SCES2230 KIMIA FIZIK 2
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B: Kinetic Energy And Temperature

Recall the ideal gas equation

$$PV = nRT = \frac{N}{N_A}RT = P = \frac{2}{3}\frac{N}{V}\overline{E}_{trans}$$

N_A=Avogadro Number (replace into the equation)

We now have,

$$\frac{2}{3}\frac{N}{V}\overline{E}_{trans}(V) = \frac{N}{N_A}RT$$

$$\therefore \overline{E}_{tarns} = \frac{3}{2}\frac{RT}{N_A} = \frac{3}{2}kT$$

Where, $R = kN_A$

Notice that,

$$\overline{E}_{trans} \propto T$$

Inference:

Two ideal gases at the same absolute temperature must have the same kinetic energy.

Random molecular motion sometimes referred as thermal motion.

$$\frac{1}{2}m\overline{v}^{2} = \frac{3}{2}\frac{RT}{N_A}$$

$$\overline{v}^{2} = \frac{3RT}{mN_A} = \frac{3RT}{m}$$

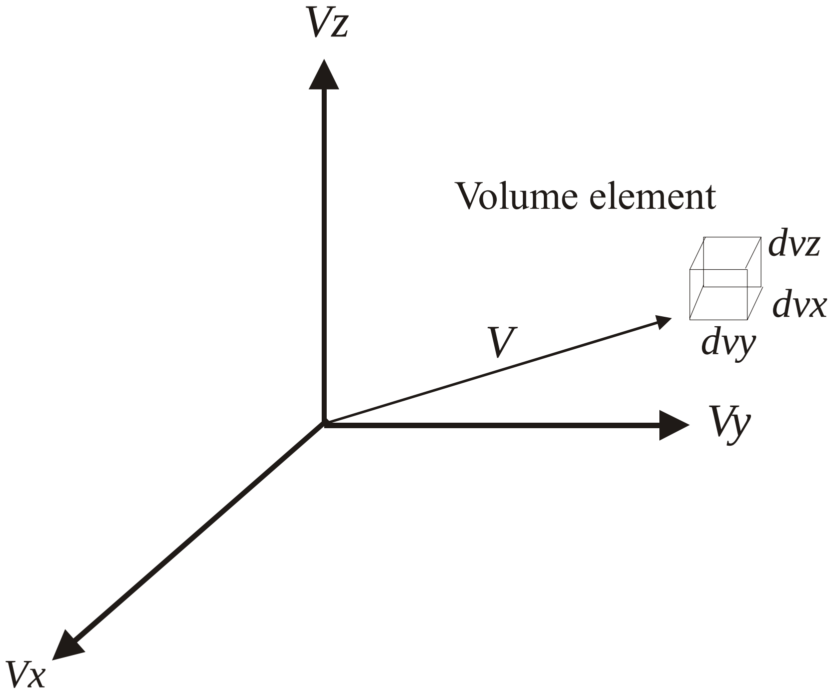
$$\therefore \sqrt{\overline{v}^{2}} = \sqrt{\frac{3RT}{m}} = v_{rms}$$

v_{rms} = root-mean-square velocity, m = molar mass

DISTRIBUTION OF MOLECULAR SPEEDS

As a result of random collisions of gaseous molecules, the molecular velocities keep on changing.

Velocity is a unit vector, with magnitude v and with a direction. The magnitude v of the velocity vector also referred as SPEED.



At a given instant, the probability of finding a molecule with a velocity in the range;

v_x to $v_x + dv_x$

v_y to $v_y + dv_y$

v_z to $v_z + dv_z$

Given by,

$f(v_x, v_y, v_z)dv_x dv_y dv_z$

where,

$dv_x dv_y dv_z$ is the infinitesimal volume in velocity space

The speed v is calculated by the Pythagoraean Theorem:

$$v = |v| = \left(v_x^2 + v_y^2 + v_z^2\right)^{\frac{1}{2}}$$

The volume element in velocity space is infinitesimal in size and it has the density point at the end of a specific velocity vector, v

The probability density - $f\left(v_x, v_y, v_z\right)$ is the probability per unit volume at appoint in velocity space. The probability for all of velocity space is unity;

$$\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} f\left(v_x, v_y, v_z\right) dv_x dv_y dv_z = 1$$

Can also be written as,

$$\int_{-\infty}^{\infty} f(v)dv = 1$$

probability density

The probability density in x direction is

$$f\left(v_x\right) dv_x$$

The kinetic energy of a molecule of mass m moving with a velocity v in x-direction,

$$E_{kin} = \frac{1}{2} m v_x^2$$

The probability density that a molecule has a velocity, v_x is given by;

$$f(v_x) = const\ e^{-\frac{m v_x^2}{2KT}}$$

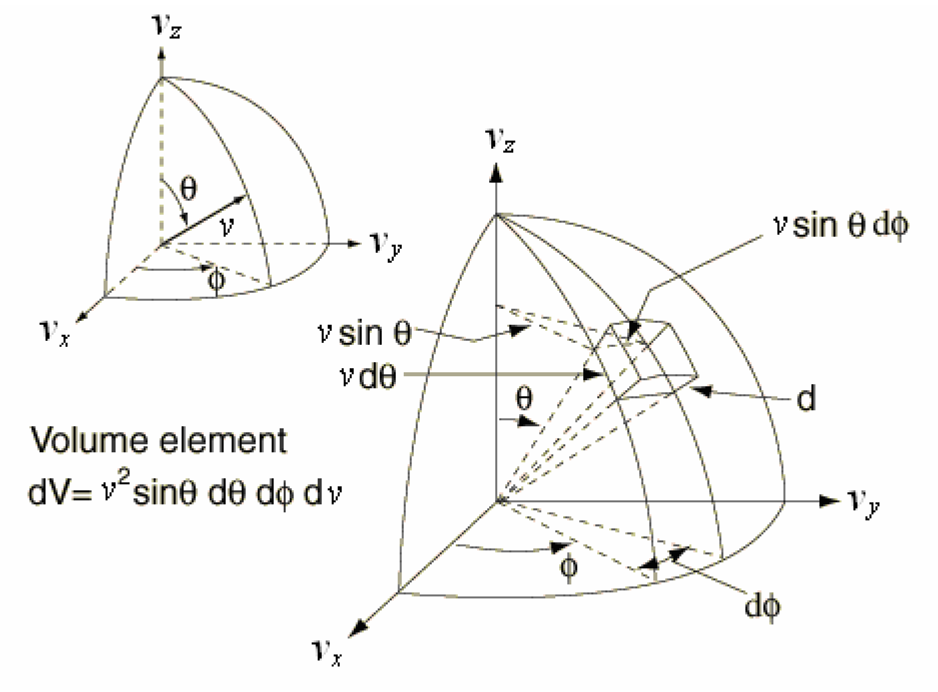
Thus,

$$\int_{-\infty}^{\infty} f(v_x) dv_x = 1 = const \int_{-\infty}^{\infty} e^{-\frac{m v_x^2}{2KT}} dv_x$$

The Maxwell-Boltzmann distribution of molecular velocities is given by:

$$f(v_x) = \left(\frac{m}{2\pi kT}\right)^{\frac{1}{2}} e^{-\frac{m v_x^2}{2KT}}$$

MAXWELL DISTRIBUTION OF SPEEDS



v_y

$$f\left(v_x, v_y, v_z\right) = \left(\frac{m}{2\pi kT}\right)^{\frac{3}{2}} \exp\left[-\frac{m}{2kT}\left(v_x^2 + v_y^2 + v_z^2\right)\right]$$

The speed is represented by the distance in velocity space at a point from origin.

The probability $f(v)d(v)$ that a molecule has a speed between v and $v + d(v)$ is given by the probable number of points in a spherical shell.

$$v_x = v\sin\theta\cos\phi$$
$$v_y = v\sin\theta\sin\phi$$
$$v_z = v\cos\theta$$

The differential volume element can be written as in spherical coordinates;

$$dv_x dv_y dv_z = v^2 dv \sin\theta d\theta d\phi$$

The probability $f(v)dv$ can now be found by integration of $f((v_x, v_y, v_z)dv_x \; dv_y dv_z$ over the angles θ and ϕ.

$$F(v)dv = \int_0^{\pi} d\theta \int_0^{2\pi} d\phi f\left(v_x^2, v_y^2, v_z^2\right) \sin\theta v^2 dv$$

Recall: $v = |v| = \left(v_x^2 + v_y^2 + v_z^2\right)^{\frac{1}{2}}$, substituting previous equation (∗)

$$F(v)dv = 4\pi v^2 \left(\frac{m}{2\pi KT}\right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2KT}\right) dv$$

The probable density $F(v)$ for the Maxwell distribution of speed is given:

$$F(v) = 4\pi v^2 \left(\frac{m}{2\pi KT}\right)^{\frac{3}{2}} \exp\left(-\frac{mv^2}{2KT}\right)$$

at $\quad v = 0 \;\; ; \;\; f(v = 0)$

Types Of Average Speeds

1. Most probable speed, v_{mp} or (C_{mp})

The speed at the maximum of $F(v)$ when $\frac{dF}{dv} = 0$

$$\frac{dF}{dv} = \left(\frac{m}{2\pi KT}\right)^{\frac{3}{2}} e^{-\frac{mv^2}{2KT}} \left[8\pi v + 4\pi v^2 \left(-\frac{mv}{KT}\right)\right] = 0$$

$$v_{mp} = \left(\frac{2KT}{m}\right)^{\frac{1}{2}}$$

$$V_{mp} = \left(\frac{2RT}{M}\right)^{\frac{1}{2}}$$

From the Maxwell speed distribution for molecules, it can be shown that:

Most probable speed, $C_p = \left(\frac{2KT}{m}\right)^{\frac{1}{2}} = \left(\frac{2RT}{M}\right)^{\frac{1}{2}}$

Mean speed, $\overline{C} = \left(\frac{8KT}{\pi m}\right)^{\frac{1}{2}} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$

rms speed, $C = \left(\frac{3KT}{m}\right)^{\frac{1}{2}} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}$

$C : \overline{C} : C_p = 1.00 : 0.92 : 0.82$

Effect Of Temperature On Molecular Speeds

As the temperature increased, the speed distribution becomes broader and more number of molecules have higher speeds.

