



9jabaz

*Download more books at 9jabaz.ng for
free!*

KINETIC MOLECULAR THEORY OF GASES

- PRESSURE OF AN IDEAL GAS
- TEMPERATURE
- APPLICATION OF KINETIC THEORY IN IDEAL GAS LAWS
- DISTRIBUTION OF MOLECULAR SPEED IN IDEAL GASES
- APPLICATION OF MAXWELL DISTRIBUTION
- COLLISION WITH A WALL & EFFUSION
- MOLECULAR COLLISION AND ~~FREE~~ MEAN ^{FREE} PATH
- PRINCIPLE OF CONTINUITY OF STATE
- CRITICAL PHENOMENAL
- IDEAL GAS
- INTRODUCTION TO VAN DER WAAL EQUATION

What is being studied is the system
What keeps or guide the system is the boundary. Other part apart from the boundary and the system is the surroundings.

KINETIC MOLECULAR THEORY OF GASES

The ~~kinetic~~ kinetic theory of gases is employed in order to interpret the properties of gas molecules in a more quantitative manner.

Any time a theory is developed to account for experimental observations in a system is first defined - In a case in which all parts of a system are not understood, the no of assumptions are made \therefore the model for the kinetic theory of gases is based on the following assumptions:

1) Gas is made of a great no of atoms or molecules separated by distances that are large compared to their size.

The molecules have mass but their volume is ^{negligible} ~~small~~ relatively small \therefore gas is made up of point-like molecules.

2) The molecules are constantly in random motion.

3) Collisions among molecules and btw molecules and the walls of the containers are elastic, i.e. K.E may be transferred from one molecule to another but not converted to another.

forms of energy

5) There are no intermolecular interactions (neither attractions or repulsion)

- Point two of the K.T.O.G means that even though a sample of gas which contains n mol of molecules is filled in volume V, each individual particles has zero volume.

- Point three and four - The gas filled the volume V because each molecule in motion such that given enough time it explore the total extent of the volume available in the container.

When the molecule collide with each other or with the walls of the container, they exchange energy and momentum, there is no loss of energy when summed over the collision partner. Hence, the collision are elastic.

Ideal Gas Law

Studying the behaviour of gases has given rise to the no of chemical and physical theories.

The molecules of ideal gas possess no ^{proper} intrinsic vol and they neither

attract nor repel one another.

The equation ^{of state} obtained i.e. the

eqn that relates ^{the} a state

variable of the gaseous system

for ideal gas is given by

$$PV = nRT$$

where n is no of moles of the gas

T is temp in kelvin

R = gas constant
V = volume

The ideal gas eqn is an eqn

of state that tells us how the

state of the gas changes with

change in conditions of a gas.

No ideal gas exists in nature but

under relatively high temp that

is $\geq 25^\circ\text{C}$ and low pressure

then this eqn roughly will be the

behaviour of most gases.

The ideal gas eqn is as the

result of the accumulation of

the works of Robert Boyle's, Jacques Charles, Gay-Lussac

BOYLE'S LAW

He observed that the vol of a given amount of a gas is inversely proportional to its pressure when kept at a constant temperature.

$$P \propto \frac{1}{V} \text{ (T constant)} \quad \text{--- (I)}$$

$$PV = \text{constant}$$

$$P_1 V_1 = P_2 V_2 \text{ (T, n, T constant)} \quad \text{--- (II)}$$

Example: When 44.8 litres of a gas is held at a pressure of 0.50 atm, we

have Soln

$$P_1 V_1 = 0.5 \times 44.8 \\ = 22.4 \text{ Latm.}$$

Equation II enable us to calculate the pressure require to compress the quantity of gas to any other volume.

For example, if you want to hold this quantity of gas (22.4L), then we must define another system.

$$P_1 V_1 = P_2 V_2 ; P_2 = \frac{P_1 V_1}{V_2}$$

$$P_2 = \frac{22.4 \text{ Latm}}{22.4 \text{ L}} \\ P_2 = 1 \text{ atm}$$

If we have different volumes and pressure and we want to make it equal the one we change is the temperature.

CHARLES LAW

Also known as the law of Charles and Gay Lussac's.

States that when the pressure exerted on a gas is held constant the volume of a fixed quantity of gas is directly proportional to the absolute temperature.

$$V \propto T \text{ (n, P constant)}$$

V is constant at T

$$\frac{V}{T} = \text{constant (provided pressure is constant)}$$

When pressure (P) and the no of moles in the sample (n) are held constant, the ratio $\frac{V}{T}$ does not change and any two combinations of volume and temperature are related as follows:

$$\frac{V_1}{T_1} = \frac{V_2}{T_2}$$

Charles law take the following form if the volume and amount of gas are kept constant

$$\frac{P}{T} = \text{constant}$$

$$\frac{P_1}{T_1} = \frac{P_2}{T_2} \text{ (for constant n, V)}$$

$$\frac{N}{T} = \text{constant}$$

Avogadro's law states that at constant pressure and temperature, equal volume of gases contain the same no. of molecules. From the eqn of state for an

ideal gas,

$$\frac{V}{n} = \text{constant} \quad (P, T)$$

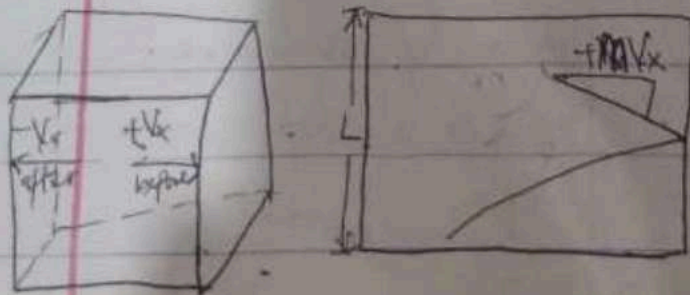
$$PV = nRT, \quad R = \frac{\text{constant}}{n}$$

PRESSURE OF A GAS

Using the model for the K.T.O.G, we

can derive an expression for the

pressure of a gas in terms of its molecular properties. Consider an ideal gas made up of N molecules each of mass, m , confined in a cubic box of length l .



At any instant the molecular motion inside

the container is completely random when a particle of mass m that is travelling with a component of velocity known as v_x parallel to the x -axis collide with the wall on the right, it is immediately reflected because the collision is elastic, the velocity after collision is the same as before. The

momentum of the molecule is $m v_x$. The change in momentum is given by $m v_x - m(-v_x) = 2m v_x$

Immediately after the collision, the molecule will take time $\frac{l}{v_x}$ to collide with the other wall.

To strike the same wall again, the molecule will take time $\frac{2l}{v_x}$.

Assumption:

We assume that the molecules does not collide with other molecules along the way. no collisions between molecules \therefore the frequency of collision b/w the molecules and the given wall is given by

$$f = \frac{V_x}{2l}$$

And change in momentum per unit time

$$= (2mV_x) \left(\frac{V_x}{2l} \right)$$

$$= \frac{mV_x^2}{l}$$

i.e. force

$$\text{Force} = \frac{\text{momentum}}{\text{time}} = \frac{mV_x^2}{l}$$

∴ the force, F , exerted by one molecule on one wall as a result of the collision

$$\text{is } \frac{mV_x^2}{l}$$

The total force, $F_{\text{total}} = \overset{\text{no. of collisions}}{N} \frac{mV_x^2}{l}$

$$\text{Pressure, } P = \frac{\text{Force}}{\text{Area}}$$

$$\text{Area} = l^2$$

$$P = \frac{NmV_x^2/l}{l^2} = \frac{NmV_x^2}{l^3}$$

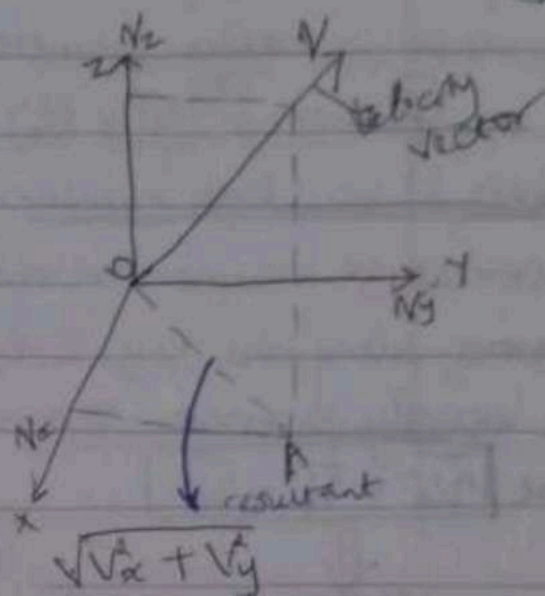
$$P = \frac{NmV_x^2}{V} \quad \text{where } V^3 = \text{Volume}$$

$$PV = NmV_x^2 \quad \text{--- (6)}$$

Let us analyze the motion of a particular molecule with velocity, N since it has both magnitude and direction,

the velocity N can be resolved in three mutually perpendicular components

V_x, V_y, V_z , these three components give the rate at which the molecule is moving along the x, y and z direction respectively, i.e. V is the resultant velocity.



The projection of the velocity on the xy plane is \overline{OA} which according to pythagoras theorem is given by

$$\overline{OA}^2 = \sqrt{V_x^2 + V_y^2}$$

$$\text{Similarly } V_x^2 = \overline{OA}^2 + V_z^2$$

$$V^2 = V_x^2 + V_y^2 + V_z^2 \quad \text{--- (7)}$$

From this consideration, V can be resolved into three mutually perpendicular components V_x, V_y and V_z . So the velocity molecule is given by equation (7)

When dealing with a large collection of molecules it is when $N = 6.2 \times 10^{23}$. Hence, it is there is a tremendous speed of molecular velocity. It is more appropriate to replace v_0^2 with the mean or average quantity v^2 .

The eqn becomes $\bar{v}^2 = \bar{v}_x^2 + \bar{v}_y^2 + \bar{v}_z^2$. When N is a large number, it is correct to assume that molecular motions along the x, y, z directions are equally probable. This means that $\bar{v}_x^2 = \bar{v}_y^2 = \bar{v}_z^2$

$$\Downarrow$$

$$3\bar{v}_x^2 = \bar{v}^2 \quad (9)$$

$$\bar{v}_x^2 = \frac{\bar{v}^2}{3} \quad (10)$$

From $P = \frac{1}{3} Nm \bar{v}^2$

Substituting $\bar{v}_x^2 = \frac{\bar{v}^2}{3}$

$$P = \frac{1}{3} Nm \bar{v}^2 \quad (11)$$

Multiply up and down by 2

$$P = \frac{2N}{3V} \left(\frac{1}{2} m \bar{v}^2 \right) \quad (12)$$

Translational Motion

is the movement of an object from one place to another.

Average Translational Motion

$$E_{\text{trans}} = \frac{1}{2} m \bar{v}^2$$

$$\therefore P = \frac{2N}{3V} E_{\text{trans}} \quad (13)$$

P is the pressure exerted by N molecule on one wall. From eqn 13,

pressure is directly proportional to the average kinetic energy OR

Considering eqn 12, pressure is directly proportional to the mean square velocity of the molecule

Hence, the larger the velocity, the more frequent the collisions and the greater the change in momentum.

KINETIC ENERGY & TEMPERATURE

If we consider the ideal gas eqn i.e $PV = nRT$

$$= \frac{N}{N_A} RT \quad (14)$$

$N_A = \text{Avogadro's constant} = 6.02 \times 10^{23} \text{ mol}^{-1}$

Combining the pressures in eqn 13 & 14,

$$\text{we get } P = \frac{2N}{3V} E_{\text{trans}}$$

$$P = \frac{N}{N_A} \frac{RT}{V}$$

$$\frac{2N}{3V} E_{\text{trans}} = \frac{N}{N_A} \frac{RT}{V}$$

$$\bar{E}_{\text{trans}} = \frac{3}{2} \frac{RT}{N_A} = \frac{3}{2} k_B T \quad (15)$$

where $k_B = \frac{R}{N_A}$ is the Boltzmann Constant

$$k_B = 1.3806488 \times 10^{-23} \text{ J K}^{-1} \\ \approx 1.381 \times 10^{-23} \text{ J K}^{-1}$$

From eqn (15) we see that the mean K.E of one molecule is proportional to absolute temperature

$$\text{i.e. } \bar{E}_{\text{trans}} \propto \frac{3}{2} k_B T$$

$$\bar{E}_{\text{trans}} \propto T$$

Eqn (15) also tells us that whenever two ideal gases are at the same temp.

T, they must have the same average kinetic energy. This means that

\bar{E}_{trans} is independent of molecular species

such as size, molar mass or amount of gas present as long as N is a large number.

$$\text{If } \bar{E}_{\text{trans}} = \frac{1}{2} m \bar{v}^2 = \frac{3}{2} \frac{RT}{N_A}$$

$$\therefore \frac{1}{2} m \bar{v}^2 = \frac{3}{2} k_B T$$

$$\bar{v}^2 = \frac{3RT}{m N_A} = \frac{3k_B T}{m}$$

Finding the square root of the sides

$$\sqrt{\bar{v}^2} = v_{\text{rms}} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3k_B T}{m}} \quad (16)$$

m = mass in kg of 1 molecule
 M = molar mass in kg mol^{-1}

where $M = m N_A$ and $v_{\text{rms}} = \sqrt{\bar{v}^2}$

Eqn (16) shows that root-mean-square

velocity is directly proportional to the square root of temp and

inversely proportional to the square root of molar mass

$$v_{\text{rms}} \propto \sqrt{T}$$

$$v_{\text{rms}} \propto \frac{1}{\sqrt{M}}$$

The heavier the molecules, the slower the motion

e.g. The root-mean-square velocity of methane is 846 m s^{-1} at 20°C is the temp. of the gas.

(1) Cal. the average translational

K.E for nitrogen molecule, N_2 (11)

and for one mole of N_2 at 20°C

Soln

$$v_{\text{rms}} = \sqrt{\frac{3RT}{M}}$$

$$846 = \sqrt{\frac{3 \times 8.314 \times T}{0.016}}$$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

Molar mass of methane = $0.016 \text{ kg mol}^{-1}$

$$846^2 = \frac{3 \times 8.314 \times T}{0.016}$$

$$T = 459.12 \text{ K}$$

25/11/2022

Soln to Q55

$$2D) E_{trans} = \frac{3}{2} k_B T \quad \text{For large number of molecules, they don't specify}$$

$$k_B = 1.381 \times 10^{-23} \text{ J K}^{-1}$$

$$T = 293 \text{ K}$$

$$E_{trans} = \frac{3}{2} \times 1.381 \times 10^{-23} \text{ J K}^{-1} \times 293 \text{ K}$$

$$= 6.07 \times 10^{-21} \text{ J}$$

$$(u) \text{ For one mol; } PV = nRT \quad n = 1 \text{ mol}$$

$$E_{trans} = \frac{3}{2} RT \quad \therefore PV = nRT \quad \therefore E_{trans} = \frac{3}{2} RT$$

$$= \frac{3}{2} \times 8.314 \text{ J K}^{-1} \times 293 \text{ K}$$

$$= 3.65 \times 10^3 \text{ J mol}^{-1}$$

25/11/2022

Soln to Q55

3) To what temp must helium atoms be cooled so that they have the same V_{rms} as O_2 at 25°C

Soln

$$V_{rms} = \sqrt{\frac{3RT}{M}} \quad , T_{oxygen} = 298 \text{ K}$$

$$\sqrt{\frac{3RT}{M}}_{oxygen} = \sqrt{\frac{3RT}{M}}_{helium}$$

$$\sqrt{\frac{3 \times 8.314 \times 298}{0.032}} = \sqrt{\frac{3 \times 8.314 \times T}{0.004}}$$

$$T = 37.25 \text{ K}$$

DISTRIBUTION OF MOLECULAR SPEED IN IDEAL GASES

While deriving the kinetic gas eqn, it was assumed that all molecules in a gas have the same velocity, but it is not so; when any two molecule collide, one molecule transfers K.E ($\frac{1}{2}mv^2$) to the other molecule. The velocity of the molecule which gains energy increases and that of the other decreases.

In studying, for example, a sample of a gas, the velocity of each individual molecule is difficult to know cuz of the huge no. of molecules and cuz the velocities of molecules are changing constantly. Due to the large no. of molecules, there is a continuous spread or distribution of velocities as a result of collision. So instead of considering individual molecular velocity, it is convenient to consider the no. of molecules moving at velocities, many

at v and $v+dv$ at any moment for a given system at some known temperature.

For example, how many molecules in a macroscopic gas sample have velocities btw 407.4 and 407.5 at any moment:

This distribution of velocity's approach was first employed by a Scottish physicist James Clerk Maxwell in 1860 and later refined by Boltzmann; they showed that for a system containing N ideal gas molecules at thermal equilibrium with its surroundings the fraction of molecule $\frac{dN}{N}$

moving at velocities btw v_x and v_x+dv_x along the x -direction is given by

$$\frac{dN}{N} = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/2k_B T} \cdot dv_x$$

$$= f(v_x) dv_x$$

where m = mass of the molecule
 k_B = Boltzmann's constant
 T = Absolute temperature

The quantity $f(v_x)$ is the Maxwell velocity distribution function in one direction.

$$f(v_x) = \left(\frac{m}{2\pi k_B T}\right)^{1/2} e^{-mv_x^2/2k_B T}$$

Velocity is a vector quantity, in any case, we need to deal only with the speed of molecule, C , which is a scalar quantity, therefore, the fraction of molecules

$\frac{dN}{N}$ moving btw speed C and

$$C+dC \text{ is given by}$$

$$\frac{dN}{N} = 4\pi C^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mC^2/2k_B T} dC$$

$$= f(C) dC$$

where $f(C)$ is the Maxwell speed distribution function is given by

$$f(C) = 4\pi C^2 \left(\frac{m}{2\pi k_B T}\right)^{3/2} e^{-mC^2/2k_B T}$$

dN = no. of molecules having speed between C and $C+dC$
 N is the total no. of molecule

16/01/2022

M = molecular mass
 T is temp in kelvin
 K_B = Boltzmann's constant

The relation above is called Maxwell law of distribution of velocities.

