Dt. 22.08.12

Rough Practical Note 15/-
Fair " " 45/-
Engineer chem part - I by Shashi Chawla
Physical chemistry through Numericals by Singh & O.P. Tondon.

STRUCTURE & BONDING

Duality: The co-existance of two contrasting properties of nature like wave nature and particle nature. In the case of light or subatomic particles like electrons is known as duality.

- For microscopic particles the wave nature is having physical significance as the λ value can be measured. But for macro object λ is too small to get it. Both this concepts are given in the form of eq. are known as de-Broglie wave eq. It is given as

$$\boxed{\lambda = \frac{h}{mv}}$$

Derivation:

For light, $E = mc^2$

From Plank's concept, $E = h\nu$

$$\Rightarrow h\nu = mc^2 \quad (c = \nu\lambda)$$

$$\Rightarrow h = m.c.\frac{c}{\nu} = mc\lambda$$

$$\Rightarrow \boxed{\lambda = \frac{h}{mc}}$$

Matter waves: These are the kind of wave associated with wave motion of any object (small or big) in space.

- These waves are having physical significance only for micro-objects (like electrons, protons) (λ is measured quantity).

Distinction betn Electromagnetic waves & Matter waves:

Matter wave	EM wave
1) Associated with the wave motion of any object.	1) These are the common forms of wave like light waves.
2) This travels with velocity less than that of light.	2) This travel with light velocity.
3) Don't contain any charged particles.	3) This contain charged particles.
4) No Deflection in electric/magnetic field.	4) Deflection in electric & magnetic field.

Effect of applying voltage:

$$\frac{1}{2}mv^2 = eV \qquad \lambda = \frac{h}{mv} \Rightarrow v = \frac{h}{m\lambda}$$

$$\Rightarrow v^2 = \frac{2eV}{m}$$

$$\Rightarrow \left(\frac{h}{m\lambda}\right)^2 = \frac{2eV}{m}$$

$$\Rightarrow \frac{h^2}{\lambda^2} = 2eVm$$

$$\Rightarrow \lambda^2 = \frac{h^2}{2eVm}$$

$$\Rightarrow \lambda = \frac{h}{\sqrt{2eVm}} = \frac{6.64\times10^{-34}\ Js}{\sqrt{2\times1.6\times10^{-19}\times V\times9.1\times10^{-31}}}$$

$$= \frac{12.25}{\sqrt{V}}\ \text{Å}$$

$$\Rightarrow \boxed{\lambda = \frac{12.25}{\sqrt{V}}\ \text{Å}} \quad [V \text{ in volt}]$$

Conclusion - The wavelength of electronic wave associated with the wave motion of an e^- in space is inversely proportional to voltage applied

to cause the wave motion.

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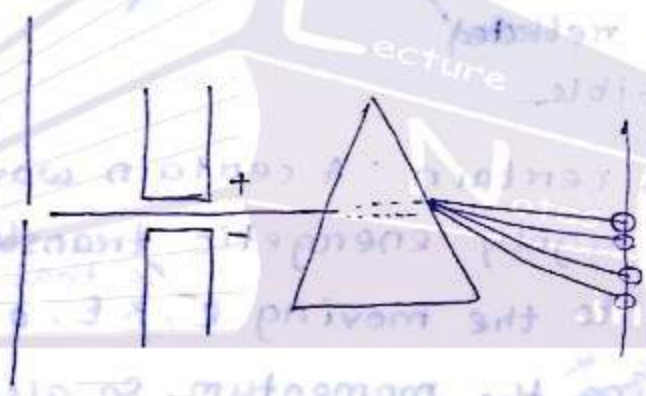
Experimental varibication of wavenature of electron (Davinson - Germer experiment):

When a single source of electron beam is allowed to fall on a crystal after being accelerated through an electric field the debracted rays are allowed to fall on a photographic plate. The debracⁿ patterns found out that they are very much similar to those found out ~~to the~~ in the case XRD [x-ray dibbracⁿ] study of crystals earlier done by William Bragg.