Effect Of Mass On Molecular Speed Distribution

Mean Speed $\langle v \rangle$

Calculated as the average of v using the probability distribution $F(v)$.

$$\langle v \rangle = \int_0^\infty v F(v) dv$$

$$\langle v \rangle = 4\pi \left(\frac{m}{2\pi KT} \right)^{\frac{3}{2}} \int_0^\infty \exp\left(-\frac{mv^2}{KT} \right) v^3 dv$$

$$\langle v \rangle = \left(\frac{8KT}{\pi m} \right)^{\frac{1}{2}}$$

$$\langle v \rangle = \left(\frac{8RT}{\pi M} \right)^{\frac{1}{2}}$$

Root-mean-square speed

Defined as the square root of $\left\langle v^2 \right\rangle$

$$\left\langle v^2 \right\rangle^{\frac{1}{2}} = \left[\int_0^\infty v^2 F(v) dv \right]^{\frac{1}{2}}$$

$$\langle v^2 \rangle^{\frac{1}{2}} = \left(\frac{3KT}{m}\right)^{\frac{1}{2}} = \left(\frac{3RT}{M}\right)^{\frac{1}{2}}$$

At any temperature, $\langle v^2 \rangle^{\frac{1}{2}} > \langle v \rangle > \langle v_{mp} \rangle$

Integral	n					
	0	1	2	3	4	5
$\int_0^\infty x^n \exp\left(-ax^2\right)dx$	$\frac{1}{2}\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$	$\frac{1}{2a}$	$\frac{1}{4}\left(\frac{\pi}{a^3}\right)^{\frac{1}{2}}$	$\frac{1}{2a^2}$	$\frac{3}{8}\left(\frac{\pi}{a^5}\right)^{\frac{1}{2}}$	$\frac{1}{a^3}$
$\int_{-\infty}^\infty x^n \exp\left(-ax^2\right)dx$	$\left(\frac{\pi}{a}\right)^{\frac{1}{2}}$	0	$\frac{1}{2}\left(\frac{\pi}{a^2}\right)^{\frac{1}{2}}$	0	$\frac{3}{4}\left(\frac{\pi}{a^5}\right)^{\frac{1}{2}}$	0

Example,

Calculate C_{mp} , C^{-} and C_{rms} for O_2 at 300K

R= 8.314 JK^{-1} mol^{-1}, M= 0.032 Kg mol^{-1}, T= 300 K

$$C_{mp} = \sqrt{\frac{2\times 8.314JK^{-1}mol^{-1}\times 300K}{0.032Kgmol^{-1}}}$$

$$= \left(1.56\times 10JKg^{-1^{5}}\right)^{\frac{1}{2}} = \left(1.56\times 10^5 m^2 s^{-2}\right)^{\frac{1}{2}} = 395ms^{-1}$$

$$C_{ave} = \sqrt{\frac{8RT}{\pi m}} = 4.46\times 10^{4}\, cms^{-1} = 446 ms^{-1}$$

$$C_{rms} = \sqrt{\frac{3RT}{M}} \quad = 484 ms^{-1}$$

Therefore, $C_{rms} > C_{ave} > C_{mp}$

The most probable speed in x-direction,

$$\langle v_x \rangle = \int_{-\infty}^{\infty} v_x f(v_x) dv_x = 0$$

Note that: $\int_{-\infty}^{\infty} x^n \exp\left(-ax^2\right) dx = \left(\frac{\pi}{a}\right)^{\frac{1}{2}}$

$n = 0$, $f(v_x)$ is symmetrical . v_x is an odd function. When T ↑ or m ↓ distribution becomes broader, area under the curve remains constant.

Probability density for the velocity of O_2.

Example: Calculate the probability density for O_2 molecule at 300 K at $v_x = 300 ms^{-1}$

$$f(v_x) = \left(\frac{M}{2\pi RT}\right)^{\frac{1}{2}} \exp\left(-\frac{Mv_x^2}{2RT}\right)$$

$$= \left[\frac{0.032 Kgmol^{-1}}{2\pi (8.314 JK^{-1})(300K)} \right]^{\frac{1}{2}} \exp\left[\frac{0.032 Kgmol^{-1} (300)^2 m^2 s^2}{2 \times 8.314 \times 300K} \right]$$

$$= 8.022 \times 10^{-4} sm^{-1}$$

$$I = \left(\frac{2RT}{M} \right)^2 \int_0^\infty x^3 e^{-x^2} dx$$

$$= \left(\frac{2RT}{M} \right)^2 \left(\frac{1}{2} \right)$$

$$\overline{C} = 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} \left(\frac{2RT}{M} \right)^2 \left(\frac{1}{2} \right) = \left(\frac{8RT}{\pi M} \right)^{\frac{1}{2}}$$

Root Mean Square –Speed, C_{rms}

$$C_{rms} = \left\langle C^2 \right\rangle^{\frac{1}{2}} = \left\{ \int_0^\infty C^2 f(c) dc \right\}^{\frac{1}{2}}$$

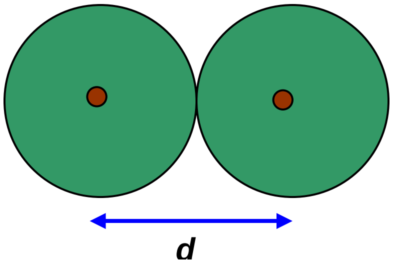
$$\int_0^\infty C^2 f(c) dc = 4\pi \left(\frac{m}{2\pi RT} \right)^{\frac{3}{2}} \left(\frac{2RT}{M} \right)^2 \left(\frac{2RT}{M} \right)^{\frac{1}{2}} \int_0^\infty x^4 e^{-x^2} dx$$

$$= 4\pi \left(\frac{M}{2\pi RT} \right)^{\frac{3}{2}} \left(\frac{2RT}{M} \right)^2 \left(\frac{2RT}{M} \right)^{\frac{1}{2}} \bullet \left(\frac{3}{8} \right) \pi^3 = \left(\frac{3RT}{M} \right)$$

$$\left\langle C^2 \right\rangle^{\frac{1}{2}} = \left\{ \int_0^\infty C^2 f(c) dc \right\}^{\frac{1}{2}} = \left(\frac{3RT}{M} \right)^{\frac{1}{2}}$$

COLLISION DIAMETER: (d)

The distance between the centers of the two molecules at the point aof their closest approach is known as collision diameter (d).



COLLISION CROSS-SECTION :(σ)

When two molecules collide, the affective area of the target is πd^2. The quantity πd^2 is called the collision cross section of the molecule, because it is the cross-sectional area of an imaginary sphere surrounding the molecule into which the center of another molecule cannot penetrate.

COLLISION NUMBER:

It is the number of collisions made by one molecule per unit time and per unit volume, It is also known as collision density.

COLLISION FREQUENCY

It is the number of collisions made by one molecule per unit time. In the following figure, collisions between the hard spheres A and B will take place, only if B approaches A within a distance of $r_A + r_B$. The hard sphere B should lie inside the cylinerical area enclosed by the cylinder of cross section $\pi (r_A + r_B)^2$. This quantity is known as collisional cross section, σ_{AB}. If $\bar{v}_{AB}$ is the average relative velocity of the hard spheres A and B, then the moving B hard spheres would travel a distance of v_{AB} in unit time. Hence, the hard sphere B would cover a volume of $\sigma_{AB} \bullet \bar{v}_{AB}$ in unit time.

Consider a system containing several molecules, in which all the molecules are stationery and only one molecule is moving. The mobile molecule moves with a mean speed $\bar{c}$ for a time Δt. It doing so it sweeps out a 'collision tube' of cross-sectional area, $\sigma = \pi d^2$ and length $\bar{C}\Delta t$, and therefore of volume $\sigma\overline{C}\,\Delta t$.

The numbers of stationery molecules inside the sphere is given by $\sigma\bar{C}\Delta t\left(\frac{N}{V}\right)$, where $\left(\frac{N}{V}\right)$ is the number density.

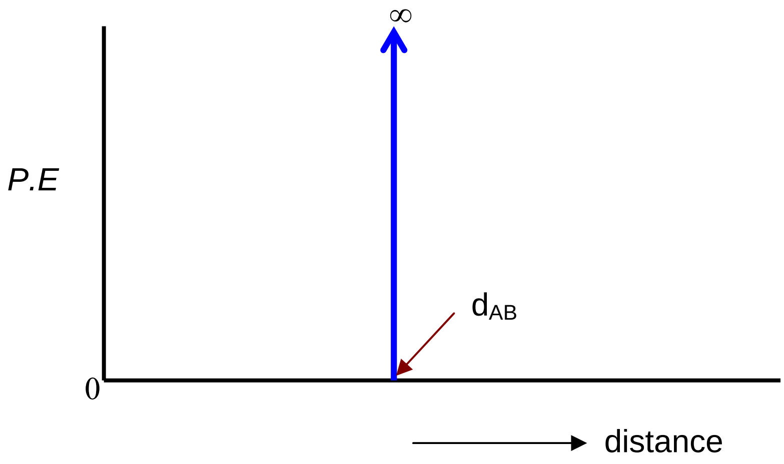
The moving molecule will hit all these molecules and hence the number of hits scored by a single molecule in the interval Δt is also $\sigma\bar{C}\Delta t\left(\frac{N}{V}\right)$. However, the molecules are not stationary and $\bar{C}_{rel} = \sqrt{2}\bar{C}$. Hence no of collisions per unit time is $Z = \sqrt{2}\bar{C}\sigma\left(\frac{N}{V}\right)$

COLLISION THEORY FOR BIMOLECULAR REACTIONS IN GAS-PHASE

Molecules are treated as hard spheres.

There are rigid and have no internal degrees of freedom

There are no forces acting between them.



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

According to simple collision theory,

reaction rate = $Z_{AB}.F$

Z_{AB} is collision frequency

F is fraction of molecules having sufficient energy for rxn.

Z_{AB} is number of molecules colliding per unit volume per unit time.

$Z^{\circ}_{AB} =$ collision number. It is the collision frequency at unit concentrations.