The dependence of the Velocity Distribution Curve on Temp. and Molecular mass

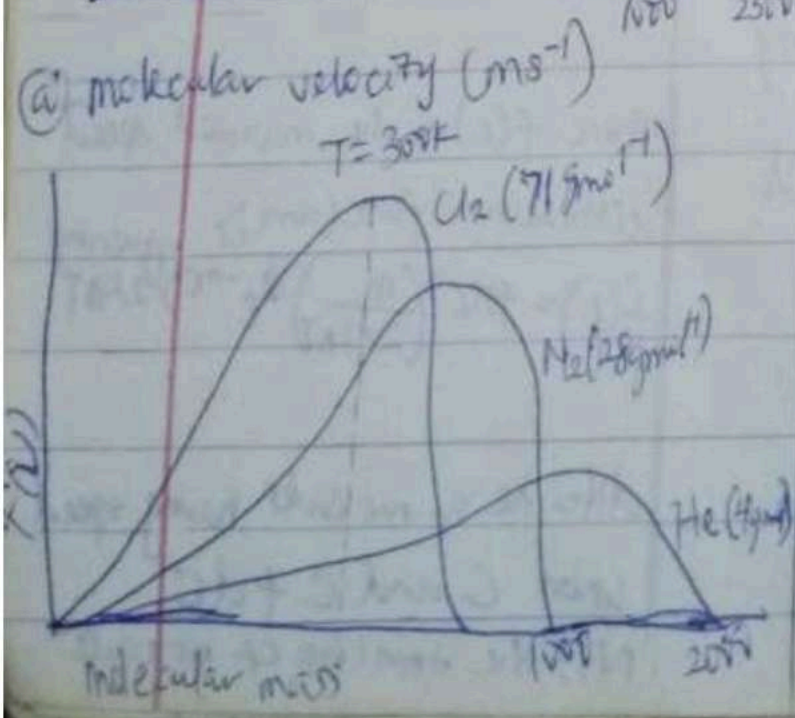
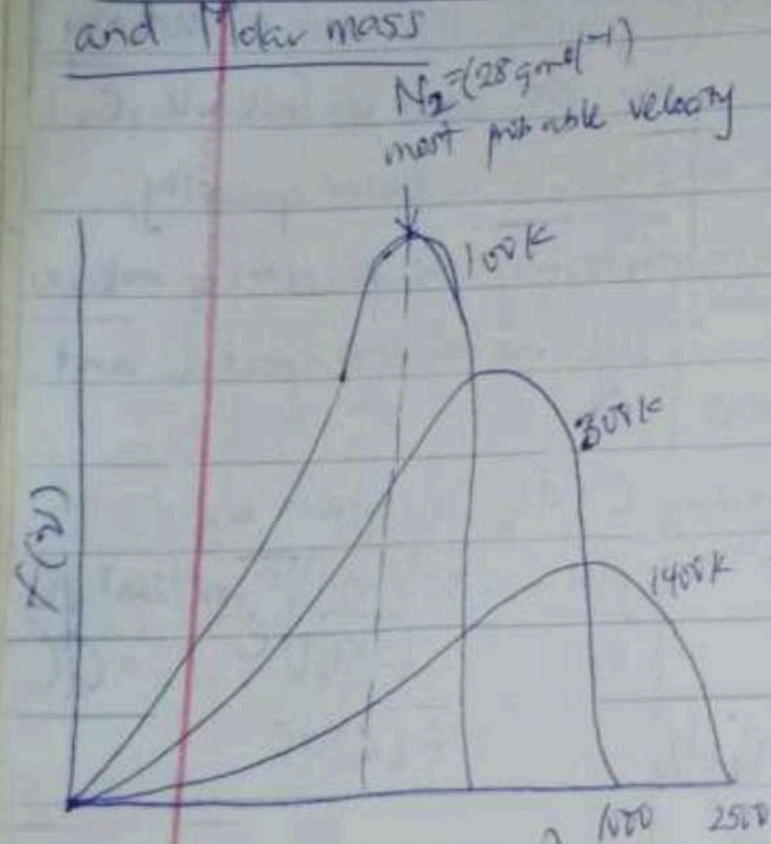


Figure (a) represents the distribution of velocities in nitrogen gas. The figure shows how the distribution curve is influenced by temperature. It can be seen that a very small fraction of molecules have either very low (close to 0) or very high velocities. At low temp the distribution has a rather narrow range. As the temp increases, the curve becomes flatter, meaning that there are now more fast moving molecules. This shows that at high temp, more molecules have higher velocities and fewer molecules have lower velocities.

The speed corresponding to the maximum value $f(v)$ is called the most probable speed i.e. C_{mp} , it is the speed possessed by the largest fraction of molecules. In figure (b) we see that heavier gases have a narrower

range of speed distribution than lighter gases at the same temperature, so heavier gases move slower. The usefulness of the Maxwell speed distribution is it enables us to cal. average quantities.

Consider the mean speed \bar{c} of a large collection of molecules at some temperature, T , the mean speed is calculated by multiplying each speed by the fraction of molecules that have that speed and then adding all the products together. But the fraction of molecules with a speed in the range c to $(c+dc)$ is $f(c)dc$; $f(c)$ is the ^{function} distribution; the product of this fraction and the speed = $c f(c)dc$

Thus, the mean speed, \bar{c} , is obtained by evaluating the integral b/w limits

$$c=0 \text{ and } c=\infty$$

$$\bar{c} = \int_0^{\infty} c f(c) dc$$

From eqn * * *

$$\bar{c} = \int_0^{\infty} \left(c \cdot 4\pi c^2 \left(\frac{m}{2\pi k_B T} \right)^{3/2} e^{-\frac{mc^2}{2k_B T}} dc \right)$$

$$\bar{c} = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \int_0^{\infty} c^3 e^{-\frac{mc^2}{2k_B T}} dc$$

From standard integrals we find that

$$\int_0^{\infty} x^3 e^{-ax^2} dx = \frac{1}{2a^2} \text{ where } a = \frac{m}{2k_B T}$$

$$\text{Thus, } \bar{c} = 4\pi \left(\frac{m}{2\pi k_B T} \right)^{3/2} \times \frac{1}{2} \left(\frac{2k_B T}{m} \right)^2$$

$$\bar{c} = \sqrt{\frac{8k_B T}{\pi m}} = \sqrt{\frac{8RT}{\pi M}} \quad \#$$

Eqn # gives the average speed, coz the square of the average velocity is a scalar quantity, then it follows that $\sqrt{\bar{v}^2} = \bar{c}$

$$\therefore \bar{c} = \sqrt{\bar{v}^2}$$

According to the cal. made by Maxwell, the most probable velocity is given by the expression

$$v_{mp} = \sqrt{\frac{2k_B T}{m}} = \sqrt{\frac{2RT}{M}} \quad \#$$

$$v_{rms} = \sqrt{\frac{3RT}{M}} \quad v_{mp} = \sqrt{\frac{2RT}{M}} \quad \bar{v} = \sqrt{\frac{8RT}{\pi M}} \quad v_{rms} = 483.5 \text{ ms}^{-1}$$

Relationship between average velocity

v_{rms} & most probable velocity

- Divide \bar{v} by v_{rms}

$$\sqrt{\frac{8RT}{\pi M}} \times \sqrt{\frac{M}{3RT}} = \sqrt{\frac{8}{3\pi}}$$

$$= 0.9213$$

$$\bar{v} = v_{rms} \times 0.9213$$

- $v_{mp} \div v_{rms}$

$$\frac{v_{mp}}{v_{rms}} = \frac{\sqrt{2RT}}{\sqrt{3RT}} \times \sqrt{\frac{M}{M}} = \sqrt{\frac{2}{3}}$$

$$= \sqrt{\frac{2}{3}} = 0.8165$$

$$v_{mp} = 0.8165 v_{rms}$$

Example: Cal. v_{mp} , \bar{v} and v_{rms}

for oxygen at 300K. $R = 8.314 \text{ J/Kmol}$

Molar mass oxygen = 0.032 kg/mol

Soln

$$v_{mp} = \sqrt{\frac{2RT}{M}} = \sqrt{\frac{2 \times 8.314 \times 300}{0.032}}$$

$$= 394.8 \text{ ms}^{-1}$$

$$v_{mp} = 0.8165 v_{rms}$$

$$v_{rms} = \frac{394.8}{0.8165}$$

$$\bar{v} = v_{rms} \times 0.9213 = 483.5 \times 0.9213 = 445.4 \text{ ms}^{-1}$$

Calculation of molecular speed when temperature is given

2) Cal. the v_{rms} of CO_2 molecule at 1000°C .
 $v_{rms} = \sqrt{\frac{3RT}{M}} = \sqrt{\frac{3 \times 8.314 \times 1273}{0.044}} = 849.5 \text{ ms}^{-1}$

3) Calculation of molecular speed when both temp. and pressure are given

In such cases, we make use of the following relation in calculating such gases

$$PV = nRT$$

$$v_{rms} = \sqrt{\frac{3PV}{M}} \quad MP = PV = RT \text{ at } n=1 \text{ mol}$$

All know that 1 mol of a gas at STP occupy a vol of 22.4 litre known as molar volume. But before applying this relation, the molar volume is reduced to the given conditions of temperature and pressure.

$$1 \text{ atm} = 760 \text{ torr} = 101,325 \text{ Pa} = 101,325 \text{ kg m}^{-1} \text{ s}^{-2}$$

Calc the rms of Cl_2 at 12°C and 780 Torr

$$1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ Torr}$$

At stp, $V = 22.4 \text{ L mol}^{-1}$, $T_1 = 273 \text{ K}$

$$P_1 = 760 \text{ Torr}$$

$$T_2 = 12 + 273 = 285 \text{ K}, P_2 = 780 \text{ Torr},$$

$$V_2 = ?$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

$$\frac{760 \times 22.4}{273} = \frac{780 \times V_2}{285}$$

$$V_2 = 22.785 \text{ L mol}^{-1} = \frac{22.785 \times 10^{-3} \text{ m}^3}{\text{mol}}$$

$$V_{\text{rms}} = \sqrt{\frac{3PV}{M}} = \sqrt{\frac{3 \times 780 \times 22.785}{M}}$$

$$760 \text{ torr} = 101,325 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$780 \text{ torr} = 103,991.45 \text{ kg m}^{-1} \text{ s}^{-2}$$

$$M = 0.071 \text{ kg mol}^{-1}$$

$$V_{\text{rms}} = \sqrt{\frac{3 \times 103,991.45 \times 22.785}{0.071}}$$

$$= 3164 \text{ m s}^{-1}$$

Calc of Molecular Velocity at STP

Calc the \bar{V} of Na at stp

$$\bar{V} = \sqrt{\frac{8PV}{\pi M}}$$

$$= \sqrt{\frac{8 \times 101,325 \times 22.4 \times 10^{-3}}{\pi \times 0.028}} \times 101,325$$

Calc. of Molecular velocity when Pressure and density are given.

$$V_{\text{rms}} = \sqrt{\frac{3PV}{M}}; \text{ Density} = \frac{M}{V}$$

$$= \sqrt{\frac{3P}{D}}$$

Oxygen at 1 atm and 0°C , has a density of 1.429 g L^{-1} . Find the root-mean square velocity of oxygen molecule

Soln $D = 1.429 \text{ g L}^{-1} = 1.429 \times 10^{-3} \text{ kg m}^{-3}$

$$V_{\text{rms}} = \sqrt{\frac{3 \times 101,325}{1.429 \times 10^{-3} \text{ kg m}^{-3}}}$$

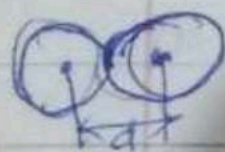
$$= 461.2 \text{ m s}^{-1}$$

Calc. the \bar{V}_{rms} of Cl_2 at

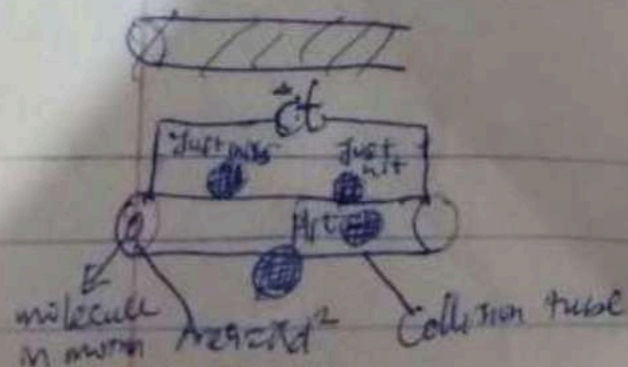
Molecular Collision &

The Mean Free Path

The collision frequency of the molecules of a gas depends on the density of a gas and the molecular velocity and \therefore on the temp. of the system. According to the kinetic theory model, each molecule is assumed to be a hard sphere of diameter, d . A molecular collision is one in which the separation b/w the two spheres measured from the centre is d . The closest distance b/w centres of the two molecules taking part in collision is known as Molecular



Diameter



If we consider the motion of a particular molecule. Let's assume that at a given instance, all molecules except this one are standing still. In time ct , this molecule moves a distance of Ct where \bar{C} is the average speed.

Cross sectional area of the cylinder is πd^2 which is the collision cross section of the molecule - The volume V will be $V = \pi d^2 (\bar{C}t)$

25/01/2022

Any molecule whose centre lies within this cylinder will collide with the moving molecule. If N is the no. of molecule in volume, V , the no. density of the gas will be given as $\frac{N}{V}$ and

the no. of collisions in time t will be given as $\pi d^2 ct \left(\frac{N}{V}\right)$

The collision frequency, Z_{11} is

no of collision per unit time is given as: $Z_1 = \pi d^2 \bar{c} \left(\frac{N}{V}\right)$

Note: Correction of the expression of the collision frequency! We had assumed that all other molecules are frozen in position, now, if we assume that the rest of the molecules are not frozen in position, then, \bar{c} should be replaced average relative velocity; $\sqrt{2}\bar{v}$

Collision frequency: $Z_1 = \sqrt{2} \pi d^2 \bar{v} \left(\frac{N}{V}\right)$ collisions s^{-1}

This is the no of collisions a single molecule makes in one second. Since there are N molecules in volume V , each will make Z_1 collisions s^{-1} . \therefore the total no of binary collisions (collisions btw two molecules) per unit volume per unit time is given as

$Z_{11} = \frac{1}{2} Z_1 \left(\frac{N}{V}\right)$
 $Z_{11} = \frac{\sqrt{2}}{2} \pi d^2 \bar{v} \left(\frac{N}{V}\right)^2$ collisions $m^{-3} s^{-1}$

The factor $\frac{1}{2}$ is introduced to ensure that we are counting each collision btw two molecules only once.

The probability of three or more molecules colliding at once is very small except at high pressure.
~~Free~~

The Mean Free Path

The distance travelled by the molecule b/w collision is termed free path. Curz the free path for a molecule varies from time to time, their mean is calculated.

Mean free path is the distance travelled by a molecule b/w successive collisions.

If $l_1, l_2, l_3 \dots$ are the free path for a molecule

$\lambda = \frac{l_1 + l_2 + l_3 \dots l_n}{n}$

n is the no of molecules with which the molecule collide

The mean free path depends on pressure, density and viscosity of the gas and it is given as

~~$\lambda = \frac{1}{\sqrt{2} Z_1}$~~
 $\lambda = \frac{1}{\sqrt{2} Z_1}$

P = Pressure of the gas

ρ = Density

η = Coefficient of viscosity of the gas

Mean density can also be given as

$$\rho = \frac{N}{V} \times \lambda = (\text{average velocity}) \times (\text{average time btw collision})$$

Note: average time btw collision is the reciprocal of the collision frequency

$$\lambda = \frac{\bar{v}}{\sqrt{2} \pi d^2 \left(\frac{N}{V}\right)}$$
$$= \frac{1}{\sqrt{2} \pi d^2 \left(\frac{N}{V}\right)}$$

From eqn f it can be seen that the mean free path is inversely proportional to the no density of the gas.

The mean free path can also be expressed in terms of the gas pressure. Assuming ideal behaviour,

$$PV = nRT$$

$$n = \frac{\text{no. molecules}}{\text{Avogadro's constant}} = \frac{N}{M_A}$$

Substituting this in eqn f

$$PV = \frac{NRT}{M_A}$$

$$\frac{N}{V} = \frac{P M_A}{RT}$$

$$\lambda = \frac{RT}{\sqrt{2} \pi d^2 P M_A}$$

E.g. The concentration of dry air at 1.0 atm and 298K is about 2.5×10^{19} molecules cm^3 . Assuming that air contains only nitrogen molecules, calc. the collision

frequency (i) the binary collision

no. (ii) the mean free path of

N_2 molecule under this condition

The collision diameter of nitrogen

is 375 \AA ; $1 \text{ \AA} = 10^{-8} \text{ cm}$

Soln

$$v_r = \sqrt{\frac{5RT}{\pi M}}$$

$$= 4.5 \times 10^2 \text{ ms}^{-1}$$

(i) Collision frequency

$$Z = \sqrt{2} \pi d^2 \bar{v} \left(\frac{N}{V}\right)$$

$$= \sqrt{2} \pi (3.75 \times 10^{-8} \text{ cm})^2 (4.8 \times 10^4 \text{ cm s}^{-1})$$

$$(2.5 \times 10^{19} \text{ molecules cm}^{-3})$$

$$= 7.5 \times 10^9 \text{ collisions s}^{-1}$$

(ii) Binary collision no

$$Z_{11} = \frac{Z_1}{2} \left(\frac{N}{V}\right)$$

$$= \frac{1}{2} Z_1 \left(\frac{N}{V}\right)$$

$$= \frac{1}{2} \times 7.5 \times 10^9 \times (2.5 \times 10^{19} \text{ molecules cm}^{-3})$$

$$= 9.4 \times 10^{28} \text{ collisions cm}^{-3} \text{ s}^{-1}$$

Note! that we have replaced the unit molecules with collision cur in the derivation of Z_1 , every molecule in the collision volume represents a collision.

(iii) Mean free path = $\frac{\text{average velocity}}{\text{collision frequency}}$

$$= \frac{4.8 \times 10^4 \text{ cm s}^{-1}}{7.5 \times 10^9 \text{ collisions s}^{-1}}$$

$$= 6.4 \times 10^{-6} \text{ cm collision}^{-1}$$

$$= 640 \text{ \AA} \text{ collision}^{-1}$$

Cal. the mean free path and the binary no. of collisions per litre per second btw hydrogen iodide molecules at 300K at 1.00 atm.

The collision diameter of the hydrogen iodide molecules may be taken to be 5.10 \AA . Assume ideal gas behaviour.

2) At 0°C and 1 atm, the molecular diameter of a gas is approximately 4 \AA . Cal. the mean free path of its molecule.

(b) If the molecular mass of the gas is 28 g mol^{-1} , what is the average speed of the gas?

3) The v_{rms} of hydrogen at s.t.p. is equal to $1.83 \times 10^5 \text{ cm s}^{-1}$ and its mean free path is $1.78 \times 10^{-5} \text{ cm}$. Cal. the collision no. at s.t.p.

Soln

1) For ideal gas behaviour

$$\lambda = \frac{RT}{\sqrt{2} \pi d^2 P N_A}$$

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

$$T = 300 \text{ K}$$

$$d = 5.10 \times 10^{-10} \text{ m}$$

$$P = 1.01325 \times 10^5 \text{ Pa}$$

$$N_A = 6.02 \times 10^{23} \text{ mol}^{-1}$$

$$\lambda = 8.538 \times 10^{-5} \text{ m}$$

$$b) PV = nRT$$

$$n = \frac{N}{N_A}$$

$$PV = \frac{N}{N_A} RT$$

$$PN_A = \frac{N}{V} RT$$

$$\frac{PN_A}{RT} = \frac{N}{V}$$

$$\frac{101325 \times 6.02 \times 10^{23}}{8.314 \times 300}$$

$$=$$

$$\text{Collision frequency } Z_1 = \sqrt{2} \pi d^2 \bar{v} \left(\frac{N}{V} \right)$$

$$\bar{v} = \frac{\sqrt{8RT}}{\sqrt{\pi M}} = \frac{\sqrt{8 \times 8.314 \times 300}}{\sqrt{\pi \times 0.028}}$$

=

$$Z_1 = \sqrt{2} \times \pi \times (5.10 \times 10^{-10})^2 \times$$

=

$$Z_{11} = \frac{Z_1}{2} \left(\frac{N}{V} \right)$$

=

=

$$= 1.27 \times 10^{29} \text{ collisions cm}^{-3} \text{ s}^{-1}$$

$$a) \lambda = \frac{l}{\sqrt{2} \pi d^2 \left(\frac{N}{V} \right)}$$

$$\text{At STP, } \frac{N}{V} = \frac{6.02 \times 10^{23} \text{ molecules}}{22400 \text{ cm}^3}$$

$$= 2.688 \times 10^{19} \text{ molecules cm}^{-3}$$

$$\lambda = \frac{l}{\sqrt{2} \times \pi \times (4 \times 10^{-8})^2 \times (2.688 \times 10^{19})}$$

$$= 5.23 \times 10^{-6} \text{ cm}$$

$$b) \bar{v} = \frac{\sqrt{8RT}}{\sqrt{\pi M}}$$

$$= \frac{\sqrt{8 \times 8.314 \times 273}}{\sqrt{\pi \times 0.028}} = 454.39 \text{ ms}^{-1}$$

$$c) \bar{v} = v_{rms} \times 0.9213$$

$$\bar{v} = 1.83 \times 10^5 \text{ cm s}^{-1} \times 0.9213$$

$$= 1.78 \times 10^5 \text{ cm s}^{-1} \quad (168597.9 \text{ cm s}^{-1})$$

$$\lambda = \frac{\bar{v}}{Z_1}$$

$$Z_1 = \frac{\bar{v}}{\lambda} = \frac{168597.9 \text{ cm s}^{-1}}{1.78 \times 10^5 \text{ cm}}$$

$$= 9.47 \times 10^9 \text{ collisions s}^{-1}$$

$$\text{Collision no: } Z_{11} = \frac{Z_1}{2} \left(\frac{N}{V} \right)$$

$$= \frac{9.47 \times 10^9}{2} \left(\frac{6.02 \times 10^{23}}{22400 \text{ cm}^3} \right)$$

$$= 1.27 \times 10^{29} \text{ collisions cm}^{-3} \text{ s}^{-1}$$

CHEMICAL KINETICS

(pseudo-first order rxn)
 where one of the reactant
 is not appreciably
 consumed (e.g. H_2O) while
 the other is consumed

Rate of reaction

mechanism of reaction

Rate of reaction is the change in conc of a reactant or product per time.

