained by treating dilute solutions of silver nitrate or gold chloride with suitable reducing agents

$$AgNO_3 \xrightarrow{\text{Reducing agent}} \text{Ag sol}$$

$$AuCl_3 \xrightarrow{\text{Reducing agent}} \text{Au sol}$$

Reducing agents could be organic reducing agents like tannic acid or formaldehyde or others.

c- Oxidation

A sol of sulphur is produced by passing hydrogen sulphide into a solution of sulphur dioxide.

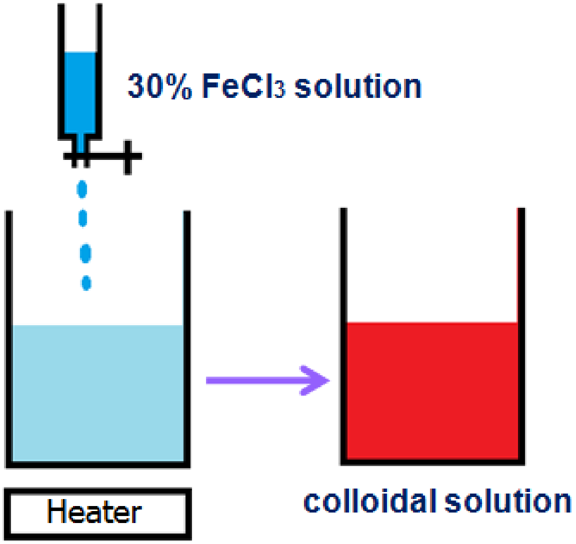
$$2H_2S + SO_2 \longrightarrow 2H_2O + S\downarrow$$

Or exploring H_2S to air for a long time

$$H_2S + O \rightarrow H_2O + S$$

d- Hydrolysis

- Sols of the hydroxides of **iron**, **chromium** and **aluminium** are readily prepared by the hydrolysis of salts of the respective metals .



- In order to obtain a red sol of ferric hydroxide, a few drops of 30% ferric chloride solution is added to a large volume of almost boiling water and stirred with a glass rod.

$$FeCl_3 + 3H_2O \longrightarrow \underset{\text{red sol}}{Fe(OH)_3} + 3HCl$$

Condensation method

Normal crystals are formed in two stages:

1. The Nucleation (formation of crystallization centers) in a supersaturated solution (like in chemical reaction that yields a slightly soluble compound.(
2. The growth of nuclei leading to the formation of sufficiently large crystals.

The nucleation rate (U) can be expressed as:

$$U = K\,(C_{sup} - C_s)/C_s$$

Condensation method

$$U = K\,(C_{sup} - C_s)/C_s$$

Where K is constant

C_{sup} = conc. of supersaturated solution

C_s = conc. of a saturated solution.

$(C_{sup}-C_s)$ is an excess of a substance which is able to form crystals, then can serve as a measure of the rate of liberation from the solution.

C_s can serve a measure of resistance to the liberation (interaction between the solute and solvent).

Condensation method

So, the grater the (C_{sup}-C_s) and the smaller Cs, the more rapidly the nuclei formed and the larger is the no. of crystallization centers, hence the smaller are colloidal particles because the liberated substance will be distributed between a large n. of crystallization centers.