Soon after the first collision, the molecule will travel l distance in time $\frac{l}{v_x}$ for the next collision with the opposite wall. The frequency of collision is the number of collisions per unit time, $= \frac{v_x}{2l}$

The change in momentume per unit time

$$\frac{\Delta P}{\Delta t} = \left(2mv_x\right)\left(\frac{v_x}{2l}\right) = \frac{m{v_x}^2}{l}$$

Newton's Second Law of motion;

Force = mass x acceleration

=mass x distance x (per unit time)^2

= momentum per unit time

$= \Delta P / \Delta t$

The force exerted by one molecule on the wall,

$$= \frac{mv_x^{\;2}}{l}$$

Total force by N molecule $= N \times \dfrac{mvx^2}{l}$

Pressure = Force / Area

$$P = \frac{Nmv_x^{\;2}}{l} \times \frac{1}{l^2} \quad = \frac{Nmv_x^{\;2}}{V} \text{ OR } \quad PV = Nmv_x^{\;2}$$

MOLECULAR COLLISIONS

The kinetic theory of gases:

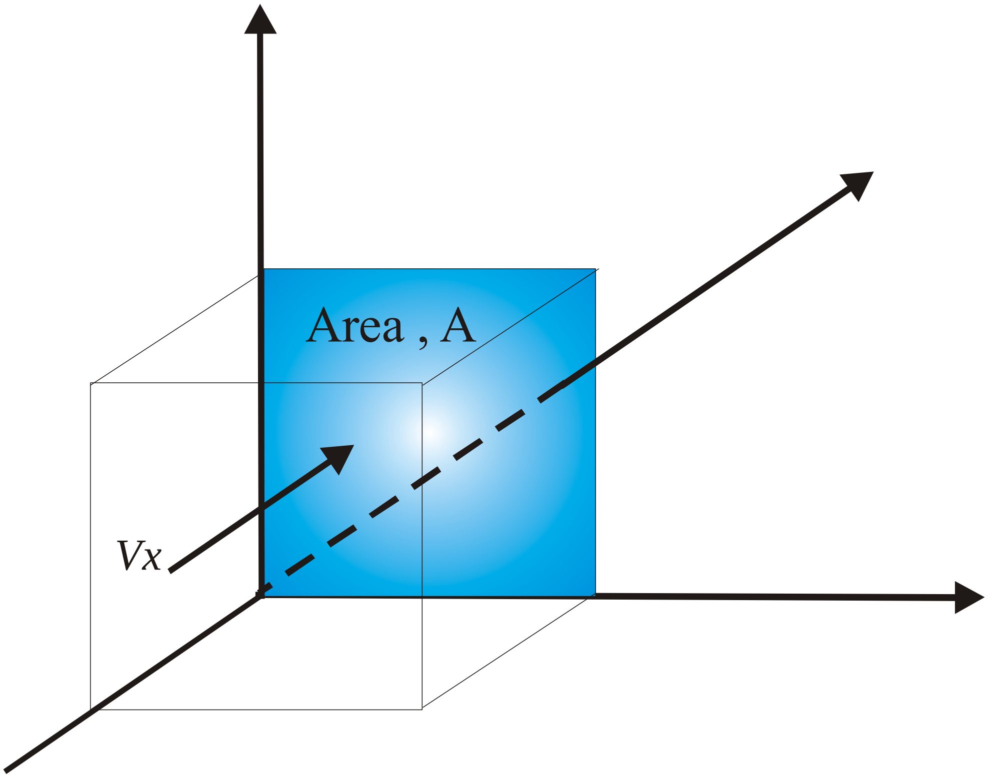
The kinetic molecular theory is based on the following postulates :

1. A gas is made up of a great number of atoms or molecules, separated by distances that are large compared to their size.
2. The molecules have mass, but their size is negligibly small.

3. The molecules are constantly in random motion.
4. Collision among molecules and between molecules and the walls of the container are elastic; i.e kinetic energy maybe transferred from one molecule to another, but is not converted to other form of energy such as heat.
5. There is no interaction, attractive or repulsive between the molecules.
6. The law of classical mechanics are applicable to the molecules.

We can now use the above model to derive an expression for the pressure of a gas in terms of molecular properties.

Consider a gas made up of ***N*** molecules each of mass ***m*** confined in a cubic box of length ***l*** **.**



A molecule with velocity ***v*** striking a wall of area A.

v is a unit vector and can be mutually resolved to its perpendicular component $\boldsymbol{v_x}$ **,** $\boldsymbol{v_y}$ **,** $\boldsymbol{v_z}$**.**

The projection of velocity vector on the ***xy*** plane is OA

$$\overline{OA}^2 = v_x^2 + v_y^2$$

similarly , $\boldsymbol{v^2} = \overline{OA}^2 + \boldsymbol{v_z^2}$

$$= \boldsymbol{v_x^2 + v_y^2 + v_z^2}$$

Consider the motion of a molecule along the *x*-direction .

Since the collision is elastic,

$\therefore$ velocity after collision = velocity after collision

momentum of molecule = mv_x

change in momentum = $mv_x - m(-v_x)$

$= 2\,mv_x$

$= \Delta P_x$

V is the volume of the cube. Now we have N number of molecules, must consider the average of v_x^2 ($\bar{v}_x^{\,2}$)

The average square velocity $\bar{v}^2$

$$\bar{v}^2 = \overline{v_x}^{\,2} + \bar{v}_y^{\,2} + \bar{v}_z^{\,2}$$

The mean-square velocity $\bar{v}^2$

$$\bar{v}^2 = \frac{v_1^{\,2} + v_2^{\,2} + \ldots. + v_N^{\,2}}{N}$$

also, $<\bar{v}^2> = \sum \frac{vi^2}{N}$ where i = 1,2,3,…N

Assume that other velocity components in x, y and z directions are equally probable.

$$\overline{v_x}^{\,2} = \bar{v}_y^{\,2} = \bar{v}_z^{\,2} = \frac{\bar{v}^2}{3}$$

Now, $P = \frac{Nm\overline{v}^2}{3V}$ kinetic gas equation $PV = \frac{1}{3}Nm\overline{v}^2$

The average kinetics energy, $\overline{E}_{trans} = \frac{1}{2}m\overline{v}^2$

Therefore, $P = 2 \times \frac{N}{3V} \times (\frac{1}{2}m\overline{v}^2)$

$$P = \frac{2}{3} \cdot \frac{N}{V} \cdot \overline{E}_{trans}$$

REACTION ORDER

Rate of reaction is define as,

$$\frac{-d[A]}{dt}$$

i.e rate of decrease of A concentration with time.

For a reaction,

$$\mathrm{A + B \rightarrow products}$$

The rate law,

$$-\frac{da}{dt} = k\ a^{\alpha}\ b^{\beta}$$

Where a and b are concentration of reactants A and B. k is the rate constant. The exponent α and β are the order of reaction with respect to A and B, which are determined experimental.

Overall order of reaction = $\alpha + \beta$

Example :

$$H_2 + I_2 \longrightarrow 2HI$$

The reaction is first order w.r.t hydrogen and iodine

NOTE : order of reaction is NOT related to (necessarily) the stoichiometry of the chemical reaction.

IODINATION OF PROPANONE

$$I_2 + H^+ + CH_3COCH_3 \longrightarrow CH_2ICOCH_3 + HI + H^+$$

$$-\frac{d[I_2]}{dt} = k[H^+][CH_3COCH_3]$$

What is the order of the reaction in I_2 , in H^+ and in CH_3COCH_3? ANSWER : zeroth-order in iodine

It is possible for a species which is not consumed in the reaction to occur in the rate law and conversely may display zeroth-order kinetics in one of the reactant.

Order of reaction is not necessarily to be integral

$$H_2 + Br_2 \longrightarrow 2HBr$$

First order in hydrogen and One-half order in bromine.

WHAT IS THE MECHANISM OF SUCH REACTION??

Stoichiometric number

- a dimensionless property. It’s value is positive for products and negative for reactants.

For a chemical reaction in general; $0 = \sum_{i=1}^{N} v_i B_i$

Where, v_i – the stoichiometric number

B_i – molecular formulas for N substances involved in the reaction.

Say, $H_2 + ½ O_2 \rightleftharpoons H_2O$

$\therefore O = -1H_2 \quad -1/2O_2 \quad +1H_20$

Extent of reaction ;

It is an expression to measure the amount of reaction that has occurred over some period of time.

Define, $n_i = n_{io} + v_i \xi$

Where, n_{io} – the amount of substance i present at $t = 0$

n_i – the amount of i at $t = t$

n are in moles

$\therefore$ Extent of reaction ξ also expressed in unit moles.

$$\frac{dn_i}{d\xi} = v_i$$

Rate of conversion : $\frac{dn_i}{dt} = v_i \frac{d\xi}{dt}$

$\therefore$ rate of conversion = $\frac{d\xi}{dt}$

Rate of conversion of *v* is defined in terms of the rate of change of the concentration of a reactant or product.

$$v = \frac{1}{V}\frac{d\xi}{dt} = \frac{1}{v_i V} \cdot \frac{dn_i}{dt} = \frac{1}{v_i} \cdot \frac{d[B_i]}{dt}$$

Say a reaction A + 2B $\rightleftharpoons$ C

Then the rate of reaction

$$v = \frac{1}{-1}\frac{d[A]}{dt} = \frac{1}{-2}\frac{d[B]}{dt} = \frac{d[C]}{dt}$$

The rate of reaction *v* is determined by using either the reactant or product. However it depends on the stoichiometric numbers and how it is written.

For a forward reaction – *v* is positive

reverse reaction – *v* is negative

at equilibrium – *v* is zero

For volume changes during the reaction, the reaction becomes ;

$$v = \frac{1}{v_i V} \cdot \frac{([B_i]V)}{dt} = \frac{1}{v_i} \cdot \frac{d[B_i]}{dt} + \frac{[B_i]}{v_i V} \cdot \frac{dV}{dt}$$

MOLECULARITY

We must distinguish between elementary and multi-step reactions.

Example : $H + Br_2 \longrightarrow HBr + Br$

Hydrogen atoms react with bromine molecules by forming a collision complex H –Br-Br.

Two reactants collide and stay together for a short period of time, before rearranging to form the products.

Molecularity of reaction – determined by the number of species involved informing the collision complex.

The above reaction is termed BIMOLECULAR.

Example : thermal dissociation of azomethane.

$$CH_3N_2CH_3 \rightarrow 2CH_3 + N_2$$

A sufficient thermal energy forces the molecule to fall apart. The process of molecules rearrangement starts to occur in a single molecule.

This type of reaction is termed UNIMOLECULAR

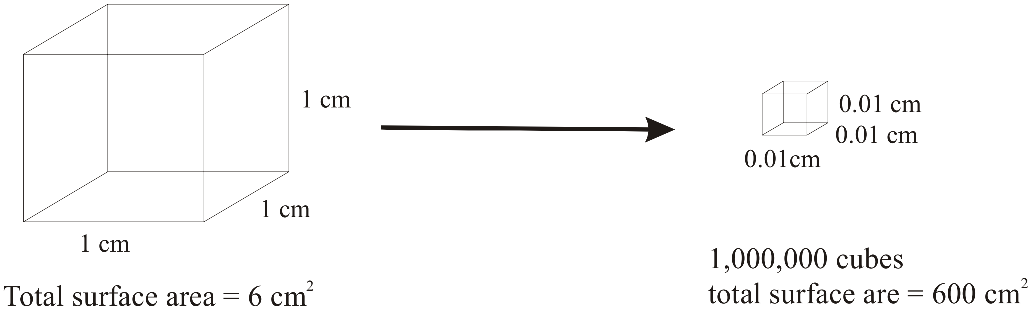
FACTORS AFFECTING RATE OF REACTION

1)Chemical nature of the reactants a freshly exposed metallic sodium surface furnishes almost instantly when explored to air and moisture – very fast reaction . Reaction between iron and moisture (air) to form rust is slow. Reason- iron do not lose electron easily. It depends on the inherent tendencies of atoms ,molecules, or ions to undergo changes in chemical bonds.