Rate = $\frac{\text{Change in concentration of reactant or product}}{\text{time taken}}$

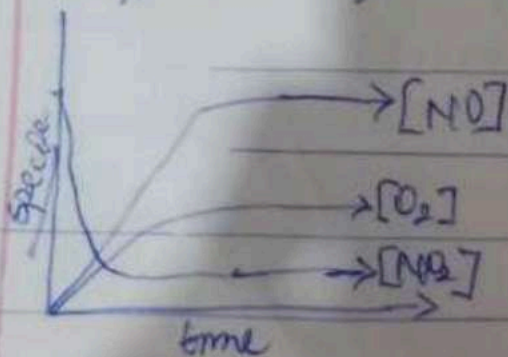
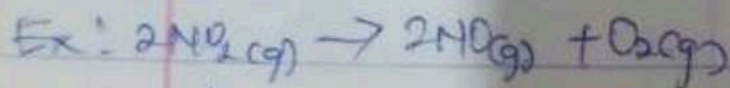
$$= \frac{\Delta[\text{reactant}] \text{ or } [\text{product}]}{\Delta t}$$

(Always positive)

$$\text{Rate} = \frac{\Delta[A]}{\Delta t} = \frac{[A]_f - [A]_i}{t}$$

given that $[A]_f < [A]_i \Rightarrow [A]_f - [A]_i = -ve$

\therefore As rate is always +ve, then $R = \frac{-\Delta[A]}{\Delta t}$



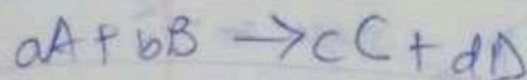
Rate constant is only a
 constant at a particular temp.
 Its magnitude is affected
 by temp. only

Average rate (up to 50 min)

$$\text{Average rate} = \frac{[\text{NO}_2]_{50\text{min}} - [\text{NO}_2]}{50\text{min}}$$

Instantaneous rate $\frac{\text{Change in concy. NO}_2}{50 \text{ min}}$

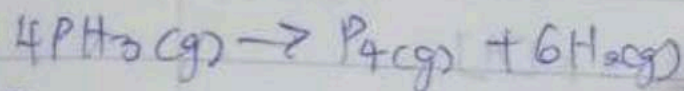
To confirm rate of rxn is always the same.



$$\text{Rate} = -\frac{1}{a} \frac{\Delta[A]}{\Delta t} = -\frac{1}{b} \frac{\Delta[B]}{\Delta t}$$

$$= +\frac{1}{c} \frac{\Delta[C]}{\Delta t} = +\frac{1}{d} \frac{\Delta[D]}{\Delta t}$$

Consider the rxn.



If in a certain experiment, over a specific time period 4.8×10^{-3} mole of PH_3 is consumed in a 2L container giving each sec of the rxn. What is the rate P_4 and H_2 in this experiment?

Soln

$$[\text{PH}_3] = \frac{4.8 \times 10^{-3} \text{ mol}}{2 \text{ dm}^3} = 2.4 \times 10^{-3} \text{ mol/dm}^3$$

$$\text{Rate} = -\frac{1}{4} \frac{\Delta[\text{PH}_3]}{\Delta t} = \frac{\Delta[\text{P}_4]}{\Delta t} = \frac{1}{6} \frac{\Delta[\text{H}_2]}{\Delta t}$$

$$\frac{\Delta[\text{P}_4]}{\Delta t} = \frac{1}{4} \text{PH}_3 \left[\frac{2.4 \times 10^{-3}}{1 \text{ s}} \right] \text{ mol/dm}^3 \text{ s}^{-1} = 6.0 \times 10^{-4} \text{ mol/dm}^3 \text{ s}^{-1}$$

Similarly, $\frac{\Delta[\text{H}_2]}{\Delta t} = \frac{6}{4} \left[\frac{2.4 \times 10^{-3} \text{ mol/dm}^3}{1 \text{ s}} \right] = 3.6 \times 10^{-3} \text{ mol/dm}^3 \text{ s}^{-1}$

$$\frac{\Delta[\text{P}_4]}{\Delta t} = \frac{1}{4} \left[\frac{2.4 \times 10^{-3} \text{ mol/dm}^3}{1 \text{ s}} \right] = 6.0 \times 10^{-4} \text{ mol/dm}^3 \text{ s}^{-1}$$

$$\frac{\Delta[\text{H}_2]}{\Delta t} = \frac{1}{6} \left[3.6 \times 10^{-3} \text{ mol/dm}^3 \right] = 6.0 \times 10^{-4} \text{ mol/dm}^3 \text{ s}^{-1}$$

Ass

Consider the general reaction $aA + bB \rightarrow cC$ and the following average rate over a specific period

$$\frac{-\Delta[A]}{\Delta t} = 0.0080 \text{ mol L}^{-1} \text{ s}^{-1}$$

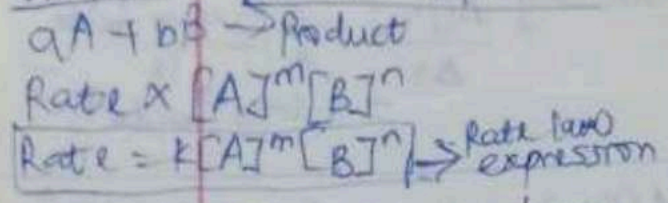
$$\frac{-\Delta[B]}{\Delta t} = 0.0120 \text{ mol L}^{-1} \text{ s}^{-1}$$

$$\frac{\Delta[C]}{\Delta t} = 0.0160 \text{ mol L}^{-1} \text{ s}^{-1}$$

Determine a set of possible coefficients to balance this general reaction.

The rate of any rxn is directly proportional to the conc of the reactant.

8/2/2022 Rate Law Expression

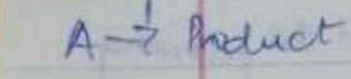


where $k \rightarrow$ Rate constant / specific rate
 $m =$ order of the rxn with respect to $[A]$

$n =$ order of the rxn with respect to B

There are several methods to determine rate of reaction:

① Integral rate method



Rate = $k[A]^m$

Since $A =$ reactant and is being consumed with time, it can be

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

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

Zeroth order (unit is $\text{mol dm}^{-3} \text{s}^{-1}$)
 If $m = 0$

$\Rightarrow -d[A] = k dt$

OR $\int d[A] = -\int k dt + C$

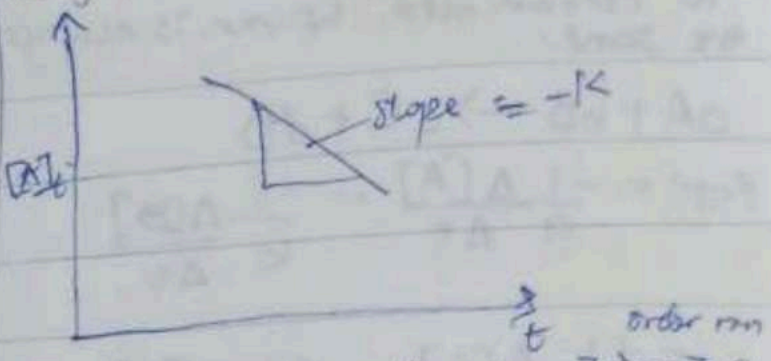
$[A]_t = -kt + C$

at time $t = 0, [A]_0 = [A]_0$

$\Rightarrow [A]_0 = 0 + C$

$[A]_t = -kt + [A]_0$
 Zero order

If a rxn is a zero order of A , the graph is given below



If the slope = $-k$, then it is a zero

If $m = 1$ (ie it is a first order rxn)

Rate = $k[A]^m$ (unit s^{-1})

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

$\int \frac{d[A]}{[A]} = -k \int dt + C$

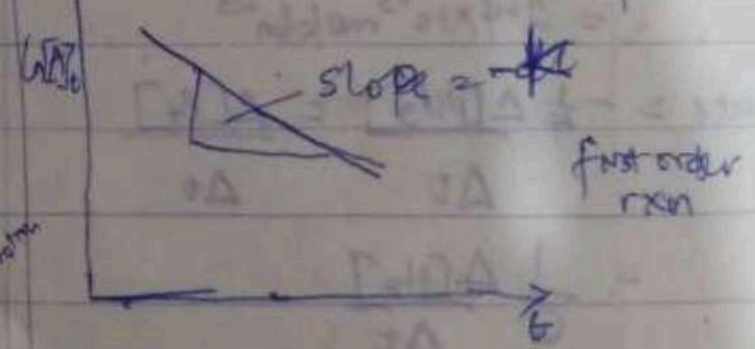
Recall $\int \frac{1}{x} dx = \ln x + C$

$\ln [A]_t = -kt + C$

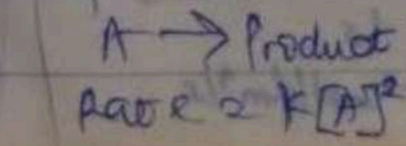
At time $t = 0$

$\ln [A]_0 = C$

implies $\ln [A]_t = -kt + \ln [A]_0$
 first order



If $m = 2$ (2nd order)



$$\text{i.e. } \int \frac{d[A]}{[A]^2} = -k \int dt + C$$

$$\int [A]^{-2} d[A] = -k \int dt + C$$

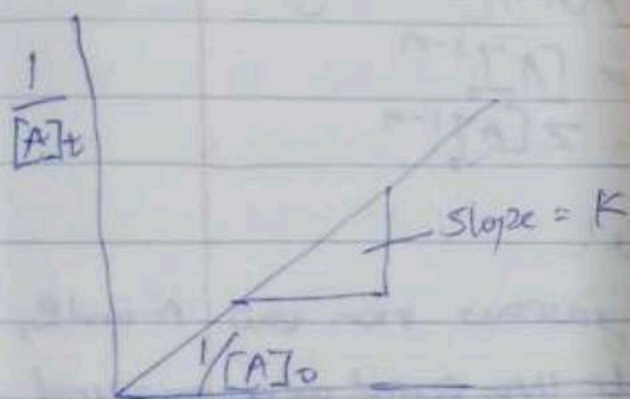
$$-\frac{1}{[A]_t} = -kt + C$$

at time $t = 0$, $[A]_t = [A]_0$

$$\Rightarrow -\frac{1}{[A]_0} = C$$

$$\Rightarrow -\frac{1}{[A]_t} = -kt - \frac{1}{[A]_0}$$

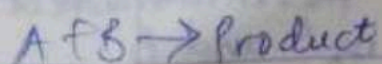
OR $\boxed{\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}}$ 2nd order



(Unit: $\text{mol}^{-1} \text{s}^{-1}$) or $\text{mol}^{-1} \text{dm}^3 \text{s}^{-1}$)

2) Isolation method:

Consider this rxn.



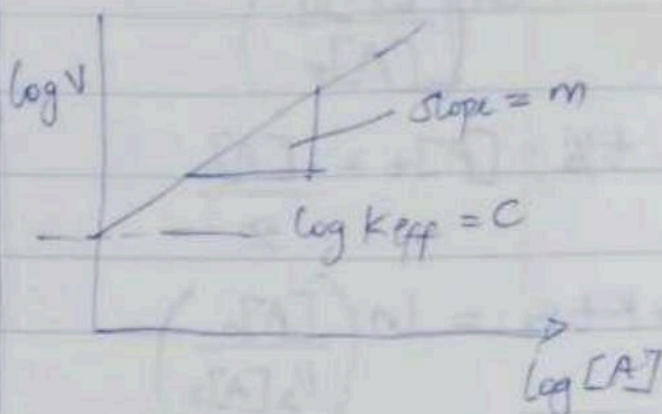
B is in excess

We can only measure the rate with respect to A

$$v = k_{\text{eff}} [A]^m \text{ where } k_{\text{eff}}$$

$$= k [B]^n = k_{\text{eff}}$$

Taking log
 $\log v = \log k_{\text{eff}} + m \log [A]$



Half-life of Reaction

The half-life of a rxn is the time taken for half of a reactant to have been consumed or time taken for the rxn to have gone half way.

For a zero-order rxn,

$$[A]_t = -kt + [A]_0$$

At half life, $[A]_t = \frac{[A]_0}{2}$

$$\Rightarrow \frac{[A]_0}{2} = -kt_{1/2} + [A]_0$$

$$\text{OR } kt_{1/2} = [A]_0 - \frac{[A]_0}{2} = \frac{[A]_0}{2}$$

$$\boxed{t_{1/2} = \frac{[A]_0}{2k}}$$
 Zero order

For 1st order:

$$\ln[A]_t = -kt + \ln[A]_0$$

$$kt = \ln[A]_0 - \ln[A]_t$$

$$= \ln\left(\frac{[A]_0}{[A]_t}\right)$$

at $t_{1/2}$; $[A]_t = \frac{[A]_0}{2}$

$$\Rightarrow kt_{1/2} = \ln\left(\frac{[A]_0}{\frac{1}{2}[A]_0}\right)$$

$$= \ln 2$$

$$= \boxed{t_{1/2} = \frac{\ln 2}{k}} \rightarrow \text{first order rxn}$$

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

For second order:

$$t_{1/2} = \frac{1}{k[A]_0}$$

$$\frac{1}{[A]_t} = kt + \frac{1}{[A]_0}$$

$$t_{1/2} \quad [A]_t = \frac{[A]_0}{2}$$

A \rightarrow Product for $n > 1$

$$-d[A] = k[A]^n$$

$$\int \frac{d[A]}{[A]^n} = -k \int dt + C$$

$$-\frac{[A]^{1-n}}{1-n} = kt + C$$

$$\frac{[A]^{1-n}}{1-n} = kt + C$$

$$\textcircled{a} \quad t=0, [A]_0 = [A]_0 \Rightarrow \frac{[A]_0^{1-n}}{1-n} = C$$

$$\frac{[A]^{1-n}}{1-n} = kt + \frac{[A]_0^{1-n}}{1-n}$$

$$[A]^{1-n} - [A]_0^{1-n} = (n-1)kt$$

$$\textcircled{a} \quad t_{1/2} \quad [A] = \frac{[A]_0}{2}$$

$$\Rightarrow \frac{[A]^{1-n}}{2^{1-n}} - [A]_0^{1-n} = (n-1)kt_{1/2}$$

$$[A]_0^{1-n} \left[\frac{1}{2^{n-1}} - 1 \right] = (n-1)kt_{1/2}$$

$$t_{1/2} = \frac{[A]_0}{k(n-1)} \left[\frac{1}{2^{n-1}} - 1 \right]$$

$$t_{1/2} \propto [A]_0^{1-n}$$

$$t_{1/2} = Z [A]_0^{1-n}$$

Example!

Ⓟ For a gaseous rxn b/w A and B,

the half-life period were measured

and the data reported are

P (atm)	① 400	② 200	③ 200
---------	-------	-------	-------

P (atm)	20	40	20
---------	----	----	----

$t_{1/2}$	40	40	20
-----------	----	----	----

Find the order of A and B

For A $t_{1/2}(1) = \left[\frac{P_A(1)}{P_A(3)} \right]^{1-n}$

$$\frac{40}{20} = \left[\frac{400}{200} \right]^{1-n}$$

$$2' = 2^{1-n}$$

$$1 = 1-n$$

$$n = 0$$

$$\text{For B } \frac{t_{1/2}(2)}{t_{1/2}(3)} = \left[\frac{[B](2)}{[B](3)} \right]$$

$$= \frac{40}{20} = \left[\frac{40}{20} \right]$$

$$2' = 2^{1-n}$$

$$1 = 1-n$$

$$n = 0$$

Q) The decomposition of ethanol on an alumina surface was studied

at 600K. Concentration vs time data were collected for this rxn and a plot of the conc of A vs time resulted in a straight line with a slope value of -4×10^{-5} mol/L/s

(a) Determine the rate law, the integrated rate law and the value of the rate constant for this rxn.

(b) if the initial conc of ethanol was 1.25×10^{-2} M, cal. the half life for this rxn

(c) How much time is required for all of the 1.25×10^{-2} M

ethanol to be decomposed.

(a) Soln Zero order rxn

$$-k = -4 \times 10^{-5} \text{ mol/L/s}$$

$$k = 4 \times 10^{-5} \text{ mol/L/s}$$

$$\text{Rate} = k[\text{C}_2\text{H}_5\text{OH}]^0$$

$$[A]_t = -kt + [A]_0$$

$$b) t_{1/2} = \frac{[A]_0}{2k} = \frac{1.25 \times 10^{-2}}{2 \times 4 \times 10^{-5}}$$

$$= 156.25 \text{ s}$$

$$c) [A]_t = -kt + [A]_0$$

$$0 = -4 \times 10^{-5} t + 1.25 \times 10^{-2}$$

$$t = \frac{1.25 \times 10^{-2}}{4 \times 10^{-5}} = 312.5 \text{ s}$$

The higher the frequency, the higher the rate of rxn

The larger the k , the faster the rxn

Factors Affecting the Rate of Rxn

- Concentration: $\uparrow \text{Conc} \rightarrow \uparrow \text{rate}$
- Temperature: $\uparrow T \rightarrow \uparrow k$

\uparrow in the frequency of the collision hence increase in the rate of the rxn.

For every 10° increase in temp, the rate doubles.

To quantitatively, for q , describe the effect of temp. on rate of rxn, Svante Arrhenius shows that the rate constant for a rxn is

$$k = Ae^{-E_a/RT}$$

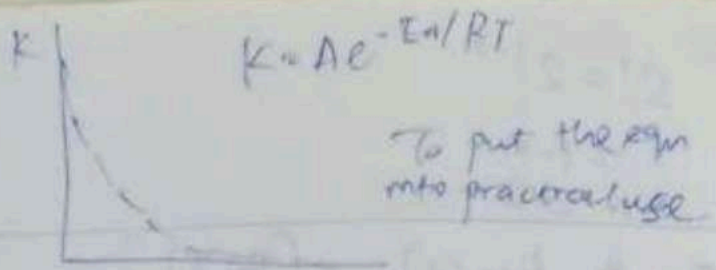
k = rate constant
 A = A (Collision parameter) a measure of collision frequency
 E_a = activation energy which is the energy barrier that one reactant molecules must overcome by transformation to product

T = Temp in absolute K scale

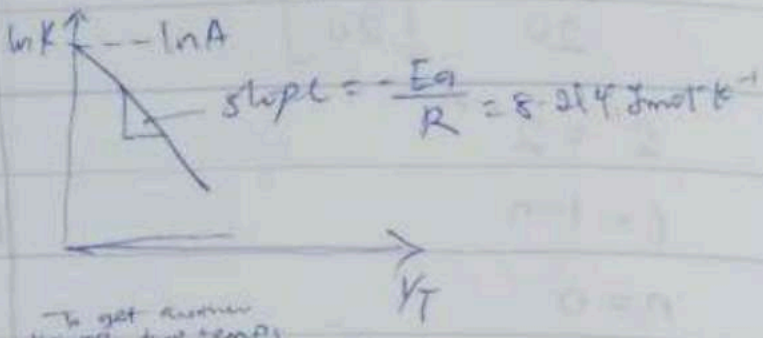
Activation Energy, E_a



Activation energy is always a positive quantity cuz slope will be negative



$$\ln k = \left(\frac{-E_a}{R} \right) \frac{1}{T} + \ln A$$



To get answer having two temps

$$k_1 = Ae^{-E_a/RT_1}$$

$$k_2 = Ae^{-E_a/RT_2}$$

$$\ln k_1 = \left(\frac{-E_a}{R} \right) \frac{1}{T_1} + \ln A \quad \text{--- (1)}$$

$$\ln k_2 = \left(\frac{-E_a}{R} \right) \frac{1}{T_2} + \ln A \quad \text{--- (2)}$$

Eqn (2) - (1)

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

$$\frac{\ln k_2}{k_1} = \frac{E_a}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$= \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

Q: A certain rxn has E_a of 54 kJ mol^{-1} . As the temp is increased from 22°C to a higher temp, the rate constant increases by a factor of 7. Cal. the higher temp.