- As x-ray is a wave form of light the electron beam that is taken also behave wave nature.



Uncertainity Principle:

- It is impossible to have two constrasting physical properties of nature like position & momentum of subatomic particle like e^- measured with 100% accuracy simultaneously with the help of one single instrument.

Mathematically,

$$\boxed{\Delta x \cdot \Delta v \geq \frac{h}{4\pi m}}$$

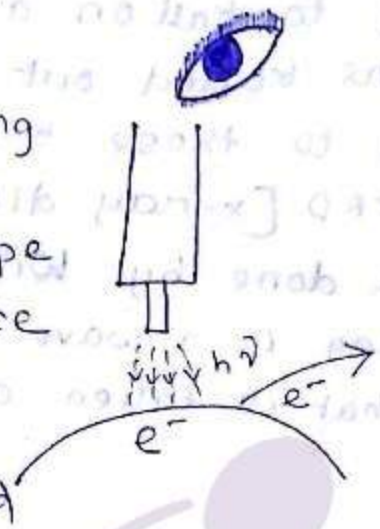
Significance of uncertainity principle:

- This concept is having physical significance only for the microscopic object, as the factor ($\Delta x \cdot \Delta v$) is having some value.

Case study:

Same amount of force is applied on an object having mass 1gm so also an e^- ($m = 9.1 \times 10^{-31}$ kg) to have same velocity. Uncertainity principle has no meaning having mass = 1gm, as ($\Delta x \times \Delta p$) is too small to measure.

Experimental verification:



When we try to make a moving e^- visible by knowing its position with the use of a subisticated e^- microscope,

i) if we use a light source of shorter wave length compare to the size of object the reflected light fall in the visible area.

So position becomes certain. A certain wave-length of light is highly energetic transfers some of its energy to the moving e^-, so that the K.E. of the moving e^- & the momentum changes, so also the path of e^-. So uncertainity w.r. to momentum increases.

ii) If we use a light of longer λ compare to the size of object reflected light doesn't fall on the visible region. So uncertainity w.r. to position (Δx) increases.

So with the help of a single instrument it is impossible to measure these two properties with 100% accuracy.

Dt. 29.8.102

Q) Calculate ~~problem~~ λ associated with an object of 2.2gm which is put into motion with velocity of 3×10^{2} m/s.

$$\lambda = \frac{h}{mv} = \frac{6.62\times10^{-34}\ Js}{2.2\times10^{-3}\times3\times10^{2}\ kgm/s}$$

$$= 10^{-34+1} = 10^{-33}\ m.$$

Q) Calculate uncertainity in position of an e^- having a mass of 9.1×10^{-31} kg & travelling with a velocity of 10^6 m/s in a discharge tube expt. with 1% accuracy.

$$\Delta x \cdot \Delta p = \frac{h}{4\pi}$$

$$\Rightarrow \Delta x = \frac{h}{4\pi m\times\Delta v} = \frac{6.62\times10^{-34}\times7}{2\times3.14\times9.1\times10^{-31}\times10^{6}\times\frac{1}{100}\times2}$$

$$= \frac{2.1}{2\times2\times9.1}\times10^{-34+31-4}$$

$$= \frac{10}{91\times2}\times10^{-7} = \frac{100}{91\times2}\times10^{-8}$$

$$= \frac{1000}{182}\times10^{-9}$$

$$= 5.8\times10^{-9}\ m.$$

[Ans - 5.8×10^{-9} m]

Q) Assuming a 0.01% in-accuracy in the determination of the velocity of a 1kg wt. object moving with a velocity of 100 m/s. Calculate the uncertainity in position & justify your ans.

(Ans) [$\Delta x \cong 5.3\times10^{-33}$ m]

The uncertainity w.r.to mass & velocity is very very small. So the product of uncertainity & momentum is very small.