2) Ability of the reactants to come in contact with each other. For reaction to occur the reactants must collide with each other:

(a) homogeneous reaction –when reactants are in the same phase, e.g liquid, gas.

(b) heterogeneous reaction –reactant only able to meet at the interface. Rate of reaction dictated by the area of contact between the phases i.e surface area plays an important role.



3) Concentration of the Reactants

The rates of both homogeneous and heterogeneous reactions are affected by the concentrations of the reactants.

4)Temperature of the system

Chemical reaction will occur faster at higher temperature. e.g chemical metabolism slows down in cooler surrounding.

5) Presence of rate promoting agents or catalysts. Catalysts are substances that increase the rate of reactions without itself being used up. Best example is enzymes.

ZERO –ORDER REACTION

Say our reaction of interest is,

$$aA + bB \rightarrow \text{products}$$

No need to specify the products since order of reaction is defined interms of the reactant concentration.

For zero-order , the rate of reaction is independent of the reactant concentrations.

$$\text{Rate} = -\frac{1}{a}\frac{d[A]}{dt} = k^{'}[A]^{\circ}[B]^{\circ} = k^{'}$$

a is only a coefficient, Thus

$$-\frac{d[A]}{dt} = k \qquad (\text{mol dm}^{-3}\ \text{s}^{-1})$$

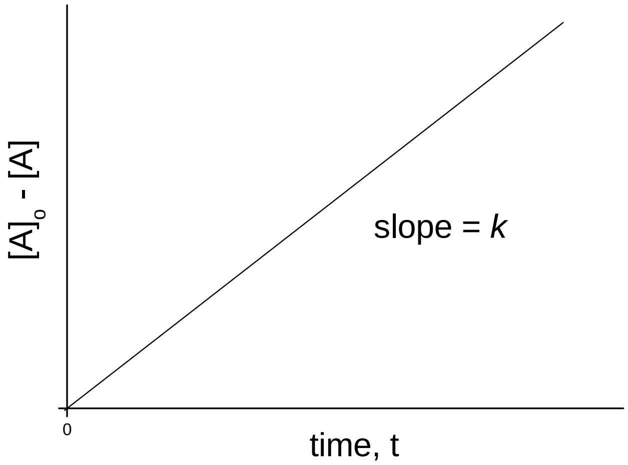
zero-order rate constant $k = ak'$

$$-d[A] = -kdt$$

intergration from t = 0 and t = t gives

$$\int_{[A]_{\circ}}^{[A]} d[A] = [A] - [A]_{\circ} = -\int_{t=0}^{t} kdt = -kt$$

or, $[A] = [A]_{\circ} - kt$



FIRST ORDER REACTION

(Tertib Pertama)

A → products

rate $= -\dfrac{d[A]}{dt} = k[A]$

intergration :

$$-\frac{d[A]}{[A]} = kdt$$

$$-\int_{[A]_1}^{[A]_2} \frac{1}{[A]} d[A] = k\int_{t_1}^{t_2} dt$$

$$\ln\frac{[A]_1}{[A]_2} = k(t_2 - t_{1)}$$

if t_1 =0 s $\quad \therefore \ln\dfrac{[A]_\circ}{[A]} = kt$

or
$$\ln[A] = [A]_\circ e^{-kt}$$
$$\ln[A] = \ln[A]_\circ - kt$$

e.g : decomposition of gaseous, N_2O_5,

$$2N_2O_5 \longrightarrow 4NO_2 + O_2 \ : \ aA \longrightarrow \text{products}$$

$$v = -\frac{1}{2}\frac{d[A]}{dt} = k[A]$$

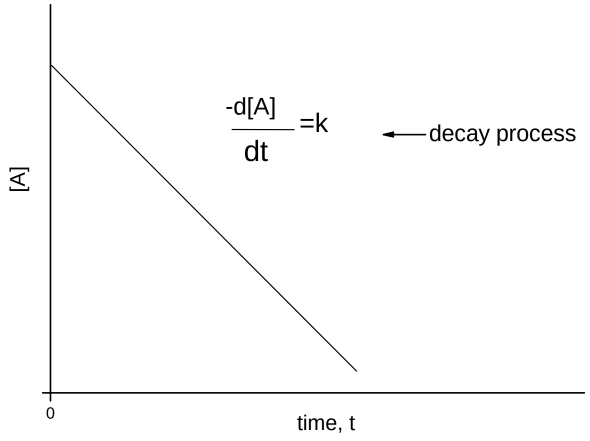
$$\therefore rate = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = k[N_2O_5]$$

can also write :

$$-\frac{d[A]}{dt} = ak[A] = K_A[A]$$
$$where K_A = ak$$

The plot of ln [A] versus t will give a slope of $-K$ (unit of K, s^{-1})

t = 0 at any point of t. changes in [A] could be changes in physical properties.



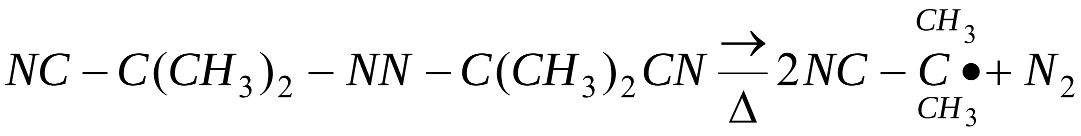
example : radioactive decays

$$^{238}_{92}U \rightarrow ^{4}_{2}He + ^{234}_{90}Th$$

rearrangement of methyl isonitrile to acetonitrile

$$H_3CNC \longrightarrow H_3C - CN$$

Example : The thermal decomposition of 2,2'-azobisisobutyronitrile (AIBN)



$$NC-C(CH_3)_2-NN-C(CH_3)_2CN \underset{\Delta}{\overset{\rightarrow}{\text{——}}} 2NC-\overset{CH_3}{\underset{CH_3}{C}}\bullet + N_2$$

Has been studied in an inert organic solvent at room temperature. The progress of reaction has been monitored by the optical absorption at 350nm. The following data are obtained.

t(s)	0	2000	4000	6000	8000	10000	12000	∞
Abs	1.50	1.26	1.07	0.92	0.81	0.72	0.65	0.40

Assuming the reaction is first order calculate the rate constant.

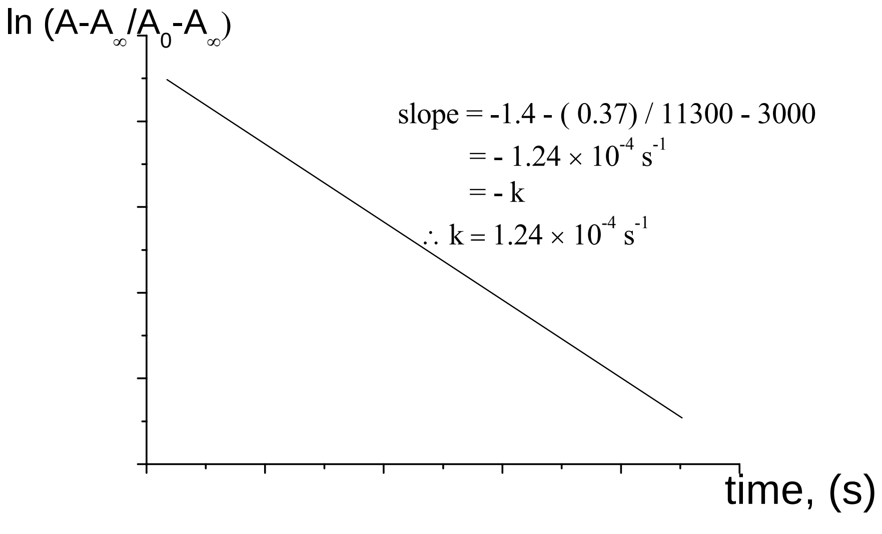
$$\ln\frac{[AIBN}{[AIBN]_{\circ}} = -kt$$

different in the absorbance t= 0 and t = ∞ , $(A_{\circ} - A_{\infty})$ is propotional to [AIBN] initially present in solution. The instantaneous concentration [AIBN]$*$ at time $t\alpha(A - A_{\infty})$

Thus, $$\ln\frac{A - A_{\infty}}{A_{\circ - A_{\infty}}} = -kt$$

since $A_{\circ}$= 1.50 and A_{∞} = 0.

t(s)	2000	4000	6000	8000	10000	12000
$\ln\left(\frac{A - A_{\infty}}{A_{\circ - A_{\infty}}}\right)$	-0.246	-0.496	-0.749	-0.987	-1.240	-1.482



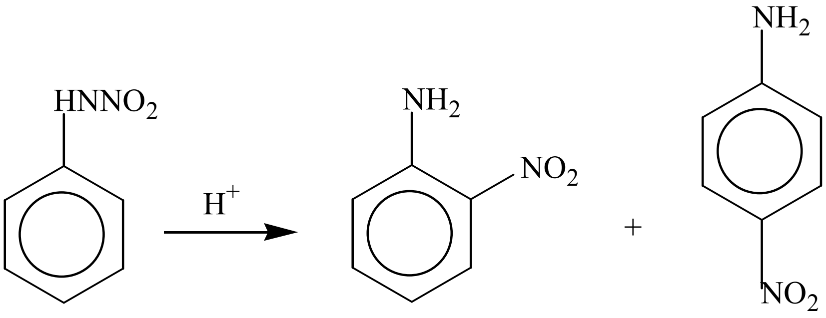
slope = -1.4 - (0.37) / 11300 - 3000

= - 1.24 × 10^{-4} s^{-1}

= - k

∴ k = 1.24 × 10^{-4} s^{-1}

Example 1:



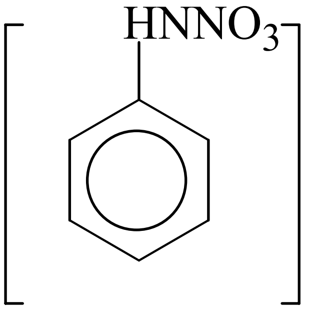
Reaction can be monitored by removing sample at suitable interval, quenching with excess alkali and measure the intensity of yellow color of the products. The following results were obtained

t (s)	0	300	780	1500	2400	3600	∞
Absorbance	0	0.036	0.074	0.120	0.162	0.199	0.249

Show that the reaction is First Order and determine the first order rate constant.

Example 2 :

Say



= a

rate constant for first order reaction, K

$$\therefore kt = 2.303\log_{10}\left(\frac{a}{a-x}\right) or \ln\frac{a}{a-x}$$

where a – concentration of reactant at $t_{\circ}$

$(a-x)$ concentration at t

assuming the Beer-Lambert Law is obeyed, decadic absorbance.