2) The E_a for the decomposition of hydrogen peroxide is 186 kJ mol^{-1} . The rate constant at 555 K is $3.52 \times 10^{-7} \text{ mol/s}$. What is the rate constant at 645 K .

Soln

$$2) \ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

$$\ln \frac{k_2}{k_1} = \frac{186000}{8.314} \left[\frac{645 - 555}{645 \times 555} \right]$$

$$\ln \left(\frac{k_2}{k_1} \right) = 5.625$$

$$\frac{k_2}{k_1} = e^{5.625}$$

$$k_2 = e^{5.625} \times 3.52 \times 10^{-7}$$

$$= 9.7 \times 10^{-5} \text{ mol/s}$$

$$1) \ln \left(\frac{k_2}{k_1} \right) = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_2 T_1} \right]$$

$$\ln 7 = \frac{54000}{8.314} \left[\frac{T_2 - 295}{295 T_2} \right]$$

$$1.95 = \frac{54000}{8.314} \left[\frac{T_2 - 295}{295 T_2} \right]$$

$$2.9 \times 10^{-4} = \frac{T_2 - 295}{295 T_2}$$

$$0.088 T_2 = T_2 - 295$$

$$295 = 0.912 T_2$$

$$T_2 = 323.6 \text{ K}$$

Lower $E_a \rightarrow$ larger $k \rightarrow$ higher rate

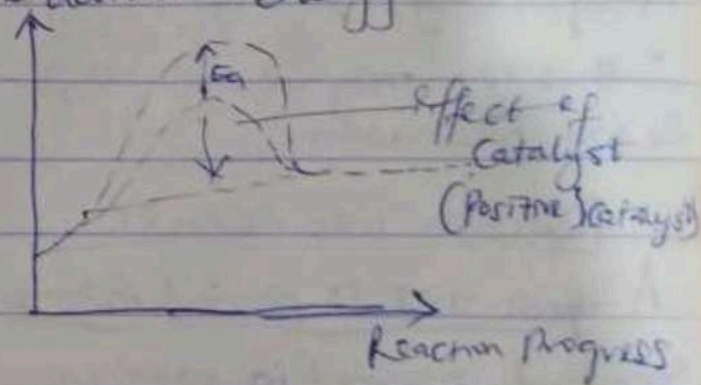
Catalyst:

- Positive catalyst:

- Negative catalyst (Inhibitor)

* Catalyst are not involved in a rxn

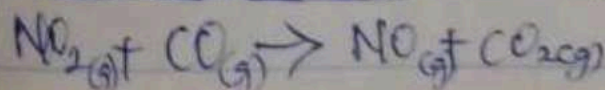
providing an alternative pathway for the rxn to occur by lowering the activation energy



REACTION MECHANISM

The series of elementary steps involved in a reaction is called

Reaction Mechanism. For instance,



Experimentally determined
 Rate law = $k[\text{NO}_2]^2$ (2nd order reaction)
 Two conditions a suitable ^{rxn} must obey

- The sum of the elementary steps must ^{give} be the overall balanced eqn for the rxn
- The mechanism must agree with the experimental rate law expression

The proposed mechanism for the rxn is as follows

$$\text{NO}_2(\text{g}) + \text{NO}_2(\text{g}) \rightarrow \text{NO}_3(\text{g}) + \text{NO}(\text{g})$$

$$\text{NO}_3(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}_2 + \text{CO}_2(\text{g})$$

This is a two step rxn mechanism

To sum the rxn:

$$\text{NO}_2(\text{g}) + \text{CO}(\text{g}) \rightarrow \text{NO}(\text{g}) + \text{CO}_2(\text{g})$$

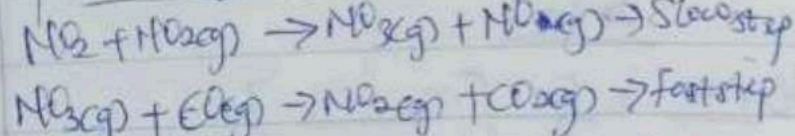
∴ this rxn may be suitable for the rxn mechanism

Reaction Intermediate

A species that is formed in one step and consumed in another step and ^{does} not appear in the overall balanced eqn is known as Reaction Intermediate. Most times, such intermediates are transient (short lived) in nature.

Molecularity

The molecularity of a rxn step is simply the no of species that are colliding in the rxn: (unimolecular or bimolecular)
 In any multi-step rxn, the step that determines the rate of rxn is the slow step

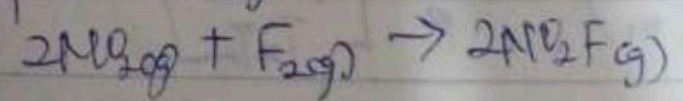


$$\therefore \frac{d[\text{NO}_2]}{dt} = k[\text{NO}_2][\text{NO}_2]$$

$$= k[\text{NO}_2]^2$$

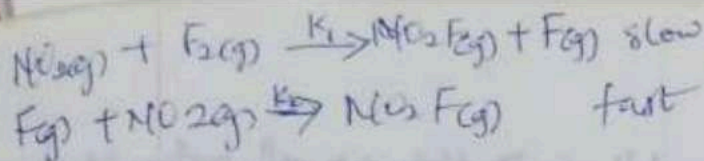
The mechanism is in agreement with the experimental rate law expression. ∴, the eqn is the suitable mechanism for the rxn.

Example! The balanced eqn for the rxn of gaseous Nitrogen dioxide and fluorine is given as



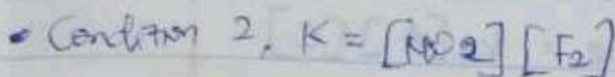
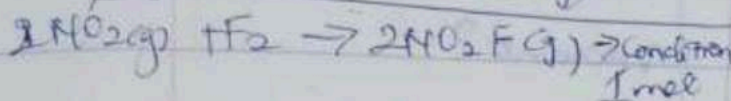
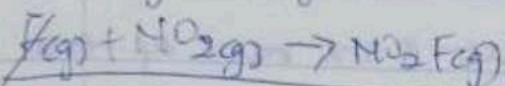
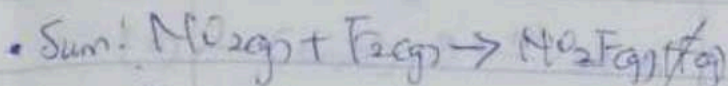
The experimentally determined rate law is: $\text{Rate} = k[\text{NO}_2][\text{F}_2]$

A suggested mechanism for the rxn is



is this an acceptable mechanism or not?

Soln

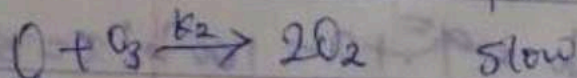
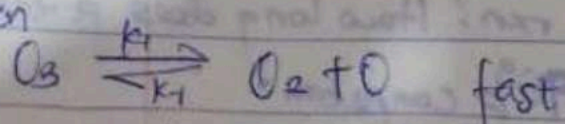


Some rxn may involve an equilibrium in one of the steps, usually fast equilibrium - for example, the conversion of O_3 to O_2



The observed rate law is Rate $= k \frac{[\text{O}_3]^2}{[\text{O}_2]}$

The proposed mechanism for this rxn



Note: Usually, the equilibrium step is usually a fast equilibrium

$$\text{Rate} = k_2 [\text{O}] [\text{O}_3]$$

† The intermediate should not feature in the rate law expression.

From step ① rate of forward rxn $= k_1 [\text{O}_3]$

$$\text{rate of reverse rxn} = k_{-1} [\text{O}_2] [\text{O}]$$

At equilibrium, the rate of forward $=$ rate of reverse rxn.

$$\text{i.e. } k_1 [\text{O}_3] = k_{-1} [\text{O}_2] [\text{O}]$$

$$\Rightarrow [\text{O}]_{\text{(intermediate)}} = \frac{k_1 [\text{O}_3]}{k_{-1} [\text{O}_2]}$$

Substituting for $[\text{O}]$ in the rate law for the slow step

$$\text{Rate} = k_2 \frac{k_1 [\text{O}_3] [\text{O}_3]}{k_{-1} [\text{O}_2]}$$

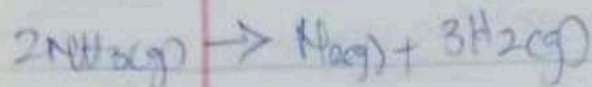
$$= k_2 k_{\text{eq}} \frac{[\text{O}_3]^2}{[\text{O}_2]} = k_{\text{eff}} \frac{[\text{O}_3]^2}{[\text{O}_2]}$$

$$\text{where } k_{\text{eff}} = \frac{k_1 k_2}{k_{-1}}$$

16/02/2022

2nd order = mol l⁻¹ s⁻¹
1st order = s⁻¹

For a rxn



It is observed that,

$$a) -\frac{d[\text{NH}_3]}{dt} = k_1 [\text{NH}_3]$$

$$b) \frac{d[\text{N}_2]}{dt} = k_2 [\text{NH}_3]$$

$$c) \frac{d[\text{H}_2]}{dt} = k_3 [\text{NH}_3]$$

$$\text{Rate} = -\frac{1}{2} \frac{d[\text{NH}_3]}{dt} = 2k_1 [\text{NH}_3]$$

Similarly,

$$\text{Rate} = \frac{d[\text{N}_2]}{dt} = k_2 [\text{NH}_3]$$

$$\text{Rate} = \frac{1}{3} \frac{d[\text{H}_2]}{dt} = 3k_3 [\text{NH}_3]$$

Comparing those with a, b, c

$$k_1 = 2k_2, k_2 = k_3, k_3 = 3k_4$$

If $k_2 = k$

$$\therefore k_1 : k_2 : k_3$$

$$2 : 1 : 3$$

Exercise!

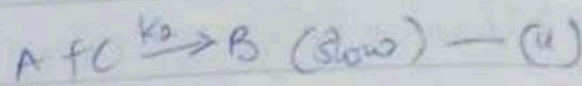
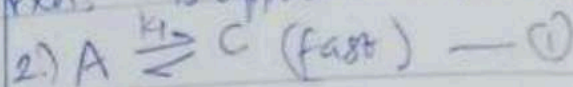
1) $2.58 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$ after 15s

$2.59 \times 10^{-5} \text{ l mol}^{-1} \text{ s}^{-1}$ after 30s

$2.57 \times 10^{-4} \text{ l mol}^{-1} \text{ s}^{-1}$ after 50s

Rate constants for a rxn $2A + B$

What is the overall order of the rxn? 2nd order coz the unit (mol⁻¹ s⁻¹) is applicable to the second order



What is the rate of the reactant?

Soln

$$\text{Rate} = k_3 [A][C]$$

From eqn (1)

$$k_1 = \frac{[C]}{[A]}$$

$$[C] = k_1 [A]$$

Substitute for [C] in Rate = $k_3 [A][C]$

$$\therefore \text{Rate} = k_3 [A] \cdot k_1 [A]$$

$$= k_3 k_1 [A]^2$$

$$= k_{\text{eff}} [A]^2$$

3) A first order rxn is 75% complete in 320s. what are the first and second half life for this rxn? How long does it take for 90% completion?

first and second half life for this rxn? How long does it take for 90% completion?

for 90% completion?

$$[A]_0 - x + a = 100\%; x = 75\%$$

$$[A]_t = a - x = 100 - 75 = 25\%$$

$$\ln\left(\frac{a}{a-x}\right) = kt$$

$$\ln[A]_t = -kt + \ln[A]_0$$

$$kt = \ln[A]_0 - \ln[A]_t = \ln\left[\frac{[A]_0}{[A]_t}\right]$$

$$k(320s) = \ln\left[\frac{100}{25}\right]$$

$$320k = \ln 4$$

$$k = \frac{\ln 4}{320} = 4.33 \times 10^{-3} s^{-1}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{\ln 2}{k} = \frac{0.693}{4.33 \times 10^{-3}}$$

$$= 160s$$

Note! After the first half-life, 50% is left. After the second half-life, $\frac{50}{2} = 25\%$ is consumed.

\therefore The total consumed after the first and second half life = 50% + 25% = 75%

Thus, the second half-life $2t_{1/2}$ = time taken for 75% to be consumed = 320s (i.e. $160s \times 2 = 320s$)

b) At 90% completion

$$[A]_0 = 100\% = a$$

$$x = 90\%$$

$$[A]_t = a - x = 100 - 90 = 10\%$$

$$\ln\left[\frac{[A]_0}{[A]_t}\right] = kt$$

$$\ln\left[\frac{100}{10}\right] = 4.33 \times 10^{-3} s^{-1} \cdot t$$

$$\ln[10] = 4.33 \times 10^{-3} s^{-1} \cdot t$$

$$t = \frac{\ln[10]}{4.33 \times 10^{-3}} = 531.8s$$

$$t = \frac{2.303}{k} \log\left(\frac{100}{100-x}\right)$$

km

State of a system is determined by four variables: (1) Pressure (P) (2) vol (V) (3) Temp (T) (4) No. of moles (n)

THERMODYNAMICS

Universe:
System
+
Surrounding
↓
Entire universe

Extensive property: depends on the amount
heat capacity, density, internal energy, mass, volume, length, shape
do not depend on the amount

Intensive property: specific heat capacity, melting point, boiling point, density & liquidness, lustre, color, pressure

* Path function: depends on path eg work & heat
* State function: depends on initial and final (eg internal energy, enthalpy, entropy)

Thermodynamic Equilibrium

* They must all be in contact
B → C / i.e. A → B
A → C

Internal energy of an ideal gas is a function of temp.

Modes of energy transfer

$$\Delta U = q + w \rightarrow \text{work}$$

$$du = dq + dw$$

State function not state function

* Volume is usually function of temp & pressure

$$w = - \int_{v_i}^{v_f} p \, dv$$

$$w = - \int p_{\text{gas}} \, dv$$

for reversible process

$$C_m = \frac{q}{n \Delta T}$$

$$\Delta U = q + w$$

$$* \text{Vol} = -w, \quad \downarrow \text{vol} = +w$$

$$w = - \int p_{\text{ext}} \, dv$$

$$\Delta U = q + \left(- \int_{v_i}^{v_f} p \, dv \right)$$

$$\Delta U = q - P (V_f - V_i)$$

$$PV = nRT$$

$$P = \frac{nRT}{V}$$

work done on = +w
work done by = -w

$$\Delta U = q - nRT$$

From $\Delta U = q - \int_{v_i}^{v_f} p \, dv$

$$\Delta U = q - P \int_{v_i}^{v_f} dv$$

$$\Delta U = q - nRT \int_{v_i}^{v_f} \frac{1}{V} \, dv$$

$$\Delta U = q - nRT \ln \left(\frac{V_f}{V_i} \right) \text{ if } V_i \text{ is}$$

bigger, it will become +ve

If work is done by the system,

then it is expansion.

Adiabatic process, $q = 0$

The heat capacity of a system at constant pressure (C_p) enthalpy is obtained.

Heat capacity, $C = \frac{q}{\Delta T}$

molar heat capacity, $C_m = \frac{q_p}{n \Delta T}$ @ constant pressure

Reversible process

$$\Delta U = q - nRT \int_{V_i}^{V_f} \frac{1}{V} dV$$

when $\Delta U = 0$

$$0 = q - nRT \ln \frac{V_f}{V_i}$$

$$q = nRT \ln \frac{V_f}{V_i}$$

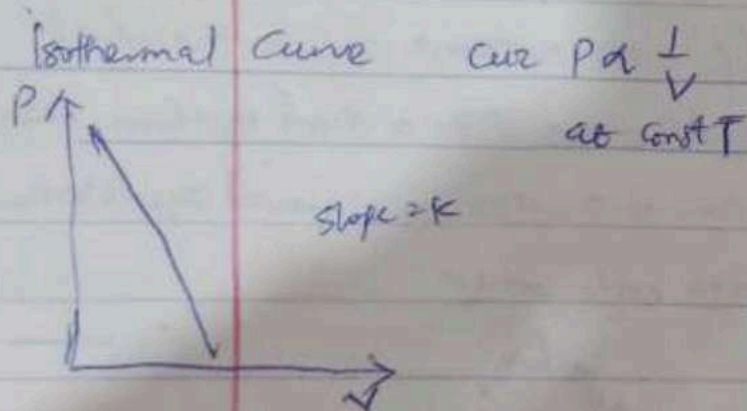
$$C_{pm} = \frac{q_p}{n \Delta T}$$

$$C_{pm} \cdot n \cdot \Delta T = q_p = \Delta H$$

$$C_{vm} \cdot n \cdot \Delta T = q_v = \Delta U$$

28/2/22

When $q_{ext} = 0$, $w_{ext} = 0$ / free expansion
 $w = -P(V_f - V_i)$ / $V = \text{const}$
 $0 = 0$ same



$n = \gamma; P V^\gamma \Rightarrow$ adiabatic, $q = 0$

$$\Delta S_T = \Delta S_{\text{system}} + \Delta S_{\text{surrounding}}$$

$\Delta S_T \geq 0$ (spontaneous)

entropy increases - spontaneous

$S_T = 0$ (equilibrium) / $\Delta S_{\text{surrounding}} < 0$ / $\Delta S_{\text{system}} > 0$
 $S_T < 0$ (non spontaneous)

$$S = \frac{q}{T}$$

when there is no transfer of energy,

$$q = 0, S = 0$$

at constant vol for V_f condition

$$S = C_v \ln \frac{T_f}{T_i} \rightarrow \text{for 1 mol}$$

$$S = C_v n \ln \frac{T_f}{T_i} \text{ for } n \text{ mol}$$

from $\Delta U = n q_{ext}$

$$\Delta S = n C_v \ln \frac{T_f}{T_i} + nRT \ln \frac{V_f}{V_i}$$

As vol increases, entropy \uparrow

$$\Delta S = \frac{q_{rev}}{T} = \int \frac{C_v dT}{T}$$

$$\frac{U}{T} = \frac{q}{T} + \frac{w}{T}$$

$$\Delta S = n C_v \ln \frac{T_f}{T_i} + nRT \ln \frac{V_f}{V_i}$$

$$= n C_v \ln \frac{T_f}{T_i} + nR \ln \frac{V_f}{V_i}$$

For enthalpy,

$$\int \frac{dH}{T} = \int \frac{C_p dT}{T} = C_p \ln \frac{T_f}{T_i}$$

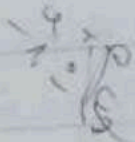
$$\Delta G = \Delta H - T\Delta S$$

heat of dissociation - endothermic process

Cyclic process, $U_{net} = 0$
i.e. $q_{net} = -w_{net}$

Example 3:

$$w = -nRT \ln \frac{V_f}{V_i}$$



7) $w = P(V_f - V_i)$

enthalpy $H = U + PV$; $H = U + PV + RT$

At constant volume, internal energy

$$U = q_v; C_{mv} = \frac{q_v}{nT} \therefore U = nC_{mv}T = w$$

At constant pressure, enthalpy

$$H = q_p; C_{mp} = \frac{q_p}{nT} \therefore H = nC_{mp}T$$

$$C_p = C_v + R$$

$$\gamma = C_p / C_v$$

ratio of molar specific heats for a gas

• Isochoric process
Since $\Delta V = 0 \therefore w = 0$
 $U = q$

• Isobaric Process - Pressure constant

$$w = -P\Delta V = -nRT$$

Entropy

• Isothermal: $\Delta S = nR \ln(V_2/V_1)$

• Isochoric: $\Delta S = nC_v \ln(T_2/T_1)$

• Isobaric: $\Delta S = nC_p \ln(T_2/T_1)$

• Adiabatic: $\Delta S = 0$ ($q_{rev} = 0$)

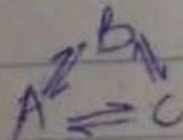
Isentropic process $\Delta S = \Delta S_{surrounding} = \Delta S_{system} = 0$

Resonance energy = $H_f(\text{actual}) - H_f(\text{calculated})$

• Zeroth law of thermodynamics

• Thermal equilibrium (no net heat flow)

If two systems are in thermal equilibrium with a third system, then those two are in thermal equilibrium with each other



Two objects at the same temp. will not exhibit heat flow when they come in contact with one another

• Diathermal walls: allows heat to flow in and out

f Thermodynamic processes

• Isothermal - Constant temp $PV = \text{constant}$

$$w = 0, q = -w$$

$$w = -2.303 nRT \log \left(\frac{P_2}{P_1} \right) = -2.303 nRT \log \left(\frac{V_1}{V_2} \right)$$

$$q = +2.303 nRT \log \left(\frac{P_1}{P_2} \right) = +2.303 nRT \log \left(\frac{V_2}{V_1} \right)$$

• Adiabatic - $q = 0$

$$PV = \text{constant}$$

$$w = \Delta U$$

$$P_1 V_1^\gamma = P_2 V_2^\gamma \rightarrow \text{adiabatic constant}$$

Adiabatic walls: - doesn't allow heat to flow in and out

Heat (q) is the energy that flows btw a system and its surroundings due to a difference in temp. Heat flows spontaneously from an area of higher temp to lower temp

$q = +ve$ (heat being absorbed by the system)
 $q = -ve$ (heat being released)

$q = \Delta H$ when T and P are constant

Non standard, ΔG value:

$$\Delta G = \Delta G^\circ + RT \ln Q$$

$\Delta G = -T\Delta S$ (a) constant temp and pressure.