If $A_{\circ}$ is the initial absorbance and A_{∞} when the reaction is complete, $A_{\infty - A_t} \alpha$ concentration at time, t

$$\therefore kt = \ln\frac{(A_{\infty - A_{\circ}})}{(A_{\infty - A_t})}$$

for first order rate constant, $\ln(A_{\infty -} A_t)$ vs t should give a straight line with slope –k

ANSWER : k $= 4.42 \times 10^{-4} s^{-1}$

Let,

$$[A] = [A]_\circ - x$$
$$[B] = [B]_\circ - x$$

where x is mol dm^{-3} of A and B consumed in time t

$$-\frac{d[A]}{dt} = -\frac{d[A]_\circ - x}{dt} = \frac{dx}{dt} = k[A][B]$$

$$= \quad k([A]_\circ - x)([B]_\circ - x)$$

$$\frac{dx}{([A]_\circ - x)([B]_\circ - x)} = kdt$$

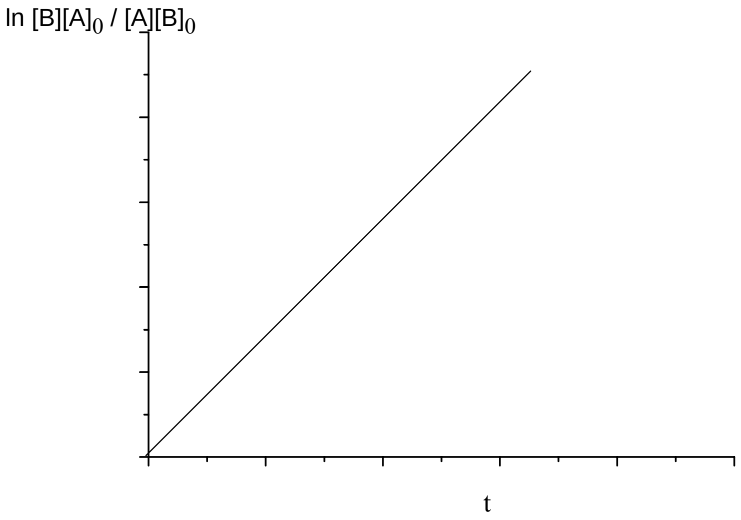
After intergration :

$$\frac{1}{[B]_\circ - [A]_\circ} \ln \frac{\left([B]_\circ - x\right)}{([A]_\circ - x)} \frac{[A]_\circ}{[B]_\circ} = kt$$

OR

$$\frac{1}{[B]_\circ - [A]_\circ} \ln \frac{[B][A]_\circ}{[A][B]_\circ} = kt$$

assuming a=b=1 and $[A]_\circ \neq [B]_\circ$



SECOND ORDER REACTION

Consider ,

$$aA + bB \rightarrow \text{product}$$

type-1

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = k'[A]^2[B]^\circ$$

$$= k'[A]^2$$

the rate is second order w.r.t A and zero-order w.r.t B

$$-\frac{d[A]}{dt} = k[A]^2$$

where $K = ak'$ in (mol dm^{-3})$^{-1}$ s^{-1}

integration :

$$\int_{[A]_\circ}^{[A]} \frac{1}{[A]^2} d[A] = -\int_0^t k dt$$

$$\frac{1}{[A]} - \frac{1}{[A]_\circ} = kt$$

type-2

$$\text{rate} = -\frac{1}{a}\frac{d[A]}{dt} = k'[A][B]$$

first-order w.r.t A and B

$$-\frac{d[A]}{dt} = k[A][B]$$

where $K = ak'$

Second order is most common reactions

Example :

$CH_3COCH_3\,(aq) + H^+\,(aq) \longrightarrow CH_3COHCH_3^+\,(aq)$

$$2NO_2\,(g) \longrightarrow 2NO\,(g) + O_2\,(g)$$

Example hydrolysis of acetyl chloride

$$CH_3COCl + H_2O \longrightarrow CH_3COOH + HCl$$

Water in excess compared to acetyl chloride molarity of $H_2O \times 55.5$ mol dm^{-3} the amount of H_2O consumed is almost negligible.

Rate is expressed

$$-\frac{d[CH_3COCl]}{dt} = k[CH_3COCl][H_2O]$$

$$= k'[CH_3COCl]$$

where $k' = k[H_2O]$ The reaction therefore appears as First- Order. Kinetics and is called a pseudo-First –Order reaction.

HALF LIFE

Consider First-order reaction $[A] = \frac{[A]_\circ}{Z}, t = t_{1/2}$

Thus, $$\ln\frac{[A]_{\circ/2}}{[A]_\circ} = -kt_{1/2}$$

$$t_{1/2} = \frac{\ln 2}{k} = \frac{0.693}{k}$$

Second-order reaction

Example :

The reaction between iodoethane and tertiary amine $C_6H_5N(CH_3)_2$ can be followed by titrating the liberated iodide ions with silver nitrate solution.

$$C_2H_5I + C_6H_5N(CH_3)_2 \rightleftharpoons C_6H_5N(CH_3)_2C2H_5^+ + I^-$$

In an experiment at $25^{\circ}C$ using equimolar amounts of reactants, the following values of the iodoethana concentration were obtained ;

Time, s	0	89	208	375	625	803	1041	1375	1875
$[C_2H_5I]$ mol dm^{-3}	1.6	1.4	1.2	1.0	0.8	0.7	0.6	0.5	0.4

Determine the order of reaction and the rate constant, k

ANSWER :

If the reaction is second –order, the rate equation,

$$-d\frac{[C_2H_5I]}{dt} = k[C_2H_5I][C_6H_5N(CH_3)_2]$$

Initial concentration for both reactants = $[A]_{\circ}$

Concentration of each reactant at $t = [A]_t$

$$\therefore kt = \frac{1}{[A]_t} - \frac{1}{[A]_t}$$

A plot of $\frac{1}{[A]_t}$ vs t should give a straight line of slope, k

t,s	0	89	208	375	625	803	1041	1375	1875
$\frac{1}{[A]}$	0.625	0.714	0.833	1.0	1.250	1.428	1.667	2.00	2.50

A straight line plot → the reaction is second-order

Slope = $k = 1.00 \times 10^{-3} dm^3 mol^{-1} s^{-1}$

ENERGY of ACTIVATION

Example :

The rate constant k for the first-order decomposition of acetone-dicarboxylic acid in aqueous solution are as follows :

Temp/$^\circ C$	0	10	20	30	40	50	60
$k, 10^5 / s$	2.46	10.8	47.5	163	576	1850	5480

Calculate the energy of activation for the reaction

The Arrhenius equation for the rate constant , k

$$k = A\exp\left(\frac{-Ea}{RT}\right)$$

Taking logarithm,

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

a plot of $\ln k$ vs $\frac{1}{T}$ should give a straight line of slope $-\frac{E_a}{R}$

or $-\frac{E_a}{2.303}$ if in $\log_{10}$

The activation energy, $E_a = 97.3 kJmol^{-1}$

$\ln k$	-10.613	-9.133	-7.652	-6.420	-5.157	-3.99
T/K	0.00366	0.00353	0.00341	0.0033	0.00319	0.0036

Slope = -11683.2 $\therefore E_a = 11683 \times 8.314$

$\ln(10.8 \times 10^{-5}) = -9.133$ $= 9.713 kJmol^{-1}$

UNIMOLECULAR REACTION

Unimolecular reactions are first-order reactions rate constant independent of pressure above pressure ≈ 1 bar.

Rate constant drops at lower pressure .

An isolated reaction of gas molecules.

Examples :

Isomerization

$CH_3NC \longrightarrow CH_3CN$ $E_a = 160.5 kJmol^{-1}$ at 470-530 K

Dissociation to stable molecules

$C_2H_5Cl \longrightarrow C_2H_4 + HCl$ $E_a = 254 kJmol^{-1}$ at 670-770 K

Dissociation to free radicals

$C_2H_6 \longrightarrow \bullet 2CH_3$ $E_a = 360 kJmol^{-1}$ at 820-1000 K

$HNO_3 \longrightarrow \bullet OH + NO_2$ $E_a = 205 kJmol^{-1}$ at 890-1200 K

Where does these high activation energies come from?

First approximation of the answer provided by Lindemann in 1922.

"When a molecule is excited to a higher energy state by a bimolecular collision, there is a time before decomposition or isomerization."

Decomposition of azomethane at high pressure

$$CH_3N_2CH_3 \longrightarrow C_2H_6 + N_2$$

shows first-order kinetics i.e : rate α $[CH_3N_2CH_3]$

However the rate increases with temperature showing the reactant must surmount an energy barrier , but first-order preclude collisional activation.

Recall, the excited molecule may lose its extra energy in a second bimolecular collision.

The reaction involves a reacting gas A with an excess of inert gas M , the excitation step and de-excitation step.

$$A + M \xrightarrow{k_1} A^* + M$$

$$A^* + M \xrightarrow{k_2} A + M$$

$$A^* \xrightarrow{k_3} B + C$$

A is a reactant molecule that can be excited on collision with M , which is either another A molecule or added diluent (bath) gas molecule in simplified form,

$$\mathrm{A} + \mathrm{M} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \mathrm{A}^* + \mathrm{M}$$

$$\mathrm{A}^* \longrightarrow \mathrm{P}$$

$$\frac{d[A^*]}{dt} = k_1[A][M] - k_2[A^*][M] - k_3[A^*]$$

$$\underset{\text{formation of A*}}{\uparrow} \qquad\qquad \underset{\text{removal of A*}}{\uparrow}$$

Low pressure limit, k_2 [M]k_3

$$-\frac{d[A]}{dt} = k_1[A][M]$$

A* isomerize or dissociate , rate determined by the number of collisions that are sufficiently energetic.

Rate determining step is bimolecular excitation. Once activated (A*) more likely to react than deactivate.

$$k = k_1[M] \qquad\qquad \text{remains constant}$$

At very low P, the reaction second-order when the partial pressure of M is changed .

However , the product can also activate or quench so that [M] is constant and the reaction is pseudo first order.

In a unimolecular dissociation, [M] increases but since the products are less efficient in energizing A, k_1 [M] ~ constant.

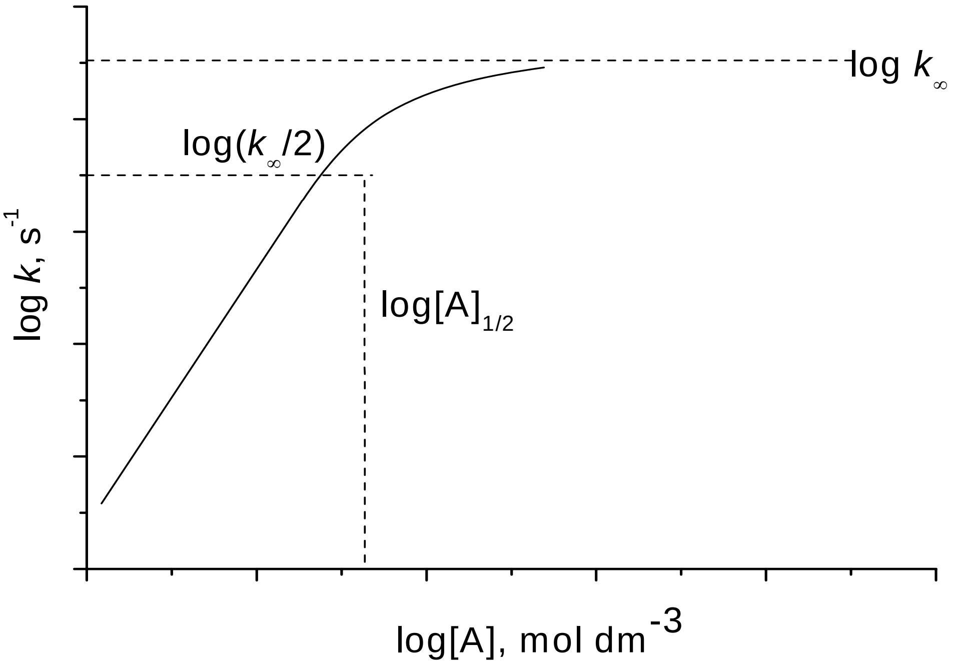
Thus, the reaction pseudo first-order.

At low pressure the rate constant of a unimolecular reaction decreases and the reaction is in the fall off region.

Since A* is never present at a very high concentration after a short build-up period, rate of consumed is the same rate at which it is produced.

$$\frac{d[A^*]}{dt} = 0$$

$$\frac{d[P]}{dt} = -\frac{d[A]}{dt} = k_3[A^*] = \frac{k_1 k_3 [A][M]}{k_2[M] + k_3} = k[A]$$



The rate constant drops with decreasing pressure for the decomposition of azomethane at 603K

The equation has two limiting forms :

1. High pressure limit, $k_2[M] << k_3$,

$$-\frac{d[A]}{dt} = k_1[A][M]$$

i.e : Collisional deactivation is much faster than the unimolecular reaction $A*$. $k \approx k_3 k_1 / k_2$ i.e : becomes independent of pressure. The rate deformining step is the first-order reaction of A* and the overall kinetics also first-order.

$$-\frac{d[A]}{dt}=\frac{k_1k_3[A][M]}{k_2[M]}$$

$$=\frac{k_1k_3[A]}{k_2}=k'[A]$$

LINDEMANN THEORY

Comparison of [M]$_{1/2}$ for unimolecular reaction.

$$k=k_\infty/(1+k_3/k_2[M]$$

The rate coefficient at high/infinite pressure

$$k_\infty=k_3k_1/k_2$$

If [M]$_{1/2}$ as the third body concentrationat which the experimental rate coefficient falls to half of its high pressure value,

$$[M]_{1/2}=k_\infty/k_1$$

We can estimate [M]$_{1/2}$ from the experimental value k_∞

assuming the collision theory rate coefficient for activation.

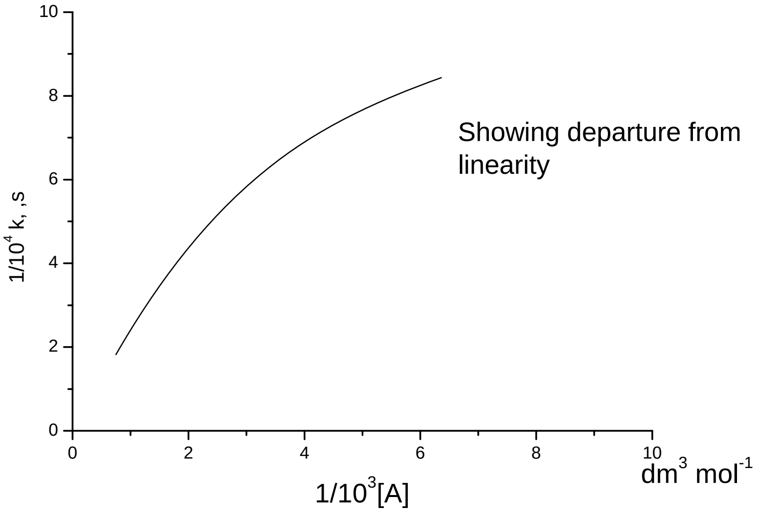
$$k_1=Z\exp(-\frac{Ea}{RT})$$

where Z is collision frequency factor

Unimolecular reaction	T/K	E, KJ mol^{-1}	$[M]_{1/2}$ exp/M	$[M]_{1/2}$ calc/M	K_1, s^{-1}
Cyclopropane → propene	760	275	3×10^{-4}	1.5×10^{4}	3×10^{15}
cyclobutane → 2 ethene	720	267	10^{-5}	2×10^{4}	4×10^{15}
$CH_3NC \longrightarrow CH_3CN$	500	161	4×10^{-4}	2×10^{2}	4×10^{13}
$C_2H_5NC \longrightarrow C_2H_5CN$	500	160	3.5×10^{-5}	3.5×10^{2}	6×10^{13}
$N_2O \longrightarrow N_2 + O$	890	256	0.8	4.0	6×10^{11}

There are discrepancies between experiment and calculated $[M]_{1/2}$ Worse when molecules get larger.

For the reaction; Trans $-C_2H_2D_2 \longrightarrow$ cis $- C_2H_2D_2$ at 794K



$$\frac{1}{k} = \frac{1}{k_1}[M] + \frac{1}{k_\infty}$$

Thus, the plot of 1/k vs [M] should give a straight line.

k_∞ can be determined by extrapolating to $\frac{1}{[M]} = 0$

The plot is far from linearity indicate another problem in Lindemann approach.

Lindemann mechanism provide simplified representation of the physical processes which involved unimolecular reactions. Its failures similar to those in collision theory, fails to take account of real molecular structure.

All subsequent models are built on the foundation of second-order activation to an energized molecule, followed by a first order reaction.

Lindemann Theory : exercise

The following values of the overall rate constant k' were obtained for the decomposition of dimethyl ether :

J_o/m mol dm^{-3}	1.20	1.89	3.55	5.42	8.18
10^4k'/s^{-1}	2.48	3.26	4.61	5.54	6.29

Use the data to demonstrate the validity of Lindemann theory and obtain the limiting value of *k'* at high pressure

ANSWER: $A + A \rightleftharpoons A^* + A$

$$A^* \xrightarrow{k_3} \text{products}$$

A and A* are normal and energized reactants respectively.

Assuming a steady state of A*

$$\text{Rate} = \frac{k_1 k_3 [A]^2}{k_2[A] + k_3} = k'[A]$$

k' is the overall first-order rate constant

therefore,

$$k' = \frac{k_1 k_3 [A]}{k_2[A] + k_3}$$

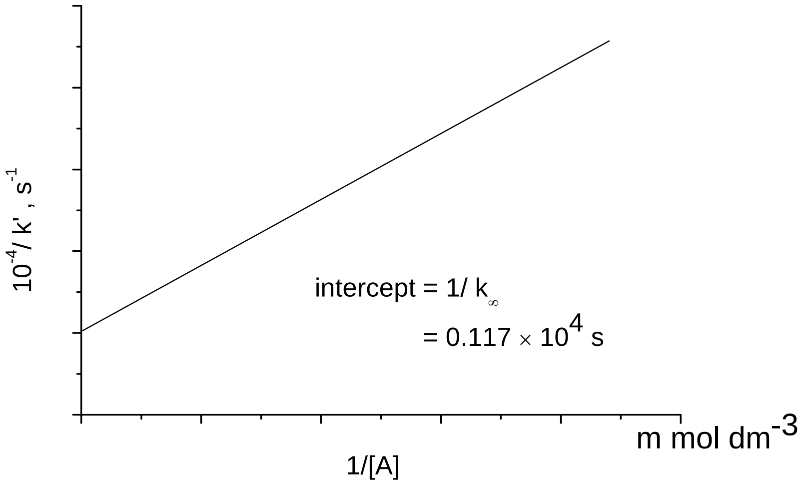
At high pressure $k_2[A] >> k_3$, the overall rate constant limits to the value,

$$k_\infty = \frac{k_1 k_3}{k_2}$$

taking the reciprocal in the expression k' gives ,

$$\frac{1}{k'} = \frac{k_2}{k_1 k_3} + \frac{1}{k_1[A]} = \frac{1}{k_\infty} + \frac{1}{k_1[A]}$$

Therefore , the plot of $\frac{1}{k'}$ against $\frac{1}{[A]}$ will gives a straight line of slope $\frac{1}{k_1}$ and intercept $\frac{1}{k_\infty}$.



The graph is a straight line , Lindemann theory is valid for this reaction.

$$\text{Intercept} = \frac{1}{k_\infty} = 0.117 \times 10^4\, s$$

$$k_\infty = 8.55 \times 10^{-4}\, s^{-1}$$

BIMOLECULAR REACTIONS

An elementary reaction that involves two molecules.

e.g : in the gas phase

$$H + H_2 \longrightarrow H_2 + H$$

$$CO + O_2 \longrightarrow CO_2 + O$$

$$K + HBr \longrightarrow KBr + H$$

$$PH_3 + B_2H_6 \longrightarrow PH_3BH_3 + BH_3$$

In solution phase

$$2CH_3COOH \longrightarrow (CH_3COOH)_2 \text{ (non polar solvent)}$$

$$Fe^{3+} + Fe^{2+} \longrightarrow Fe^{2+} + Fe^{3+}$$

The predominant force between two non polar , unchanged molecules is a strong repulsion.

If the molecule can react in an exothermic reaction, the activation energy is a measure of the energy required to deform the electron clouds of the reactants so that the reaction can occur.

E_a for exothermic Bimolecular Reactions

Reaction type	Electronic structure	E_a , $kJmol^{-1}$
Molecule+ molecule	Two closed shells	80-200
Radical +molecule	One closed shell/ one open shell	0-60
Radical + radical	Two open shells	~ 0

Radicals refer to molecules with at least one orbital vacancy in their valence shells and to atoms.

Most reactions in gas phase involve radicals.

Arrhenius parameters for bimolecular reactions

Reaction	Log $\left(\frac{A}{Lmol^{-1}s^{-1}}\right)$	E_a, $kJmol^{-1}$
$Br + H_2 \rightarrow HBr + H$	10.8	76.2
$I + H_2 \rightarrow HI + H$	11.4	143.0
$Cl + H_2 \rightarrow HCl + H$	10.9	23.0
$N + NO \rightarrow N_2 + O$	10.2	0
$CH_3 + C_2H_6 \rightarrow CH_4 + C_2H_5$	8.5	45.2
$2CH_3 \rightarrow C_2H_6$	10.5	0
$CH_3 + NO \rightarrow CH_3NO$	8.8	0

The pre exponential factor involving atoms in the range of $10^{10.5} - 10^{11.5}$ L $mol^{-1}s^{-1}$ but the activation energies differ appreciably.