* Capacity & molar capacity

Cyclic process: $\Delta U = 0$

$$q_{net} = -w_{net}$$

Enthalpy, $H = U + PV$

Heat capacity, $C = \frac{q}{\Delta T}$

Molar heat capacity, $C = \frac{q}{n\Delta T}$

(a) constant pressure, $C_p = \frac{q_p}{n\Delta T}$
 $\Delta H = q_p$

(b) constant volume, $C_v = \frac{q_v}{n\Delta T}$
 $\Delta U = q_v$

Resonance energy = $\Delta H_f^\circ(\text{actual}) - \Delta H_f^\circ(\text{calculated})$

Effusion $\frac{k T G}{M}$

During effusion a gas travels from a high pressure to low pressure through orifice or a thin hole.

For effusion to occur the mean free path must be large compared to the diameter of the orifice.
* The no of molecules passing through the orifice is equal to the no that would normally strike an area of wall equal to the area of the hole.

Thomas Graham found experimentally that under the same condition of temp. and pressure the rate of diffusion (effusion) of a gas is inversely proportional to the square root of their molar masses. Thus for two gases,

(I) and (II) we have.

$$r \propto \frac{1}{M}$$

$$r_1 = \sqrt{\frac{k}{M_1}}$$

$$r_2 = \sqrt{\frac{k}{M_2}}$$

$$\therefore \frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}}$$

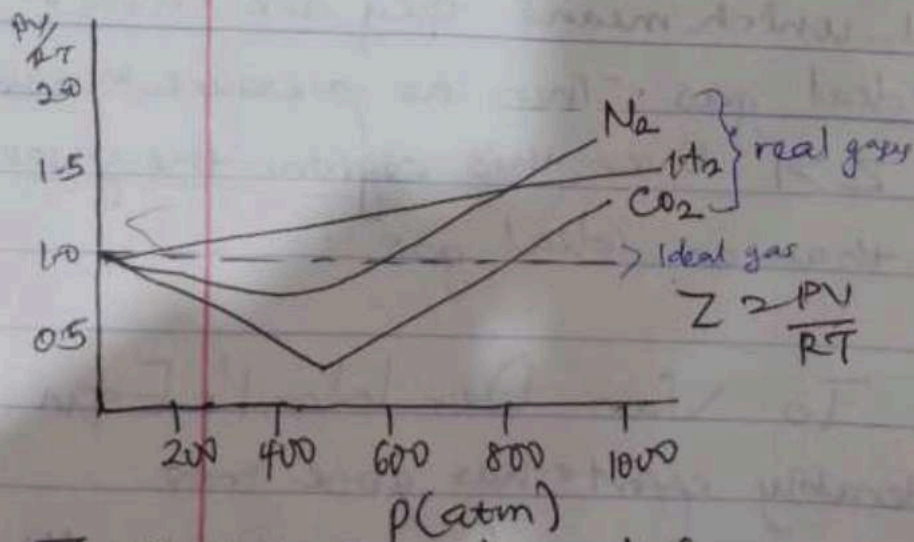
$$\frac{r_1}{r_2} = \sqrt{\frac{M_2}{M_1}} \text{ or } \sqrt{\frac{d_2}{d_1}}$$

r_1, r_2 = rate of diffusion of the two gases.

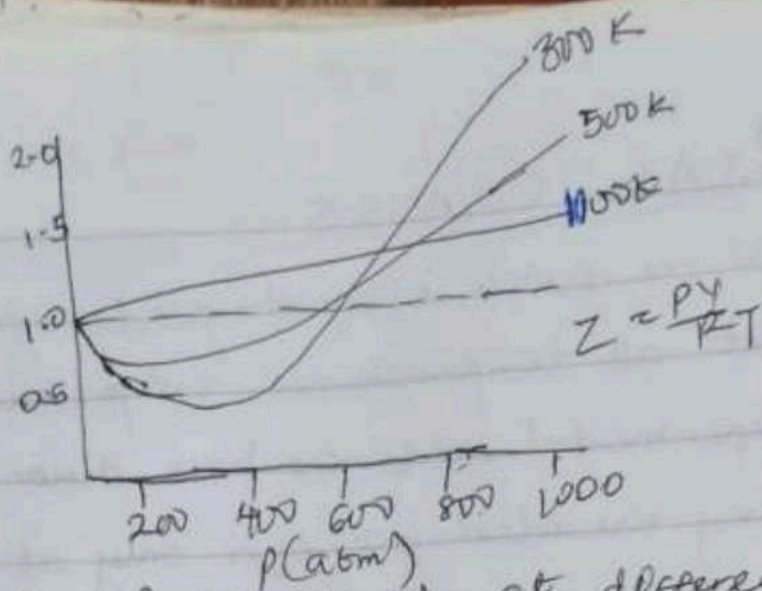
REAL GASES

An ideal gas is one which obeys the gas laws or gas eqn. $PV = nRT$ at all temperatures and pressures. For real gases, experimental evidences have shown that very few gases obey the ideal gas eqn only at low pressure and high temp. and that most gases shows substantial deviation from the ideal behaviour at high pressure and low temperature. Thus all gases which fail to obey the ideal gas eqn are termed not ideal or real gases.

The extent to which a real gas departs from the ideal behaviour may be depicted in terms of a new function called the compressibility factor, $Z = \frac{PV}{RT}$



Z vs plot for Na and C₂ at 300K for 1 mol of an ideal gas, $Z=1$ and it is independent of temp.



Z vs P plot for N_2 at different temp.

For an ideal gas, $Z = 1$ for any value of P at a given temp T . However, the compressibility factors for real gases exhibit fairly divergent dependence on pressure.

At low pressure, the compressibility factor of most gases are close to unity. In fact in the limit of P approaching zero, we have $Z = 1$ for all gases. However, as P increases, some gases have $Z < 1$ which means they are easier to compress than an ideal gas. Then as pressure increases further all gases have $Z > 1$. Over this region, the gases are harder to compress than an ideal gas.

Introduction To Van Der Waal's Eqn

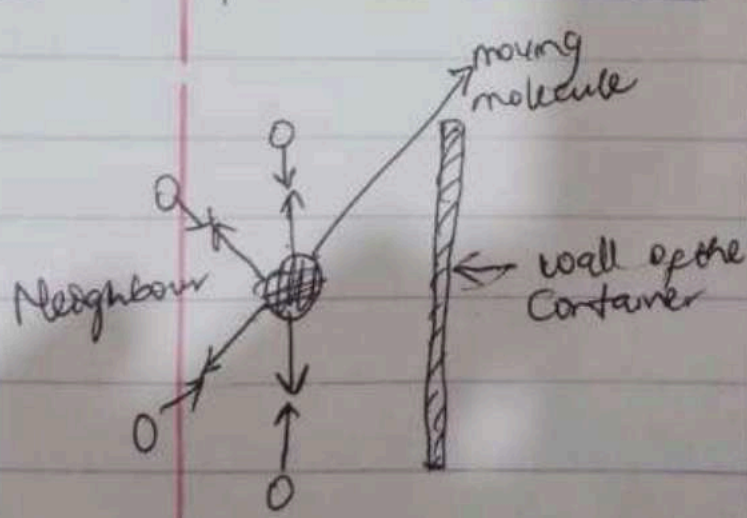
Over the years, considerably efforts has gone into modifying the ideal gas eqn for real gases. One of the numerous such eqns ^{be} proposed is the van der waal eqn of state (after the Dutch physicist) Johannes Diderich Van der Waals (1837-1923)

Van der Waals attributed the deviation of real gases from ideal behaviour to two erroneous postulates of the kinetic theory

(1) the molecules in a gas are point masses and possess low volume

(2) there are no intermolecular attraction in a gas. ∴ the ideal gas eqn $PV = nRT$ derived from kinetic theory could not hold for real gases.

Van der Waals eqn of state attempt to account for the finite volume for molecules in individual of individual molecules in a non-ideal gas and the attractive forces between them.



The pressure exerted by the individual molecules on the walls of the container depends on both the frequency of molecular collision with the walls and the momentum impacted by the molecules to the wall. ^{Both} Most contributions are diminished by the attractive intermolecular forces.

In ^{each} this case, the reduction in pressure depends on the no of molecules present or the density of the gas (m/v).

Now, reduction in pressure due to attractive forces is proportional to the impact the number density has on frequency and momentum frequency and the impact number i.e.

reduction in pressure due to attractive forces $\propto \left(\frac{N}{V}\right) \left(\frac{N}{V}\right)$

$$\propto \frac{N^2}{V^2} = a \frac{N^2}{V^2}$$

where $a =$ proportionality constant
Hence, the ideal gas eqn will be

Hence, $PV = nRT$ becomes:

$$\left(P + a \frac{n^2}{V^2}\right)(V - nb) = nRT$$

If P in the eqn above is the experimentally measured pressure of the gas and $\left(P + a \frac{n^2}{V^2}\right)$ would be the pressure of the gas if there were no intermolecular forces present. To allow for finite volume of molecules, V in the ideal gas eqn is replaced with $(V - nb)$ where nb represents the total effective volume of n moles of the gas. Both a and b are constants characteristic of the gas under study.

Example: The molar volume of ethane C_2H_6 at $350K$ is $0.1379 \text{ L mol}^{-1}$. Cal. the pressure of the gas using
 (a) the ideal gas eqn
 (b) the van der Waals eqn
 $a = 5.47 \text{ atm L}^2 \text{ mol}^{-2}$

$b = 0.0651 \text{ L mol}^{-1}$
 $R = 0.08206 \text{ Latm K}^{-1} \text{ mol}^{-1}$
Soln

a) $PV = nRT$

$$P = \frac{nRT}{V} = \frac{0.0821 \times 350}{0.1379}$$

$$P = 208.3 \text{ atm}$$

b) $\left(P + a \frac{n^2}{V^2}\right)(V - nb) = nRT$

Since $n = 1$

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT$$

$$\left(P + \frac{a}{V^2}\right) = \frac{RT}{V - b}$$

$$P = \frac{RT}{V - b} - \frac{a}{V^2}$$

$$= \frac{0.08206 \times 350}{0.1379 - 0.0651} - \frac{5.47}{(0.1379)^2}$$

$$= 106.9 \text{ atm}$$

2) Cal. the pressure exerted by 1 mole of methane CH_4 in a 250ml container at $300K$ using van der Waals eqn (b) what pressure will be predicted by ideal gas eqn?
 $a = 2.253 \text{ L}^2 \text{ atm}$
 $b = 0.0428 \text{ L mol}^{-1}$

3) One mol of water vapour is confined to a 20m flask at 27°C. Cal. its pressure using

(i) Van der waal eqn (ii) Ideal gas eqn

$$a = 5.464 \text{ L}^2 \text{ atm mol}^{-2}$$

$$b = 0.0305 \text{ L mol}^{-1}$$

$r =$

4) ~~Two~~ moles of NH_3 are in a 5L flask at 27°C. Cal.

the pressure exerted by the gas assuming that (i) the gas behaves like an ideal gas

(ii) the gas behaves like a real gas.

$$a = 4.14 \text{ L}^2 \text{ atm mol}^{-2}$$

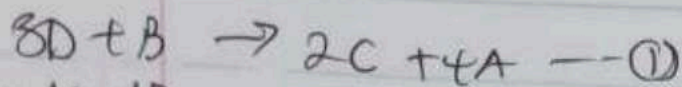
$$b = 0.037 \text{ L mol}^{-1}$$

Rate of rxn

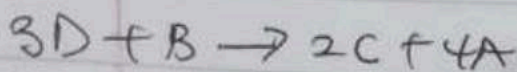
The rate of a rxn may be expressed as

$$+\frac{1}{2} \frac{dC}{dt} = -\frac{1}{3} \frac{dD}{dt} = +\frac{1}{4} \frac{dA}{dt} = -\frac{dB}{dt}$$

what is the eqn of the rxn involved



$$-\frac{1}{3} \frac{dD}{dt} = -\frac{dB}{dt} = +\frac{1}{2} \frac{dC}{dt} = +\frac{1}{4} \frac{dA}{dt}$$



The rate of a rxn is a function of the conc. of a rxn.

The rate of rxn ^{increases} by a factor of 1.837 when the conc of X is increase by 1.5 times. The order of the rxn with respect to X is ?



$$\text{Rate}_1 = k[X]_1^a$$

$$\text{Rate}_2 = 1.837 R_1, \text{ when } X_2 = 1.5X_1$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[X]_2^a}{k[X]_1^a}$$

$$\frac{\text{Rate}_2}{\text{Rate}_1} = \frac{k[X]_2^a}{k[X]_1^a}$$

$$\frac{1.837 R_1}{R_1} = \left[\frac{1.5 X_1}{X_1} \right]^a$$

$$1.837 = 1.5^a$$

$$\log 1.837 = \log 1.5^a$$

$$\log 1.837 = a \log 1.5$$

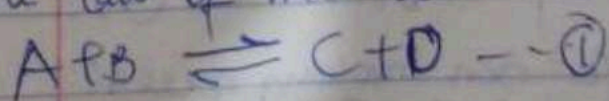
$$a = \frac{\log 1.837}{\log 1.5}$$

$$a = 1.5$$

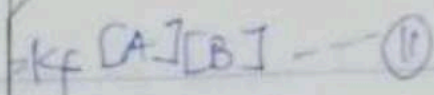
CHEMICAL EQUILIBRIUM

Generally, a rxn in which the starting materials are reproduced upon formation of sufficient amounts of products is said to be a reversible rxn - reversible rxn are generally expressed in the form of $aA + bB \rightleftharpoons cC + dD$ where a, b, c, d are stoichiometric coefficient of the species A, B, C, D respectively. In the course of forward and backward rxn, a point might be reached at which forward & backward rxn rate are equal at this point the rxn is said to be at equilibrium.

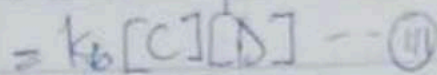
This rate of rxn are taken to be proportional to the concentration of the species in what is known as the law of mass action.



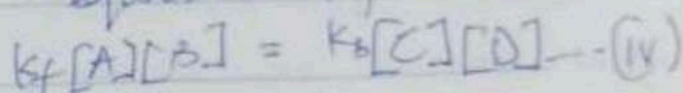
The rate of forward rxn, R_f



The rate of backward rxn, R_b



At equilibrium $R_f = R_b$

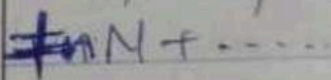


$$\frac{k_f}{k_b} = \frac{[C][D]}{[A][B]}$$

$$K = \frac{[C][D]}{[A][B]}$$

In more general formation for such chemical ^{reaction} ~~to be~~ written as

the form of $aA + bB \rightleftharpoons mM$



and the corresponding equilibrium constant becomes

$$K = \frac{[M]^m [N]^n}{[A]^a [B]^b} \quad \text{--- (v)}$$

A constant K is known in this context as the mass

action equilibrium constant expressed in terms of concentration species.

$$K = \frac{[C][D]}{[A][B]} \quad \text{--- (vi)}$$

The problem with the mass action above is that rxn rates

are not expressed based on simple mass action law ~~of~~ ^{the} over all rxn but rather depends on the detailed rxn path or mechanism. equilibrium constant, K expressed in terms of concentration of the specie is only an approximation.

Application of Thermodynamics which deals with only initial and final state of chemical equilibrium separates the subject (from that of chemical kinetics).

The exact definition of K , based on thermodynamics

We can express K , in terms of activities at

$$K = \frac{a_M^m a_N^n}{a_A^a a_B^b} \quad \text{--- (VII)}$$

where a_i may be defined as $a_i = \gamma_i x_i$ or $a_i = \gamma_i C_i$ (VIII)

$\gamma_i \Rightarrow$ activity coefficient for specie i , in the rxn.

$x_i \Rightarrow$ the mole fraction

$C_i =$ the molarity/molar conc.