Some bimolecular reaction are very complex. Some cases the rate of reaction depends on the pressure – indicates the reaction leads to a collision complex. This is a weakly bound molecule that survives for a short time but longer than the characteristic periods of its vibration and rotations.

$$A + B \rightleftharpoons AB \longrightarrow \text{products}$$

When AB is formed, the reaction is no longer a bimolecular. At low pressure the unimolecular dissociation of AB is in the fall off region, the overall reaction may approach third-order reaction.

Example of such reaction:

$$ClO + NO \rightleftharpoons ClONO \longrightarrow Cl + NO_2$$

Rate constant = 6.2×10^{-12} cm3 s^{-1} exp $\left(\frac{294K}{T}\right)$

Example :

$$A + B \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AB \xrightarrow{k_3} C$$

say a weak complex AB is formed assuming k2 >> k3 , the first step remains in equilibrium . Thus , the rate equation is,

$$\frac{d[C]}{dt} = k_2[AB]$$

$$\therefore \frac{k_1}{k_2} = K_c(c^\circ)^{\Sigma vi} = K_c / c^\circ$$

c° *- a standard concentration in one mole per liter.*

$$K_c = \frac{[AB]c^\circ}{[A][B]}$$

$$\frac{k_1}{k_2} = \frac{[AB]}{[A][B]}$$

We eliminate [AB]

$$\frac{d[C]}{dt} = \frac{k_1 k_3}{k_2}[A][B] = k_3(K_c / c^\circ)[A][B]$$

TRIMOLECULAR REACTIONS

Two atoms cannot combine in a bimolecular reaction in the gas phase to form a diatomic molecule because the energy release causes the molecules to dissociate.

Need a third atom to carry away the energy produced.

Atoms recombination reactions are third order in the gas phase.

The third order elementary reaction

$$2A + M \longrightarrow A_2 + M$$

$$A + B + M \longrightarrow AB + M$$

Rate equation :

$$\frac{d[A_2]}{dt} = k[A]^2[M]$$

$$\frac{d[AB]}{dt} = k[A][B][M]$$

Trimolecular reactions by avoiding three – body collision.

$$A + M \underset{k_2}{\overset{k_1}{\rightleftharpoons}} AM$$

M is a polyatomic molecule capable of forming a complex.

AM can dissociate with rate constant k_2 to regenerate A and B or to form A_2 with rate constant k_3

$$AM + A \xrightarrow{k_3} A_2 + M$$

The steady rate equation :

$$\frac{d[A_2]}{dt} = \frac{k_1 k_3 [A]^2[M]}{k_2 + k_3[A]}$$

The intermediate is short lived . Thus, $k_2 >> k_3 [A]$

$$\frac{d[A_2]}{dt} = \frac{k_1}{k_2} \cdot k_3 [A]^2 [M]$$

since, $\frac{k_1}{k_2} = K_c (c^\circ)^{\Sigma vi}$

where $K_c = \frac{[AM]c^\circ}{[A][M]}$

Now, $\frac{d[A_2]}{dt} = (K_1 / c^\circ) k_3 [A]^2 [M]$

If k_2 follows Arrhenius equation with E_{a2} .

$\therefore$ the activation energy for trimolecular reaction ,

$$E_a = RT^2 \frac{d \ln k_1}{dT} + RT^2 \frac{d \ln k_2}{dT}$$

$$= \Delta H_1^\circ + E_{a2}$$

If the first step is exothermic and the E_a for second step not too large, E_a can be negtive.

If the combination of atom with another atom or diatomic is trimolecular, the reverse reaction is bimolecular, and the Arrhenius equation for the reverse reaction may be calculated using K_c (see bimolecular reaction).

Reaction	T/K	$\log\left(\frac{K}{L^2 mol^{-2} s^{-1})}\right)$
$H + H + M \longrightarrow H_2 + M$	300	10.0 (H_2)
$O + O + M \longrightarrow O_2 + M$	300	8.9 (O_2)
$O + O_2 + M \longrightarrow O_3 + M$	380	8.1 (O_2)
$O + NO + M \longrightarrow NO_2 + M$	300	10.46 (O_2)
$H + NO + M \longrightarrow HNO + M$	300	10.7 (H_2)

CHAIN REACTIONS

Involving radicals and exothermic

Example:

$$H_2 + Br_2 \rightleftharpoons 2HBr$$

At 500 – 1500 K, typical of unbranched chain reaction.

The empirical rate equation :

$$\text{Rate} = \frac{1}{2}\frac{d[HBr]}{dt} = \frac{k[H_2][Br_2]^{1/2}}{1 + k'[HBr]/[Br_2]}$$

If NO HBr at t= 0 , rate at t= 0

$$\alpha[H_2][Br]^{1/2}$$

If sufficient HBr is added, $k'[HBr]/[Br_2] >> 1$,

Then initial rate, $\dfrac{\alpha[H_2][Br_2]^{3/2}}{[HBr]}$

The presence of product inhibits the forward reaction.

$$2 \times [HBr] \longrightarrow 1/2 \times \text{initial rate}$$

At low [HBr] , rate $\alpha[Br_2]^{1/2}$, thus Br_2 dissociates, suggest that Br atom plays role in the mechanism.

IF the dissociation is in equilibrium:

$$[Br] = K^{1/2}[Br_2]^{1/2}$$

Christiansen, Herzfed and Polanyi (1919) :

Br could react with H_2 to start reaction.

Proposed mechanism :

Initiation

$$Br_2 + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2Br + M$$

Propagation

$$Br + H_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} HBr + H$$

$$H + Br_2 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} HBr + Br$$

The carrier gas is M. The net reaction is the sum of step 2 and 3. The reaction is initiated by Br_2 NOT H_2 because bond in bromine is much weaker.

k_2 is endothermic, E_{ac} is high , slower reaction.

k_{-2} is fast , destroys product, inhibition reaction.

Termination $Br^{\cdot} + Br^{\cdot} \rightarrow Br_2$

Chain reaction rapidly reaches steady state when;

$$\frac{d[Br]}{dt} \approx \frac{d[H]}{dt} \approx 0$$

Then , $k_{-3} = 0$

The steady-state rate equation :

$$\frac{1}{2}\frac{d[HBr]}{dt} = \frac{k_2(k_1/k_{-1})^{1/2}[H_2][Br_2]^{1/2}}{1+\dfrac{k_{-2}[HBr]}{k_3[Br_2]}}$$

$\dfrac{k_1}{k_{-1}}$ is the dissociation constant of bromine

$k = k_2(k_1/k_{-1})^{1/2}$

IF k_{-3} is included ,

$$\frac{1}{2}\frac{d[HBr]}{dt} = \frac{k_2(k_1/k_{-1})^{1/2}[H_2][Br_2]^{1/2}}{1+k_{-2}[HBr]/k_3[Br_2]}\left(\frac{1-[HBr]^2}{K[H_2][Br_2]}\right)$$

where , $K = k_2k_3/k_{-2}k_{-3}$

The equilibrium constant for the overall reaction.

For low extent of reaction, the steady-state law becomes the rate law for the reverse reaction. Under condition [HBr] $>>K[H_2][Br_2]^{1/2}$

$$-\frac{1}{2}\frac{d[HBr]}{dt} = k_{-3}\left(\frac{k_1}{k_{-1}}\right)^{1/2}[HBr][Br_2]^{1/2}$$

First order in [HBr] at constant [Br2]

The steady state law at equilibrium is still applicable whether we start from

H_2 + Br OR HBr

PYROLYSIS OF HYDROCARBON

EXAMPLE: Production of ethylene from ethane, cracking process of higher hydrocarbons to produce butadiene, butene and propylene.

Generally heterogeneous reaction with solid catalysts.

Homogeneous reaction of ethane ⟶ ethylene pyrolysis.

$$C_2H_6 \longrightarrow C_2H_4 + H_2$$

reaction at 700 – 900K ,P >0.2 bar

Reaction Mechanism :

Initiation : $C_2H_6 \xrightarrow{k_1} 2CH_3$

Chain transfer $CH_3 + C_2H_6 \xrightarrow{k_2} CH_4 + C_2H_5$

propagation $C_2H_5 \xrightarrow{k_3} C_2H_4 + H$

$$H + C_2H_5 \xrightarrow{k_4} H_2 + C_2H_5$$

Termination $\quad H + C_2H_5 \xrightarrow{k_5} C_2H_6$

The rate of equation of ethane ;

$$\frac{d[C_2H_6]}{dt} = -(k_1 + k_2[CH_3] + k_4[H])[C_2H_6]$$

The rate of formation of ethane in the last step is ignored because termination occurs after long chain of reactions.

In the steady state, the rates of change of the radical concentrations ≈ zero.

$$\frac{d[CH_3]}{dt} = 2k_1[C_2H_6] - k_2[CH_3][C_2H_6] = 0$$

$$\frac{d[C_2H_5]}{dt} = (k_2[CH_3] + k_4[H])[C_2H_6] - (k_3 + k_5[H])[C_2H_5] = 0$$

$$\frac{d[H]}{dt} = k_3[C_2H_5] - k_4[H][C_2H_6] - k_5[H][C_2H_5] = 0$$

Therefore, the steady state concentration of the radicals, $^{\bullet}$CH3 , $^{\bullet}C_2H_5$, $^{\bullet}$H can be obtained from these simultaneous equation.

$$[CH_3] = \frac{2k_1}{k_2}$$

$$[C_2H_5] = \frac{2k_1 + k_4[H]}{k_3 + k_5[H]}[C_2H_6]$$

$$[H] = \frac{2k_1k_5 \pm \sqrt{(2k_1k_5)^5 + 16k_1k_3k_4k_5}}{-4k_4k_5}$$

k_1 is small so that ,

$$[H] = \left(\frac{k_1k_3}{k_4k_5}\right)^{1/2}$$

$\therefore$ Rate of reaction of ethane

$$\frac{d[C_2H_6]}{dt} = -\left[3k_1 = k_4\left(\frac{k_1k_3}{k_4k_5}\right)^{1/2}\right][C_2H_6]$$

The reaction is first-order!

HARPOON MECHANISM

Consider the reaction ,

K + Br2 ⟶ KBr + Br

The first stage of the reaction is the transfer of valence electron of the alkali atom to the halogen molecule. Such a transfer is possible even when the reactants are far apart (5 –10 $\overset{\circ}{A}$). Once the transfer takes place, the strongly attractive Coulombic force brings the two oppositely charged ions togethers, followed by the formation of the products.