Sub a_i in eqn (VII);

$$K = \frac{\gamma_M^m C_M^m \gamma_N^n C_N^n}{\gamma_A^a C_A^a \gamma_B^b C_B^b}$$

$$= \left(\frac{\gamma_M^m \gamma_N^n}{\gamma_A^a \gamma_B^b} \right) \frac{C_M^m C_N^n}{C_A^a C_B^b}$$

$$K = K_f K_c \quad \text{--- (IX)}$$

With the assumption that $K_f = 1$

then $K \approx K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b}$ (X)

Gas-Phase Equilibria

The equilibrium constant is better expressed in terms of fugacity of its gases

fugacity, f

$$f_i = \gamma_i P_i \quad \text{--- (XI)}$$

for rxn involving gases:

$$K = \frac{\gamma_M^m P_M^m \gamma_N^n P_N^n}{\gamma_A^a P_A^a \gamma_B^b P_B^b}$$

$$= \left(\frac{\gamma_M^m \gamma_N^n}{\gamma_A^a \gamma_B^b} \right) \left(\frac{P_M^m P_N^n}{P_A^a P_B^b} \right) \quad (12)$$

$$K = K_c K_p \quad (13)$$

for $K_f = 1$

$$K \approx K_p$$

$$\therefore K_p = \frac{P_M^m P_N^n}{P_A^a P_B^b} \quad (14)$$

Assuming the ideal behaviour of gases

Recall: $PV = nRT$

$$\left(\frac{n}{V} \right) = \frac{P}{RT} \rightarrow \text{concentration}$$

$$K_c = \frac{[M]^m [N]^n}{[A]^a [B]^b} = \frac{\left(\frac{P_M}{RT} \right)^m \left(\frac{P_N}{RT} \right)^n}{\left(\frac{P_A}{RT} \right)^a \left(\frac{P_B}{RT} \right)^b}$$

$$K_c = K_p \cdot (RT)^{-\Delta n}$$

$$K_c = K_p \cdot \frac{(RT)^{-\Delta n}}{(RT)^{-(a+b)}}$$

$$K_c = K_p \cdot (RT)^{-[\Delta n] - (a+b)} \quad (15)$$

$$\text{Let } \Delta n = (m+n) - (a+b)$$

$$K_c = K_p (RT)^{-\Delta n} \quad (16)$$

$$P = \sum_{i=1}^n P_i \quad \left. \begin{array}{l} \text{Dalton's law} \\ \text{of Partial} \\ \text{Pressure} \end{array} \right\}$$

$$P_i = x_i P$$

where $P =$ Total pressure

$P_i =$ Partial pressure for species i

$x_i =$ mole fraction

$$K_p = \frac{(x_M P)^m (x_N P)^n}{(x_A P)^a (x_B P)^b}$$

$$= \left(\frac{x_M^m x_N^n}{x_A^a x_B^b} \right) \frac{P^m P^n}{P^a P^b}$$

$$K_{xi} P^{(m+n) - (a+b)}$$

$$\Delta n = (m+n) - (a+b) \quad (17)$$

$$K_p = K_{xi} P^{\Delta n} \quad (18)$$

From eqn 18

$$K_p = K_n \left(\frac{P}{N} \right)^{\Delta n}$$

$$N = \sum_{i=1}^n n_i \quad ; \quad x_i = \frac{n_i}{N} \quad (19)$$

$$\text{where } K_n = \frac{P_M^m \cdot P_N^n}{P_A^a \cdot P_B^b}$$

EFFECT OF AN INERT GAS ON EQUILIBRIUM

Let's consider an equilibrium mixture of gases in a vessel, addition of an inert gas would increase the total number of mole (N) as well as (P) the total pressure, both of them would be increased proportionally. However (P/N) would remain constant.

Likewise "n" for the reactive species in the system will not change in other word "K_n" would also remain constant.

∴ K_p would not be affected by the addition of the inert gas provided (P/N) remain constant.

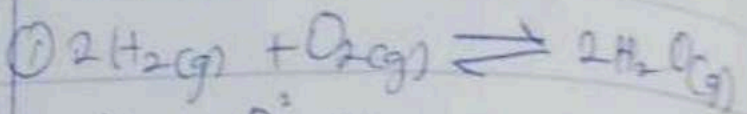
If however, the inert gas is added while keeping P constant, then only the total number of molecules (N) would change.

If N increase, then K_n would increase for Δn > 0. i.e. if n is +ve N↑ K_n↑ Δn > 0

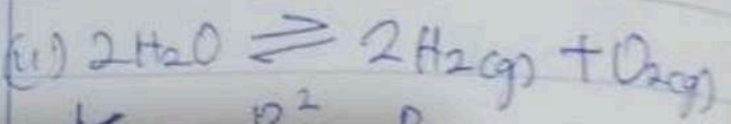
Also if N increases, K_n would decrease for Δn < 0 i.e. if n is negative N↑, K_n↓ Δn < 0

Example!

Consider the rxn



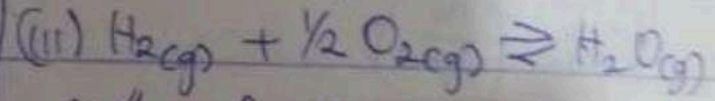
$$K_p = \frac{P_{\text{H}_2\text{O}}^2}{P_{\text{H}_2}^2 \cdot P_{\text{O}_2}}$$



$$K_p = \frac{P_{\text{H}_2}^2 \cdot P_{\text{O}_2}}{P_{\text{H}_2\text{O}}^2}$$

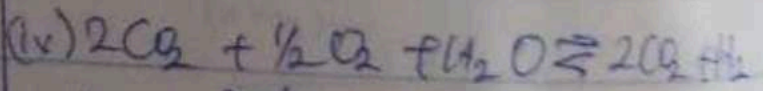
(i) and (ii) are related inversely

$$K_p = 1/K_p$$

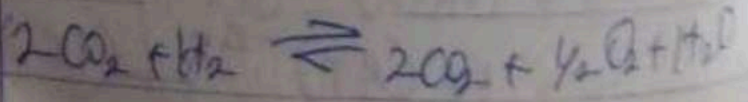


$$K_p'' = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2} \cdot P_{\text{O}_2}^{1/2}}$$

$$K_p'' = \sqrt{K_p} = (K_p)^{1/2}$$

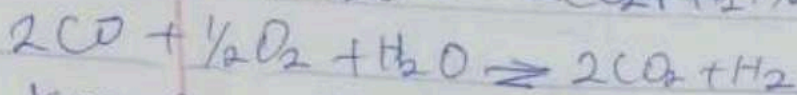
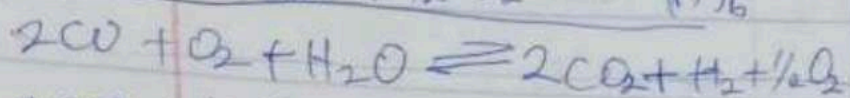
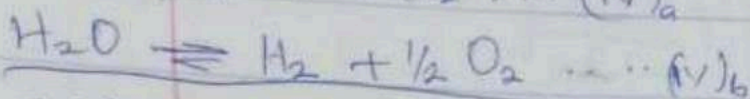
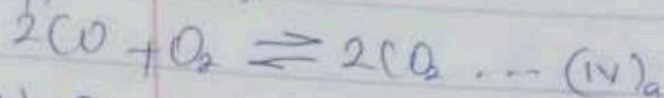


$$K_p = \frac{P_{\text{CO}}^2 \cdot P_{\text{H}_2}}{P_{\text{CO}_2}^2 \cdot P_{\text{O}_2}^{1/2} \cdot P_{\text{H}_2\text{O}}}$$



$$K_p = 1/K_p$$

Suppose (iv)



$$K_{p(iv_a)} = \frac{P_{CO_2}^2}{P_{CO}^2 \cdot P_{O_2}}$$

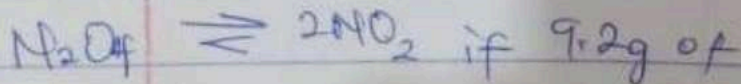
$$K_{p(iv_b)} = \frac{P_{H_2} \cdot P_{O_2}^{1/2}}{P_{H_2O}}$$

$$K_{p(iv_a)} \cdot K_{p(iv_b)} = \frac{P_{CO_2}^2 \cdot P_{H_2} \cdot P_{O_2}^{1/2}}{P_{CO}^2 \cdot P_{O_2} \cdot P_{H_2O}}$$

$$= \frac{P_{CO_2}^2 \cdot P_{H_2}}{P_{CO}^2 \cdot P_{O_2}^{1/2} \cdot P_{H_2O}}$$

$$K_p = K_{p(iv_a)} \cdot K_{p(iv_b)}$$

Consider the rxn:



NO_2 is introduced into a 36 L flask

at $25^\circ C$, the equilibrium pressure is

found to be at 0.1 atm. Find K_p

for the system assuming ideal behaviour

of the gases.

Soln

$$PV = nRT \text{ @ equilibrium}$$

$$n = \frac{PV}{RT} = \frac{0.1 \times 36}{0.082056 \times 298}$$

$$= 0.147 \text{ moles}$$

$$n_{NO_2} = \frac{\text{Reacting mass}}{\text{molar mass}}$$

$$= \frac{9.2}{46} = 0.2 \text{ moles}$$



Initial — 0.2

Equilibrium x · 0.2 - 2x

$$x + 0.2 - 2x = 0.147$$

$$x = 0.053$$

$$n_{N_2O_4} = 0.053$$

$$n_{NO_2} = 0.094 = 0.2 - 2(0.053)$$

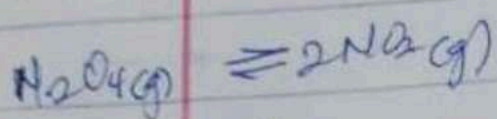
$$K_p = K_n \left(\frac{P}{N}\right)^{\Delta n}$$

$$\Delta n = 1$$

$$K_p = K_n \left(\frac{P}{N}\right)^1$$

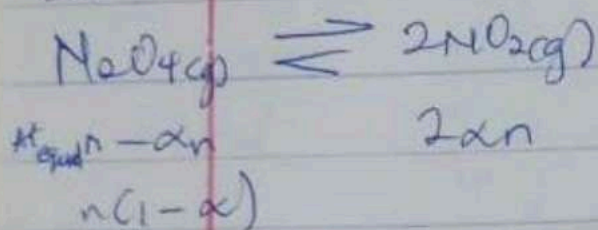
$$= \frac{(0.094)^2}{0.053} \cdot \frac{0.1}{0.147}$$

$$= 0.113$$



Starting with n moles of N_2O_4 .

Let degree of dissociation be α .



$$n_e = n - \alpha n + 2\alpha n = n(1 + \alpha)$$

Mole fraction at equilibrium

$$X_{\text{N}_2\text{O}_4} = \frac{n(1-\alpha)}{n(1+\alpha)} = \frac{(1-\alpha)}{(1+\alpha)}$$

$$X_{\text{NO}_2} = \frac{2\alpha n}{n(1+\alpha)} = \frac{2\alpha}{1+\alpha}$$

and K_p , equilibrium constant in

terms of partial pressure:

$$K_p = \frac{P_{\text{NO}_2}^2}{P_{\text{N}_2\text{O}_4}} = \frac{(X_{\text{NO}_2} P)^2}{X_{\text{N}_2\text{O}_4} P}$$

$$= \frac{X_{\text{NO}_2}^2 P^2}{X_{\text{N}_2\text{O}_4} P}$$

$$K_p = \frac{X_{\text{NO}_2} P}{X_{\text{N}_2\text{O}_4}} = \frac{2\alpha \left(\frac{2\alpha}{1+\alpha}\right)^2 P}{\frac{(1-\alpha)}{1+\alpha}}$$

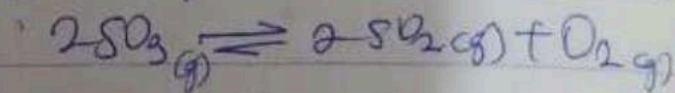
$$= \frac{4\alpha^2 P (1+\alpha)}{(1+\alpha)^2 (1-\alpha)}$$

$$K_p = \frac{4\alpha^2 P}{1-\alpha^2}$$

$$\alpha = \left[\frac{K_p}{K_p + 4P} \right]^{1/2}$$

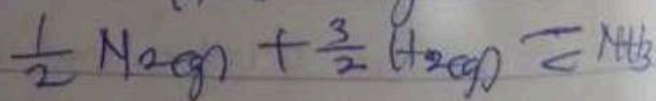
Example. If 0.0600 moles of $\text{SO}_3(\text{g})$ is placed in a 1 litre container at 1000K, 36.7% of SO_3 is dissociated

when equilibrium is established.



What are the equilibrium concentrations of the three species

Consider the formation of 1 mole NH_3 as given



based on this stoic combination at equilibrium the pressure of hydrogen gas is three

times that of nitrogen. Let the total pressure p , be expressed as

$$p = P_{N_2} + P_{H_2} + P_{NH_3}$$

$$\Rightarrow P_{NH_3} = p - (P_{N_2} + P_{H_2})$$

$$P_{NH_3} = p - (P_{N_2} + 3P_{N_2})$$

$$= p - 4P_{N_2}$$

$$P_{N_2} = \frac{1}{4} [p - P_{NH_3}]$$

$$P_{H_2} = \frac{3}{4} [p - P_{NH_3}]$$

$$K_p = \frac{P_{NH_3}}{P_{N_2}^{1/2} \cdot P_{H_2}^{3/2}}$$

$$= \frac{P_{NH_3}}{\left[\frac{1}{4} (p - P_{NH_3}) \right]^{1/2} \left[\frac{3}{4} (p - P_{NH_3}) \right]^{3/2}}$$

$$K_p = \frac{16 P_{NH_3}}{3 \sqrt{3} [p - P_{NH_3}]^2}$$

$$0.325 K_p = \frac{P_{NH_3}}{[p - P_{NH_3}]^2}$$

For $P_{NH_3} \ll p \Rightarrow p - P_{NH_3} \approx p$

$$0.325 K_p = \frac{P_{NH_3}}{p^2}$$

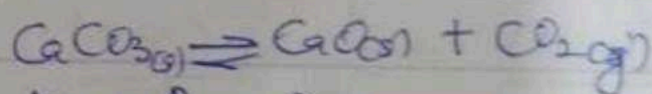
$$P_{NH_3} = 0.325 K_p \cdot p^2$$

Heterogeneous ^{Equilibrium} Equation

For equilibrium involving more than one phase, the concentration or pressure of pure solids or liquids are constants

Hence, ~~should be embedded~~ in K_c or K_p such that they do not appear explicitly for the expression in an equation

For example, ~~de~~ decomposition of Calcium carbonate



$$K = \frac{P_{CaO} P_{CO_2}}{P_{CaCO_3}}$$

$$\frac{P_{CaO}}{P_{CaCO_3}} = \text{constant} \approx K^*$$

$$K = K^* P_{CO_2}$$

$$\therefore \frac{K}{K^*} = P_{CO_2}$$

$$K_p = P_{CO_2}$$

Temperature Dependence
Of Equilibrium Constant
Equilibrium constant is only

fixed at a fixed temperature.

A change in temp. will change the magnitude or equilibrium constant.

From thermodynamic, we recall:

$$\Delta G = \Delta G^\circ + RT \ln K_p$$

At equilibrium, $\Delta G = 0$

$$\Delta G^\circ = -RT \ln K_p$$

$$-\frac{\Delta G^\circ}{RT} = \ln K_p$$

Differentiating both sides

$$\frac{d(\ln K_p)}{dT} = -\frac{1}{R} \frac{d(\Delta G^\circ)}{dT}$$

$$\text{But } \left[\frac{\partial \left(\frac{G}{T} \right)}{\partial T} \right]_P = -\frac{1}{T^2} G + \frac{1}{T} \left(\frac{\partial G}{\partial T} \right)_P$$
$$= -\frac{1}{T^2} (G + TS)$$

Since $G = H - TS$

$$\left(\frac{\partial \left(\frac{G}{T} \right)}{\partial T} \right)_P = -\frac{H}{T^2}$$

$$\therefore \frac{d(\ln K_p)}{dT} = \frac{\Delta H}{RT^2}$$

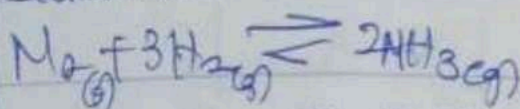
$$\int_{T_1}^{T_2} d(\ln K_p) = \frac{1}{R} \int_{T_1}^{T_2} \frac{\Delta H}{T^2} dT$$

$$\ln K_{p_2} - \ln K_{p_1} = \frac{1}{R} \Delta H^\circ \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

$$\therefore \ln \left(\frac{K_{p_2}}{K_{p_1}} \right) = \frac{\Delta H^\circ}{R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right]$$

Van't Hoff Equation

Question! For the rxn



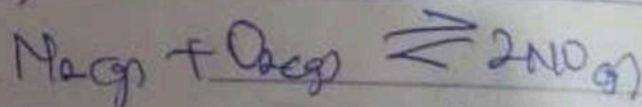
$$\Delta H = -92.4 \text{ kJ at}$$

equilibrium, $K_c = 9.6$ at

300°C . What is the value of K_c at 600°C given

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1}$$

e) For the equilibrium rxn



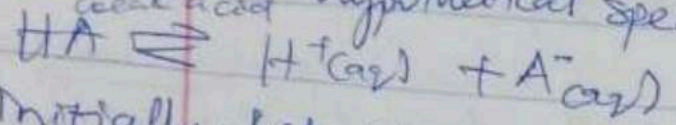
K_c is 4.05×10^{-4} at 2000K ,

at ~~the same~~ K_c is 3.60×10^{-3} at 2500K . Is the forward

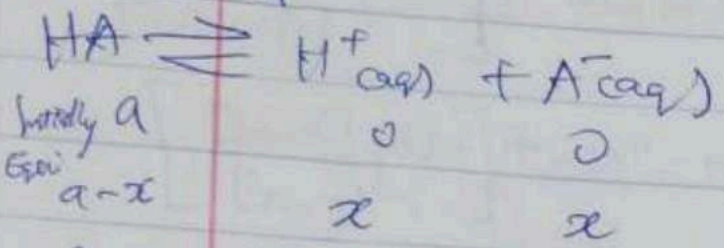
rxn as written, exothermic or endothermic

IONIC EQUILIBRIUM

Consider an hypothetical species



Initially, let the amount of HA be a



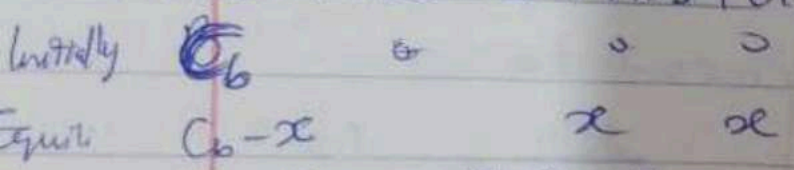
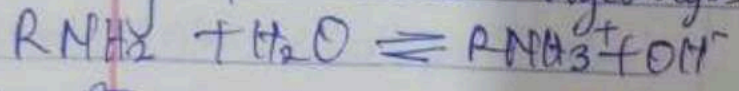
$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{x^2}{a-x}$$

$$x \ll a, \Rightarrow a-x \approx a$$

$$K_a = \frac{x^2}{a}$$

$$x = \sqrt{aK_a}$$

Similarly for a base hydrolysis



$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$

$$= \frac{x^2}{C_b - x}$$

$$x \ll C_b \Rightarrow C_b - x \approx C_b$$

$$\therefore K_b = \frac{x^2}{C_b} \text{ ; hence } x = \sqrt{C_b K_b}$$

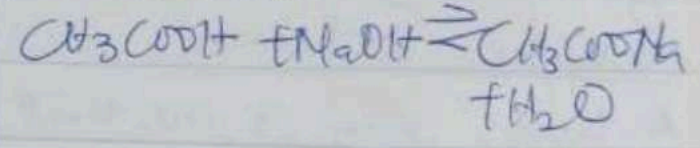
$$\therefore [H^+] = \sqrt{aK_a}$$

$$[OH^-] = \sqrt{C_b K_b}$$

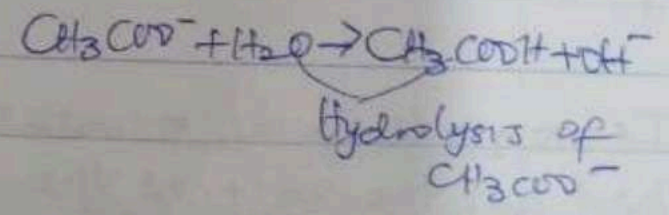
$$[H^+][OH^-] = K_w = \sqrt{aC_b K_a K_b}$$

$$K_w = 1 \times 10^{-14} \rightarrow \text{acid hydrolysis}$$

For the rxn:



He can express the dissociation of the salt as:

$$CH_3COONa \rightarrow CH_3COO^- + Na^+$$


$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]}$$

This can be related to K_a by multiplying both the numerator and denominator by $[H^+]$

$$K_h = \frac{[CH_3COOH][OH^-][H^+]}{[CH_3COO^-][H^+]}$$

$$K_h = \frac{K_w \cdot [CH_3COOH]}{[CH_3COO^-][H^+]}$$

But $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
dissociates partially

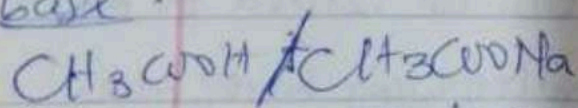
$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$\therefore K_h = \frac{K_w}{K_a}$$

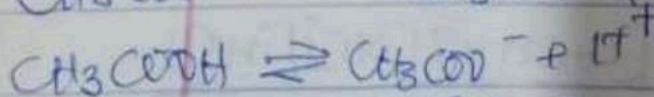
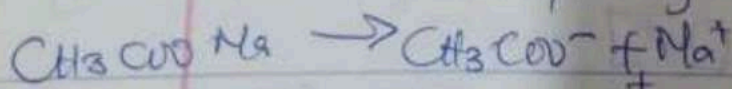
Buffer Solution

A buffer soln is one that resists a change in its pH upon addition of a small amount of an acid or base.

It is made up of a weak acid and the salt of the weak acid or a weak base and the salt of the weak base.



$\text{CH}_3\text{COONa} \rightarrow$ dissociates completely.



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$[\text{H}^+] = \frac{K_a [\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

$$\log [\text{H}^+] = \log K_a + \log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$$

multiplying both sides by -1

$$= \log [\text{H}^+] = -\log K_a + \left[-\log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \right]$$

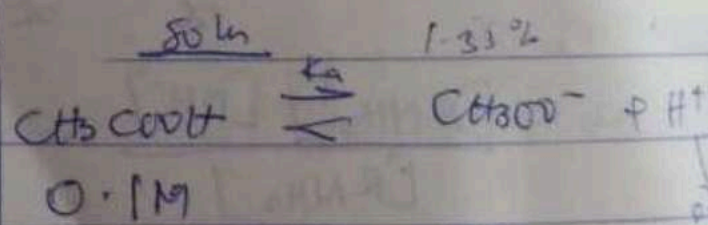
$$\text{pH} = \text{p}K_a + \left[-\log \frac{[\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]} \right]$$

$$\therefore \text{pH} = \text{p}K_a + \left[-\log \frac{[\text{Acid}]}{[\text{Salt}]} \right]$$

$$\text{pH} = \text{p}K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} \rightarrow \text{Henderson-Hasselbalch equation}$$

Example: The dissociation of 0.1M acetic acid solution is 1.33%. Calculate the acid dissociation constant K_a .



* substitution $0.1 - 0.00133$ $\frac{1.33}{100} \times 0.1 = 0.00133$

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}^+]}{[\text{CH}_3\text{COOH}]}$$

$$= \frac{(0.00133)^2}{(0.1 - 0.00133)} = 1.77$$

2) Using formic acid and sodium formate suggests the recipe for a buffer solution of pH 3. Given that the acid dissociation constant for formic acid is 1.8×10^{-4}

Soln

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\begin{aligned} \text{pK}_a &= -\log K_a \\ &= -\log (1.8 \times 10^{-4}) \\ &= 3.745 \end{aligned}$$

$$3 = 3.745 + \log \frac{[\text{Salt}]}{[\text{Acid}]}$$

$$\log \frac{[\text{Salt}]}{[\text{Acid}]} = 0.18$$

$$\frac{[\text{Salt}]}{[\text{Acid}]} = 0.18 \div 1$$

$1.8 \text{ ml}^{\text{salt}}$ and 10 ml of acid

The Relationship Between Reaction Quotient, Q and Equilibrium Constant, K_c - Predicting the direction of Equilibrium

Let us consider a general case

of an hypothetical rxn

$$aA + bB \rightleftharpoons cC + dD$$

For which we can write a non-equilibrium rxn quotient

Q, where the concs of A, B, C and D are non-equilibrium values

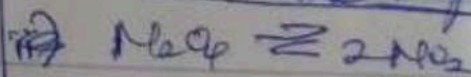
$$Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \rightarrow \text{non-equilibrium point}$$

There are three possibilities

i) $Q < K_c$

We would need to increase Q in order to get the equilibrium and it's either by increasing the product [C+D] or you increase the reactant [A+B]

To drive the rxn to equilibrium, the rxn must be driven to the right



$$Q = \frac{[NO_2]^2}{[N_2O_4]}$$

We can increase NO_2 by adding more reactant (N_2O_4) or removing NO_2 to make N_2O_4 react faster.

ii) $Q = K_c$: At equilibrium
Le Chatelier principle is applied here

iii) $Q > K_c$:

For such a system, the rxn must be driven leftwards i.e. more of A and B must be produced in order for the system to reach equilibrium.

Le Chatelier's Principle

ELECTROCHEMISTRY

All chemical rxns are fundamentally electrical in nature since electrons are involved in various ways in the rxn. Electrochemistry deals with electrical energy and chemical change. It primarily involves redox processes.

Chemical rxns can be used to produce electrical energy as in voltage or galvanic cells.

Conversely, electrical energy can be used to bring about chemical transformation (as in an electrolytic cell)

Ohm's Law and Electrical Charge

An electrical current I is a rate of flow of electrical charge Q

$$\text{i.e. } I = \frac{dQ}{dt} \quad \text{--- (1)}$$

I will be generated when Q passes through a system over a period of time
where I is in ampere (A)

Q in Coulombs (C)

t in seconds (s)

— for a current of $1A = 1C/s$

The current is forced through an electrical cycle by an electrical potential difference E , which is otherwise known as electromotive force (e.m.f) and it is measured in volts (V)

It takes 1 Joules of work to move 1 Coulomb charge through a potential difference of 1 volt i.e

$1J = 1C \cdot 1V$ and charge must move from a point of lower potential to a point of higher potential

Work done is moving charge Q through an electric potential

$$W = EQ \dots \textcircled{2} \quad (W = \overset{\text{volts}}{V} Q)$$

$$\text{Power, } P = \frac{W}{t} = \frac{EQ}{t}$$

$$P = E \left(\frac{Q}{t} \right) = EI \quad (VI) = I^2 R$$

$$\text{Watt} = \text{Volt-Ampere} = J s^{-1}$$

The higher the potential difference btw two points in a given wire,

the more current the wire will carry btw those two point

The quantitative relation btw potential E and current I is such that E is directly proportional to current I

$$E \propto I \dots \textcircled{4}$$

$$E = IR \dots \textcircled{5}$$

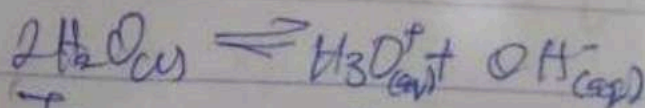
R is the proportionality constant

It is the resistance of the materials and it is measured in ohms.

$$R = V/A$$

SOLUTIONS OF ELECTROLYSIS

If an aqueous solution contains ions, it will conduct electricity. Pure water is slightly ionized partially to hydroxonium ion and hydroxide ion.



It is regarded as a poor conductor.

The solute of an aqueous solution that is a better electric conductor than ordinary pure water is called AN ELECTROLYTE.

An electrolyte is wholly or partially ionized in aqueous solution.

Covalent solute that do not ionize in solution do not enhance the conductivity of the solvent.

They are called non electrolyte e.g. sucrose or any other simple sugar.

An electrolyte can be strong or weak, depending on the degree of ionization. Strong electrolytes are virtually completely ionic in aqueous solution e.g. NaCl.

Weak electrolytes are polar covalent substances that dissociate only partially in aqueous solution e.g. CH_3COOH .

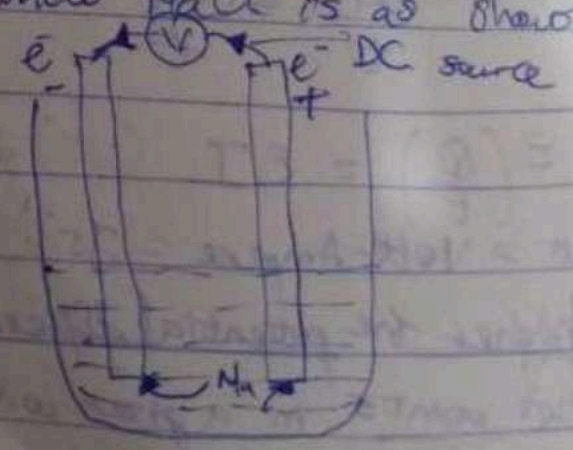
METALLIC & ELECTROLYTIC CONDUCTION

An electric current is the flow of electric charge. In metals, this charge is carried by electrons and the electrical conduction of this type is called metallic conduction.

When electric charge is carried by mobile ions in molten salt or aqueous solution of electrolyte, the electrical conduction is said to be ELECTROLYTIC.

Chemical change must accompany the movement of ions through the electrolyte if the flow of current is to be sustained.

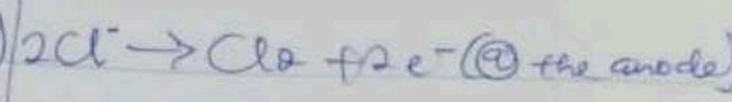
A typical electrolytic cell for the electrolysis of molten sodium chloride NaCl is as shown below.



The direct current source (DC) pumps electrons into the left hand electrode which therefore may be considered to be negatively charged. Electrons are drawn from the right hand electrode which may be considered to be positively charged, in this way, electric field is generated which brings about the attraction of sodium ions i.e. cations towards the negative pole i.e. the cathode.

And chloride ions (anions) move towards to the positive pole, thus the electric charge in electrolytic conduction is caused by cations moving towards the cathode and anions moving towards the anode.

The chemical change that sustains the flow of current in the above cell



CONDUCTANCE OF SOLUTIONS & DETERMINATION OF CELL CONSTANT

The resistance R of a material is directly proportional to its length L and inversely proportional to the cross sectional A

$$R \propto L$$

$$R \propto \frac{1}{A}$$

$$\text{i.e. } R \propto \frac{L}{A}$$

Conductance of Solutions and Determination of Cell Constant

The resistance, R of a material is directly proportional ^{to length} l and inversely proportional ^{to area} to A . $R \propto \frac{l}{A}$

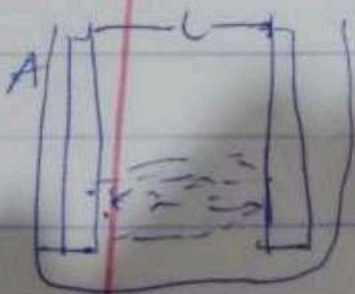
$$R = \rho \frac{l}{A} \quad \text{--- (6)}$$

where ρ is the proportionality constant called resistivity or specific resistance

ρ is an intensive property of a material. The reciprocal of resistivity is called conductivity or specific conductance

$$K = \frac{1}{\rho} \quad \text{--- (7)}$$

The conductivity of a solution btw parallel plates of area A and length l can be determined from its measured resistance



$$\text{as } K = \frac{l}{AR} \quad \text{--- (8)}$$

$$K = \frac{1}{A} \left(\frac{l}{R} \right) = \left(\frac{l}{A} \right) G \quad \text{--- (9)}$$

$$\text{where } G = \frac{1}{R} \quad \text{--- (10)}$$

G = conductance (reciprocal of resistance)

It is possible to change the type of the electrolyte solution contained in a particular electrolytic cell, while its l and A remains the same

In other words, the architectural designs of the parallel plates remain the same, while

Cells of different Physical Configurations ~~consideration~~ are characterized by their cell constants. It should be noted that the cell constant is not just a function of electrode area and separating distance. It is also influenced

by the electric field pattern between the electrodes. This is called the fringe field effect which affects the electrode area by an amount $AR = \text{Area} \times \text{resistance of solution}$ such that the proper determination of the cell constant $K = \frac{L}{A - AR}$ - (12)

which implies that

$$K \approx \frac{L}{A}$$

is only an approximation when $AR \ll A$. However, it is

practically impossible to measure the fringe field effect AR .

The actual value of K

for a particular cell is

determined by measuring the resistance R of a cell containing a solution of known conductivity.

It is usually potassium chloride solution cuz its conductivity is already known at various conc. and temp.

$$K = \left(\frac{L}{A}\right) \frac{1}{R} = K \left(\frac{1}{R}\right)$$

$$\Rightarrow K = FR \quad \text{--- (13)}$$

$$K_1 R_1 = K_2 R_2 = \dots = K_n R_n$$

Example: Cell, the conductivity of the solution of resistance 7.85Ω placed in a cell with plates having cross-sectional area of 5.75 cm^2 and are separated by 1.32 cm

Soln

$$K = \frac{L}{AR} = \frac{1.32}{5.75 \times 7.85} = 2.92 \times 10^{-2} \Omega^{-1} \text{ cm}^{-1}$$

Molar Conductivity

Conductivity of a solution depends on the no of vacuum which include the degree of dissociation of the solution, the mobility of the ion, nature of the solvent, temperature and concentration.

A function that reduces conductivity to a common basis concentration basis is called the molar conductivity,

Λ_m

Molar conductivity can be defined as the ratio of specific conductivity K and the concentration of the electrolyte solution.

$$\Lambda_m = \frac{K}{C} \quad (14)$$

$(\text{cm}^2 \Omega^{-1} \text{mol}^{-1})$

Note that C here is measured in mol cm^{-3} and if the specific conductivity is expressed in the usual unit of $\Omega^{-1} \text{cm}^{-1}$ and the molar conc. of the electrolyte is expressed in the usual unit of mol dm^{-3} , the direct expression of molar conductivity as we have in (14) requires a conversion factor of $\frac{1000 \text{ cm}^3}{\text{dm}^3}$ such that

molar conductivity, $\Lambda_m = \frac{1000 K}{C}$ (14)

$(\text{cm}^2 \Omega^{-1} \text{mol}^{-1})$

for $C = \text{mol dm}^{-3}$, $K = \Omega^{-1} \text{cm}^{-1}$

In order to account for the fact that the charge of an ion in solution determines the

strength in terms of conductivity, the term equivalent conductivity, Λ_{eq} was defined as $\frac{K}{C_{eq}}$ which

is measured in $\text{cm}^2 \Omega^{-1} \text{eq}^{-1}$

$$\Lambda_{eq} = \frac{K}{C_{eq}}$$

The C_{eq} can be defined

$$C_{eq} = \frac{V_i |Z_i| C}{1}$$

where V_i is the no. of moles of ion i in solution

Z_i is the charge of ion, i

Example! Cal. the resistance at 25°C of a conductivity cell with plate having area 7.2 cm^2 separated by a distance of 1.2 cm apart

if it is filled with 0.1 mol/dm^3 soln of sodium chloride whose molar conductivity is $106.74 \text{ cm}^2 \Omega^{-1} \text{mol}^{-1}$

Soln

$$\Lambda_m = \frac{1000 k}{C}$$

$$k = \frac{\Lambda_m C}{1000}$$

$$= \frac{106.74 \times 0.1}{1000} = 0.010674$$

$$R = \frac{L}{A k} = \frac{1.2}{7.2 \times 0.010674} = 15.614$$

Limiting Conductivity and Molar Conductivity at Infinite Dilution

For strong electrolytes, eqn (14) can be expressed as a linear relationship between k and C where the molar conductivity can be seen as the proportionality constant

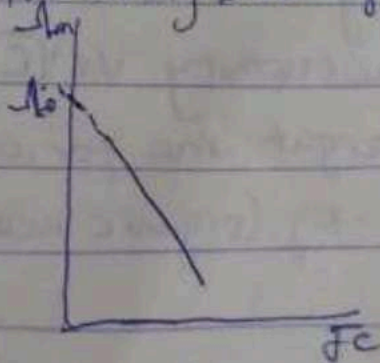
$$k \propto C$$

$$k = \Lambda_m C$$

However, molar conductivity is never constant, it decreases as conc. increases and vice versa.

Therefore

for strong electrolyte



Λ_0 is limiting conductivity.

The plot of molar conductivity against square root of conc.

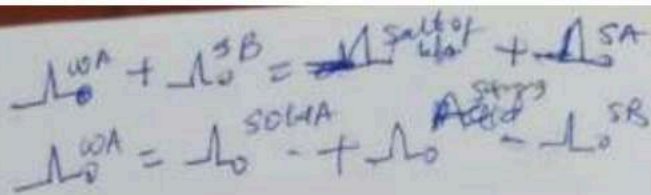
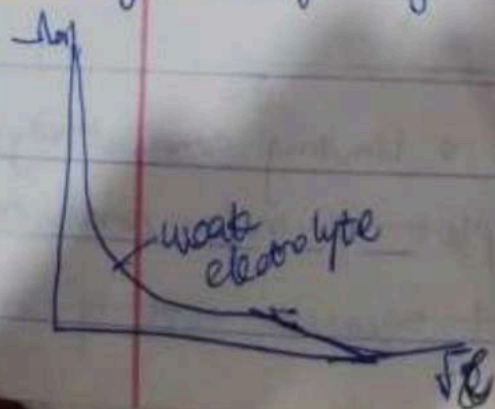
Soln

$$k = \frac{\Lambda_m C}{1000}$$

2) Calc the specific conductivity of a $0.002 \text{ mol dm}^{-3}$ solution of sodium nitrate whose molar conductivity at 25°C is $12.1 \text{ m S m}^2 \text{ mol}^{-1}$ ($12.1 \text{ m S cm}^2 \text{ mol}^{-1}$)

was presented from series of experimental measurement made by current and for a strong electrolyte the plot of Λ_m against \sqrt{C} is a straight line which upon extrapolation to the vertical axis gives an intercept known as the limiting molar conductivity, Λ_0 of the electrolyte.

Kohlrausch proposed the square-root law of the form: $\Lambda_m = \Lambda_0 - k\sqrt{C}$ (17) where k is an experimental constant. Unfortunately, this law could not be applied to weak electrolytes cuz the molar conductivity vs \sqrt{C} is not a straight line for weak electrolytes. eg (organic acid)



In the limit of very small concentrations

$$\Lambda_m = \Lambda_0 \quad (18)$$

$$\text{Cuz } \Lambda_m = \Lambda_0 - k\sqrt{C}$$

Kohlrausch's Law of Independent Migration of Ion

The molar conductivity @ infinite dilution is the sum of partial molar conductivities of independently migrating opp ions.

$$\Lambda_0 = \sum \Lambda_i^2$$

$$\Lambda_0 = \Lambda_0^+ + \Lambda_0^- \quad (19)$$

The underlying assumption here is that each ion migrates in soln without interaction to the other ion, the unique statement in this law is that the ionic conductivity at infinite dilution is a property of the ion alone and it is independent of the counter ion. This is evident in the nearly constant difference in the

molar conductivity Λ_m for pairs of salts having common ion

$$\Lambda_0^{KCl} - \Lambda_0^{NaCl} = 23.4 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$$

$$\Lambda_0^{KNO_3} - \Lambda_0^{NaNO_3} = 23.4 \Omega^{-1} \text{mol}^{-1} \text{cm}^2$$

$$\Lambda_0^{KCl} = \Lambda_0^{K^+} + \Lambda_0^{Cl^-}$$

$$\Lambda_0^{NaCl} = \Lambda_0^{Na^+} + \Lambda_0^{Cl^-}$$

$$\Lambda_0^{KCl} - \Lambda_0^{NaCl} = \Lambda_0^{K^+} + \Lambda_0^{Cl^-} - \Lambda_0^{Na^+} - \Lambda_0^{Cl^-}$$

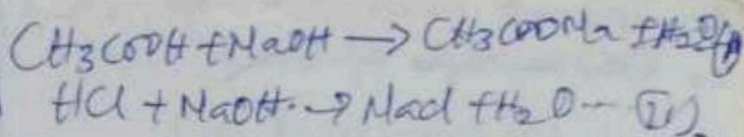
$$= \Lambda_0^{K^+} - \Lambda_0^{Na^+}$$

This statement however is only true @ infinite dilution but not exact @ finite concentration

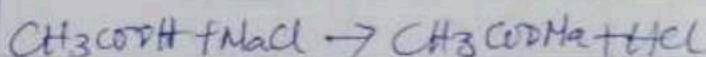
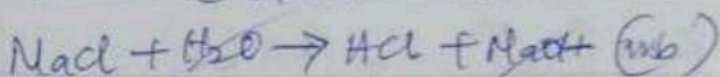
It is impossible to extrapolate Λ_m vs \sqrt{c} of weak electrolytes due to incomplete dissociation leading to steep increase in molar conductivity @ infinite dilution. However, Kohlrausch's law makes it possible to deduce Λ_0 for weak electrolytes from the corresponding value of the related strong electrolytes.

eg $\Lambda_0(\text{CH}_3\text{COOH}) = \Lambda_0(\text{CH}_3\text{COONa}) + \Lambda_0(\text{HCl}) - \Lambda_0(\text{NaCl})$

This follows from!