The metal atom uses its valence electron as a “harpoon” in order to pull in the halogen molecule, employing the coulombic interionic attraction as a “rope” . There are three energy contributions to the charge transfer process.

ionization energy of K, $\longrightarrow$ I

electron affinity of $Br_{2,}$ $\longrightarrow$ E_{ea}

coulombic interaction energy between the ions

$$\longrightarrow -\frac{e_2}{4\pi\varepsilon_\circ R}$$

e = electronic charge

$\varepsilon_\circ$ = permittivity of vacuum

The charge transfer occurs when the difference between I and E_{ea}

Is balanced by the coulombic interaction energy.

i.e :
$$\frac{e^2}{4\pi\varepsilon_\circ R_x} = I - Eea = \Delta E$$

R_x is the critical distance at which charge transfer takes place. By solving the above equation, the value of R_x can be obtained.

From R_x , the collision cross-section can be obtained as, $\sigma^* = \pi R_x^2$

And $P = \frac{\sigma^*}{\sigma}$ substituting the values of e and $\varepsilon_\circ$,

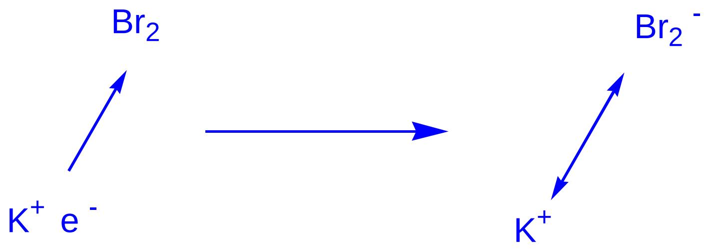
$$R_x = \frac{(1.602 \times 10^{-19})^2}{4\pi(8.854 \times 10^{-12}) \cdot \Delta E / N_A}$$

$$R_x(in - m) = \frac{2.3066 \times 10^{-28} \times N_A}{\Delta E(in - J)}$$

$$R_x(in - \overset{\circ}{A}) = \frac{14.4}{\Delta E(in - eV)}$$

Harpoon Mechanism :

e.g $\mathrm{K + Br2 \longrightarrow KBr + Br}$



The electron is like a harpoon, and the attraction due to coulombic attraction is the line of the harpoon.

The attractive force creates a larger cross-sectional reactive area than predicted by collision theory.

Before : Br_2

Energy = E

• K After

After : electrostatic attraction

Br_2^-

Energy = E’

• K^+

Since energy cannot be created nor destroyed.

Hence,

$$\Delta E' = 0 = I - E_a - \frac{e^2}{4\pi\varepsilon_\circ R_x} = 0$$

or, $$\Delta E = \frac{e_2}{4\pi\varepsilon_\circ R_x}$$

Harpoon Mechanism Calculation

$\rho = \frac{\sigma *}{\sigma}$ (apparent = $\sigma * / \sigma$ from simple collision theory) $R^* = R_x$ where d= R (K) + R (Br_2)

$$= \frac{R*^2}{d^2} = \left(\frac{e^2}{4\pi\varepsilon_\circ d(I - E_a)} \right)^2 \qquad (\textit{general formula})$$

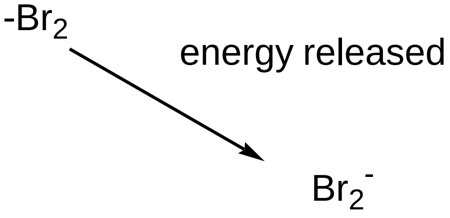
$$\sigma* = \pi R*^2$$

$$P = \frac{\sigma *}{\sigma} = \frac{R*^2}{d^2} = \left(\frac{e^2}{4\pi\varepsilon_\circ d(I - E_a)} \right)^2$$

$$d = R(K) + R(Br_2)$$

$\therefore$ -E_a

because energy has to be put in



= 250kJ mol-1

$\therefore$ -E_a I is +ve because energy has to be put in.

With I = 420 kJ mol^{-1} , Ea = 250kJ mol^{-1}

d= 400pm , P≈12

SCES 2230 Kimia Fizik 2.

1. Calculate the means speed and root-mean square speed of oxygen at 25 ^{o}C. Given gas constant = 8.314 J K mol^{-1}.
2. Use the means speed from question 1, calculate,
    a. Maxwell-boltzmann distribution of molecular velocity of O_2.
    b. Maxwellian probable distribution of speed.
    c. Probability density of oxygen.

3. With suitable diagram, describe
    a. collision diameter.
    b. Collision cross-section.

Answer to Class test (22/09/2003)

Q1. The Average (means) speed $\bar{c}$ is defined as $\bar{c} = \dfrac{c_1 + c_2 + ... + c_N}{N}$

$$\bar{c} = \sqrt{\frac{8kT}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} = \sqrt{\frac{8 \times 8.314 \times 298}{0.032\pi}} = 444.0ms^{-1}$$

Most probable speed,

$$c_{mp} = \sqrt{\frac{2kT}{m}} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times 8.314 \times 298}{0.032}} = 393.5ms^{-1}.$$

Root-means-square-speed $= c_{rms} = \sqrt{\dfrac{3RT}{M}} = \sqrt{\dfrac{3 \times 8.314 \times 298}{0.032}} = 481.9ms^{-1}$

Q2. Maxwell boltzmann distribution of molecular speed,

O_2= 32×10^{-3} kg mol^{-1}. T=25 ^{o}C=273+25=298 K, R=8.314 J K mol^{-1}.

k=1.38×10^{-23}. kt=4.11×10^{-21} J.

The mass of one oxygen molecule = 0.032/6.022×10^{23}=5.31×10^{-26} kg.

$$f(v_x)=\left(\frac{m}{2\pi kT}\right)^{1/2} e^{\left(-mv_x^2/2kT\right)}=\left(\frac{5.31\times10^{-26}}{2\pi\times4.11\times10^{-21}}\right)^{1/2} e^{\left(-5.31\times10^{-26}\times(293.5)^2/8.22\times10^{-21}\right)}$$

$f(v_x) = (2.056\text{x}10^{-6})^{0.5}\, e^{(-0.5546)} = (1.434\text{x}10^{-3})(0.57323) = 8.235\text{x}10^{-4}$ s m^{-1}.

k=J K^{-1} , J= kg m^2 s^{-2}

$$f(v_x)=4\pi v_x^2\left(\frac{m}{2\pi kT}\right)^{3/2} e^{\left(-mv_x^2/2kT\right)}=\left(\frac{5.31\times10^{-26}}{2\pi\times4.11\times10^{-21}}\right)^{1/2} e^{\left(-5.31\times10^{-26}\times(293.5)^2/8.22\times10^{-21}\right)}$$

Q3.

The decomposition of urea in 0.1 M HCl occurs according to reaction
$NH_2CONH_2 \;+\; 2H_2O \longrightarrow 2NH_4^+ \;+\; CO_3^{2-}$
The first order rate constant for this reaction was measured as a function of temperature, with the following results:

Temperature, °C	k, mins^{-1}
61.0	0.713×10^{-5}
71.2	2.77×10^{-5}

Calculate the activation energy, E_a, and the pre-exponential coefficient factor, A for this reaction.

Since, $k = Ae^{-E_a/RT} \Rightarrow \ln k = \ln A - \dfrac{E_a}{RT}$,

$1/T$, K^{-1}	ln k,
2.992×10^{-3}	-11.85
2.904×10^{-3}	2-10.49

WE can write, $\ln k_2 - \ln k_1 = -\dfrac{E_a}{R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$

Therefore we obtain, $E_a = -\dfrac{R.(\ln k_2 - \ln k_1)}{1/T_2 - 1/T_1}$

$$E_a = -\frac{\left(8.314JK^{-1}mol^{-1}\right)(-10.49 + 11.85)}{(2.904 - 2.992)\times 10^{-3}K^{-1}} = 128.5kJmol^{-1}$$

Rearrange the equation to obtain ln A,

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

$$\ln A = -10.49 + \frac{128.5}{0.008314 \times 344.4} = -10.49 + 44.84 = 34.35$$

therefore, A = 8.28×10^{14} min^{-1} = 1.38×10^{13} s^{-1}.

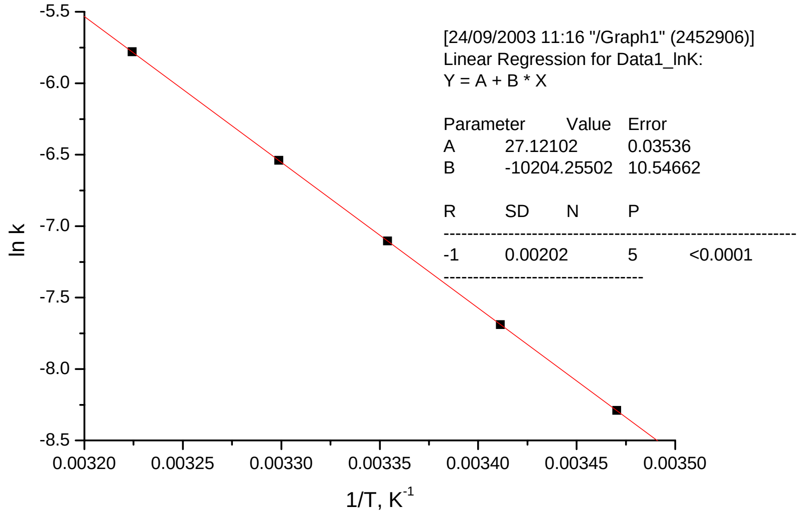
Question: An unstable metabolite decomposed very rapidly in aqueous solution at pH 7. At all temperature in the range 15 to 37 ^{o}C, the decomposition proceeded with first order kinetics and the following values were obtained for its 1st order rate constant.

Temperature/^{o}C	*Rate constant, k/s^{-1}*
15	2.51×10^{-4}
20	4.57×10^{-4}
25	8.22×10^{-4}
30	1.445×10^{-3}
37	3.09×10^{-3}

Determine from this findings the energy of activation of the decomposition.

Answer: $k = Ae^{-E_a/RT} \Rightarrow \ln k = \ln A - \dfrac{E_a}{RT}$

T, ^{o}C	k, s^{-1}	T, K	1/T, K^{-1}	ln k
15	2.51E-4	288.15	0.00347	-8.29006
20	4.57E-4	293.15	0.00341	-7.69083
25	8.22E-4	298.15	0.00335	-7.10377
30	0.00145	303.15	0.0033	-6.53965
37	0.00309	310.15	0.00322	-5.77958



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[24/09/2003 11:16 "/Graph1" (2452906)]
Linear Regression for Data1_lnK:
Y = A + B * X

Parameter       Value       Error
A          27.12102         0.03536
B          -10204.25502     10.54662

R          SD         N          P
------------------------------------------------------------
-1         0.00202               5          <0.0001
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```

$$slope = -\frac{E_a}{R} = \text{-}10204.255,$$

Therefore E$_a$ = (10204.255×8.314) = 84.84 kJ mol^{-1}.