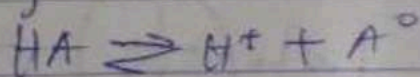
Reverse (ii), then add to (i)



∴ an important application of Kohlrausch's law is the determination of limiting molar conductivity of weak electrolytes which cannot be determined accurately as the intercept of molar conductivity vs \sqrt{c}

Degree Of Dissociation of Weak Electrolytes

Consider a weak electrolyte HA which dissociates partially as



Initially c 0 0

@ equil $(1-\alpha)c$ αc αc

An apparent degree of dissociation was defined for weak electrolyte as

$$\alpha = \frac{\Lambda - \Lambda_0}{\Lambda_0} \quad \text{any conc.}$$

$$\Lambda_0 \quad \text{@ infinite}$$

An apparent dissociation constant K_a can be expressed as

can be expressed as

$$K = \frac{(\alpha C)^2}{(1-\alpha)C} = \frac{\left(\frac{\Lambda C}{\Lambda_0}\right)^2}{\left(1 - \frac{\Lambda}{\Lambda_0}\right)C}$$

from which we can express K to be!

$$K = \frac{\Lambda^2 C}{\Lambda_0(\Lambda_0 - \Lambda)} \quad (21)$$

The Λ value are known for electrolyte @ various concentration along a conductivity cell,

then K can be obtained from the plot of the linear form of eqn 21.

$$\frac{1}{\Lambda C} = \frac{\Lambda_0}{\Lambda^2} - \frac{1}{\Lambda_0 K} \quad (22)$$

In other conductance of an aqueous acetic acid solution as concentration of 0.10 M is $5.2 \frac{\Omega^{-1} \text{cm}^2}{\text{mol}}$ at 25°C, the dissociation constant of acetic acid given that $\Lambda_0 = 390.71$

$$\begin{aligned} K &= \frac{8064}{\frac{5.2^2 C}{390.71(390.71 - 5.2)}} \\ &= \frac{5.2^2 \times 0.10}{390.71(390.71 - 5.2)} \\ &= 1.795 \times 10^{-5} \end{aligned}$$

Ionic Mobility

The molar conductance of a solution depends on the ease of ionic movement. Ionic velocity is not a constant, however it depends on the strength of electric field E ,

they are given by

$$\Lambda_0 = \Lambda_0^+ + \Lambda_0^-$$

$$t_+ = \frac{\Lambda_0^+}{\Lambda_0}$$

$$t_- = \frac{\Lambda_0^-}{\Lambda_0}$$

i.e. $t_+ = \frac{\Lambda_0^+}{\Lambda_0}$, $t_- = \frac{\Lambda_0^-}{\Lambda_0}$

On the other hand, ionic mobility, u , defined as the ionic velocity per unit electric field is a constant. Thus, for a cation

$$u_+ = \frac{v_+}{E}$$

Anim: $\frac{v_+}{E} < u$

where V_+ is the vol of cation moving in an E-F of strength E & V_- is the vol of anion moving in an electric field of strength E.

The ionic mobility, u , has a unit of $\frac{\text{cm/s}}{\text{V cm}^{-1}} = \text{cm}^2 \text{s}^{-1} \text{V}^{-1}$

It is related to the molar ionic conductance at infinite dilution

$$u_+ = \frac{\lambda_+^0}{F}$$

$$u_- = \frac{\lambda_-^0}{F}$$

where F is the faraday constant

Question! The mobility of a chloride ion in water at 75°C is

$$7.91 \times 10^{-4} \text{ cm}^2 \text{ s}^{-1} \text{ V}^{-1}$$

(a) Cal. the molar conductance of the ion at infinite dilution

(b) How long will it take for the ion to travel btw two electrodes

separated by 4.0 cm if the electric field is 20 V/cm

Soln

$$\begin{aligned} \lambda_0 &= F u \\ &= 9650 \times 7.91 \times 10^{-4} \\ &= 76.3 \text{ C s}^{-1} \text{ V}^{-1} \text{ mol}^{-1} \text{ cm}^2 \\ &\approx 76.3 \Omega^{-1} \text{ mol}^{-1} \text{ cm}^2 \end{aligned}$$

$$V = E d$$

$$V = 20 \times 7.91 \times 10^{-4} = 1.58 \times 10^{-2} \text{ cm}^2 \text{ V}^{-1}$$

Solubility Determination

It is defined as molar conductivity $(\Lambda) = \frac{F}{C}$

$$\Lambda = \frac{F}{S}$$

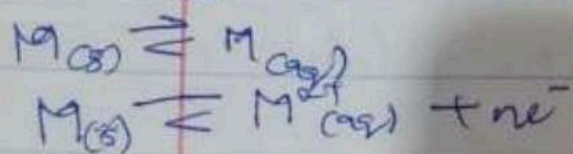
where S is molar solubility
For a sparingly soluble salt, concentration is very low.

$$\Lambda \approx \Lambda_0$$

$$S = \frac{K}{\Lambda_0}$$

Electrochemical Cell

An electrochemical cell is an assemblage consisting of electrodes dipped into an electrolyte and brings about a chemical rxn that either uses or generates electric current. When a metal dips into a solution containing the ion of the metal and equilibrium occur b/w the metal and the metal ion.

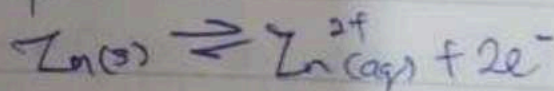


The rxn b/w the metal and its soln @ half rxn eqn

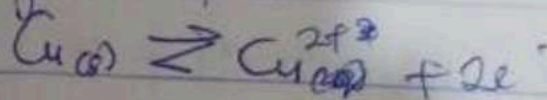
Ions enter solution from the metal leaving electrons behind and metal ions in the solution combine with the electrons of the metal.

A voltage cell consists of two half cells that are electrically connected. Each half cell is the portion of an electrochemical cell in which a half rxn takes place.

Left Half Cell:

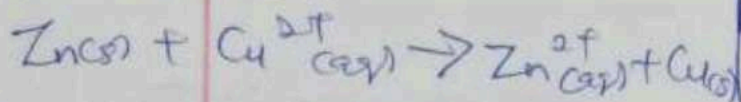


Right Half Cell:



For this cell, zinc loses electron more readily than copper, \therefore zinc metal is ~~dissolving~~ undergoing oxidation, copper undergoing reduction.

Overall cell rxn!



This voltage cell can be written in a shorthand notation as $\text{Zn(s)} / \text{Zn}^{2+}(\text{aq}) \parallel \text{Cu}^{2+}(\text{aq}) / \text{Cu(s)}$

where zinc metal and zinc ion is anode and Cu \rightarrow cathode $\parallel \rightarrow$ salt bridge. It should be noted that!

(i) Anode or oxidation half cell is always written on the left-hand side.

(ii) Cathode or reduction half cell is always written on the right-hand side.

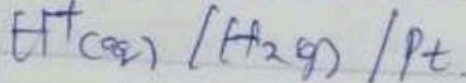
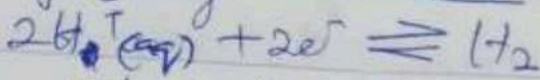
(iii) That the two electrodes are electrically connected by a salt bridge denoted by \parallel

(iv) A single vertical bar $|$ indicates a phase boundary

In a situation where a gas is involved in the half cell such that an ^{unreactive} inert material is used as an electrode surface. The inert material should also be

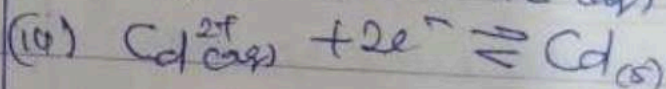
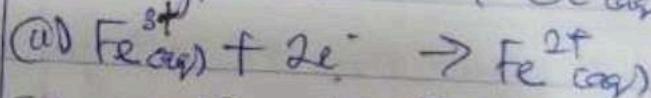
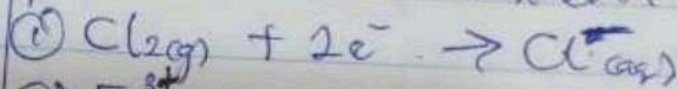
represented in the cell notation

eg hydrogen electrode

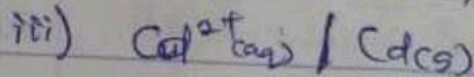
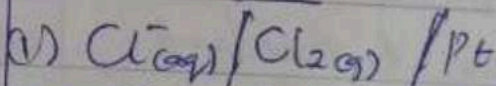


Examples!

Express the following half cell rxn in half cell notation assuming platinum is used as an inert.



soln



ELECTROMOTIVE FORCE

The maximum potential difference between electrodes of a voltage cell is known as the electromotive force of the cell. It is denoted by E_{cell} and it is measured in volts. This maximum voltage or

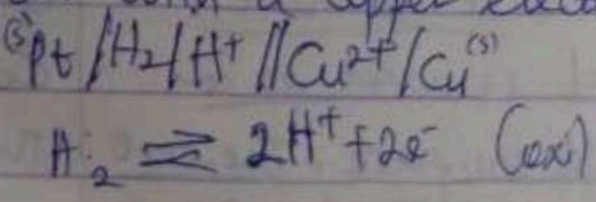
or potential difference is only assumed by the cell when ~~no~~ current moves through the cell. The e.m.f. is measured by a potentiometer. A potentiometer has an adjustable voltage which is varied until it just balances the cell voltage. When the two voltage sources are imbalanced, no current flows from the voltage cell and the e.m.f. of the cell is the balancing voltage of the potentiometer. A standard e.m.f. denoted by E_{cell}° is the e.m.f. of a cell in which all reactants and products are in their standard state.

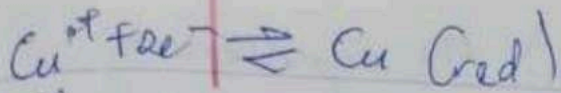
Electrode Potentials & E.M.F.

Each half cell has electrode potential. When two half cells are connected electrically, the e.m.f. of the cell is the sum of the electrode potential of two

half cell. However, it is impossible to determine the absolute value of the electrode potential of a single half cell. All half cell potentials are expressed relative to a referenced electrode potential. The commonly used referenced half cell is the standard hydrogen electrode which is assigned a electrode potential of 0 volts. The standard hydrogen electrode, consists of hydrogen gas @ 1 atm bubbling over a platinum surface. The electrode potentials of other half cells are the measured e.m.f. of the cells when the other half cell is

electrically connected to the hydrogen electrode. For example, let us combine hydrogen electrode cell with a copper electrode cell:





$$E^\circ(\text{ox}) = 0.00\text{V}$$

$$E^\circ(\text{red}) = ?$$

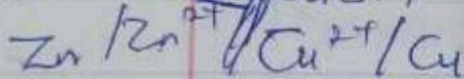
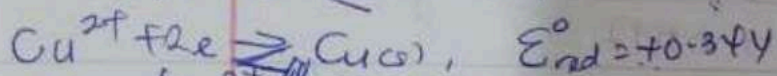
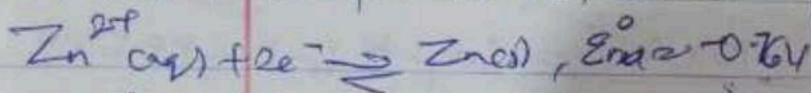
$$E^\circ_{\text{cell}} = E^\circ_{\text{oxi}} + E^\circ_{\text{red}}$$

$$= +0.34\text{V}$$

$$\Rightarrow \text{V of } E^\circ_{\text{cell}} = 0.34\text{V}$$

$$E_{\text{cell}} = 0.34\text{V}$$

Ex! Given E° for two half cell as



Generally; $E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{oxi}}$

$$E^\circ_{\text{cell}} = +0.34 - (-0.76)$$

$$= +1.10\text{V}$$

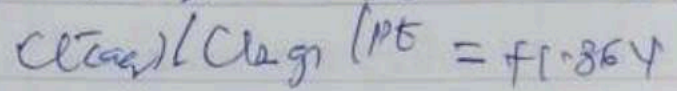
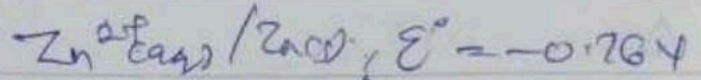
The general convention for writing electrode potential is reduction.

(the one that is most negative is the ^{electrode potential} _{one} undergoing oxidation)

Cal the E°_{cell} with the short

hand notation $\text{Zn} / \text{Zn}^{2+}(\text{aq}) // \text{Cl}^-(\text{aq}) / \text{Cl}_2(\text{g}) / \text{Pt}$ provided the reactants and

Given the standard electrode potential



$$E^\circ_{\text{cell}} = E^\circ_{\text{red}} - E^\circ_{\text{oxi}}$$

$$= +1.36 - (-0.76)$$

$$= +2.12\text{V}$$

Is that a workable cell? ^{Yes, it is workable as each} free

It is workable only if the

overall e.m.f. gives the workdone and ΔG is -ve.

$$(\Delta G = -nFE^\circ)$$

FREE ENERGY, EQUILIBRIUM CONSTANT & E.M.F

The change in ^{free energy} e.m.f, ΔG

for a rxn

ΔG can be related to the

e.m.f of a cell as

$$\Delta G^\circ = -nFE^\circ$$

products are in their standard states

$$\Delta G = -nFE_{cell}^{\circ}$$

n = no of electrons transferred in the overall cell rxn.

F = Faraday constant

E_{cell}° = standard e.m.f of the cell

$$\Delta G = -RT \ln K$$

Then we can equate the maximum work done by the cell such that the e.m.f of the cell

$$\left[E_{cell}^{\circ} = \frac{RT}{nF} \ln K \right]$$

OR

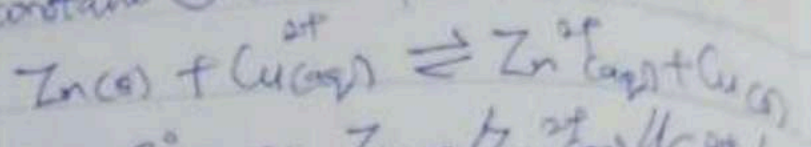
$$E_{cell}^{\circ} = \frac{2.303 RT}{nF} \log K$$

By sub- the constants $R = 8.314 \text{ mol}^{-1} \text{ K}^{-1}$, $T = 298 \text{ K}$, $F = 96500 \text{ C}$

Sub- these values in E_{cell}°

$$E_{cell}^{\circ} = \frac{0.0592}{n} \log K$$

Example 1) Cal- the equilibrium constant @ 25°C for the rxn



If E_{cell}° of $\text{Zn(s)} / \text{Zn}^{2+}(\text{aq}) // \text{Cu}^{2+}(\text{aq}) / \text{Cu(s)}$ = $+1.10 \text{ V}$

Soln

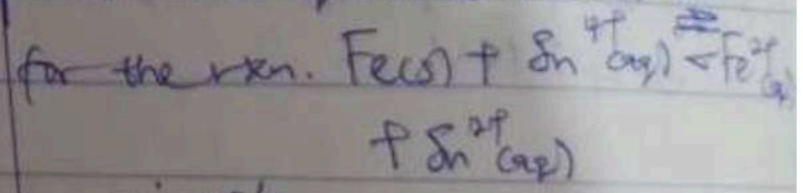
$$E_{cell}^{\circ} = \frac{0.0592}{n} \log K \frac{RT}{nF} \ln K, n=2$$

$$1.10 = \frac{0.0592}{2} \log K \frac{8.314 \times 298}{2 \times 96500} \ln K$$

$$\frac{1.10 \times 2}{0.0592} = \log K \ln K = 85.689$$

$$K = 1.64 \times 10^{37}$$

2) Cal- the equilibrium constant



$\text{Sn}^{4+} / \text{Sn}^{2+} / \text{Pt}$, $E^{\circ} = +0.15 \text{ V}$

$\text{Fe}^{2+} / \text{Fe}$, $E^{\circ} = -0.41 \text{ V}$

Soln

$$E_{oxi}^{\circ} = -0.41 \text{ V}$$

$$E_{red}^{\circ} = +0.15 \text{ V}$$

$$E_{cell}^{\circ} = +0.15 - (-0.41)$$

$$= +0.56 \text{ V}$$

$$0.56 = \frac{0.0592}{2} \log K$$

$$K = 8 \times 10^{18}$$

Spontaneity of Cell Rxn

A cell rxn is spontaneous when its ΔG° is -ve. In other words, a cell will only be able to do work only when its ΔG° is -ve. For ΔG to be negative, E_{cell} must be +ve. If the cell is +ve, it is workable, if otherwise, it is not workable.

The Nernst Eqn

Let us consider a cell rxn
 $aA + bB \rightleftharpoons cC + dD$

$$\Delta G = \Delta G^\circ + RT \ln \frac{a_c^c a_d^d}{a_a^a a_b^b}$$

$$\Delta G = -nFE_{\text{cell}}$$

$$\therefore -nFE = -nFE^\circ + RT \ln \frac{a_c^c a_d^d}{a_a^a a_b^b}$$

$$E = E^\circ - \frac{RT}{nF} \ln \frac{a_c^c a_d^d}{a_a^a a_b^b}$$

This eqn is known as the Nernst eqn.

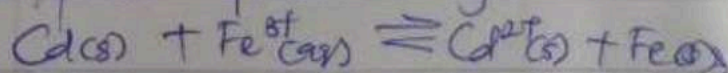
A cell which

At equilibrium, the activity is equal to 1 and $E = 0$

$$E^\circ = \frac{RT}{nF} \ln K$$

$$E^\circ = \frac{-\Delta G}{nF}$$

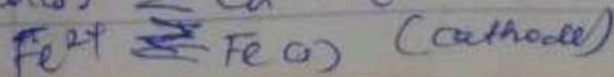
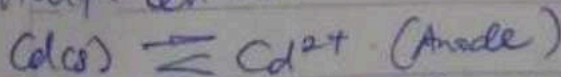
Predict whether the following rxn will proceed spontaneously.



$$[\text{Cd}^{2+}] = 0.1519, [\text{Fe}^{2+}] = 0.6819$$

$$\text{Cd}^{2+}/\text{Cd} = -0.403 \text{ V}$$

Half-cell rxn!



$$E^{\circ} = -0.447 - (-0.403)$$
$$= -0.044 \text{ V}$$

$$E = E^{\circ} - \frac{RT}{nF} \ln \frac{[\text{Cd}^{2+}]}{[\text{Fe}^{3+}]}$$

$$= -0.044 - \frac{0.0257}{2} \ln \left(\frac{0.15}{0.68} \right)$$

$$E = -0.025 \text{ V}$$

Since E is $-ve$, ΔG would be ve

$\therefore R$ is not workable.

① QUANTIZATION OF ENERGY

Existing in discrete & non-continuous form.