Q) Justify when the velocity of e^- is 1840 times the velocity of proton, then only the λ associated with an e^- becomes equal to that of proton.

Put de-Broglie eq. , Find λ_p , λ_e .

$\lambda_p = \frac{h}{m_p v_p}$ & $\lambda_e = \frac{h}{m_e v_e}$ then take :

$$\frac{\lambda_p}{\lambda_e} = \frac{m_e v_e}{m_p v_p} = \frac{m_e \times 1840 v_p}{1840 m_e \times v_p} = 1$$

Q) Calculate the λ of e^- which is accelerated from rest ($v=0$) with application of a P.d. of 1000 V. [Ans- 38.7 pm]

$$\lambda = \frac{h}{\sqrt{2meV}} \text{ Å} = \frac{12.25}{\sqrt{V}} \text{ Å}.$$

$= 0.387$ Å

$$\lambda = \frac{12.25}{\sqrt{1000}} = \underline{12.25}$$

Plank's quantum theory :

1) Energy absorbed or emitted by any object is always discontinuous.
2) In the case of light the emission or absorption takes place in the form of packets or bundles of energy.
3) Each packet consist of a large no. of photons with energy equal to $\boxed{E = nh\nu}$ where n - pure positive number.

So a photon can have energy $= 1h\nu, 2h\nu$ but never a value of $1.5h\nu, 2.3h\nu$.

~~Photoelectric effect:~~

Photoelectric effect :

- It is the phenomenon by means of which photoelectrons are emitted from metallic surface having a low ionisation potential high melting pt. with the incident of radiation having frequency more than a minium value. (threshold frequency) which is a characteristic of the metal surface.

(ν_0 is a fun. of IE of metal surface).

Dt. 30.8.12

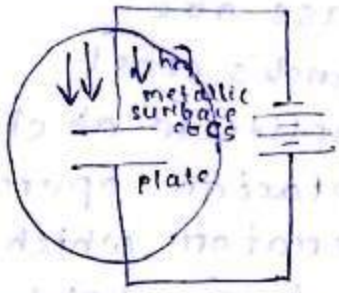
Conditions :

1) Thresh-hold frequency(ν_0) is a characteristic of metal

Low the IE less the ν_0.

2) Metal should have low IE & higher M.P.

3) A small gap is maintained betn the metal surface & the 2nd plate.



- All the incoming photons transfer their energy to make the valance e^- come out of metallic surface. These amount of energy is known as work fun. & the rest is added to the KE of the emerging photo-electrons.

$$h\nu = h\nu_0 + \frac{1}{2}mv^2$$

where $h\nu_0$ = work function i.e. Ionisation potential.

$$\Rightarrow h(\nu - \nu_0) = \frac{1}{2}mv^2$$

$$\Rightarrow \nu > \nu_0$$

~~Collision~~

- The collision betn the incident photon & valance e^- is purely elastic in nature. The fall of the photon & emmission of photo e^- is simultaneous. That is why we use very small space betn metallic surface & plate.
- K.E. of photoelectrons depend on frequency of radiation where as the amount of photoelectric current is dependent on the no. of ~~photoelectron~~ photo e^-s which is a fun of intensity of radiation.
- The least potential required to bring the photoelectrons to rest ($\frac{1}{2}mv^2 = 0$).

Dt. 5.9.12

Time independent Schrondingen's wave eq.:

$$\boxed{\nabla^2\psi + \frac{8\pi^2 m}{h^2}(E-V)\psi = 0}$$

E = Total energy of the atomic state (KE, PE, IE internal energy etc.)

V = potential energy

m = mass of e⁻

h = Planck's const.

ψ = Amplitude of electronic wave.

∇ = Laplacian operator (A mathematical operator which can be operated upon any funⁿ, taking into account all the 3 co-ordinate axes)

$$\nabla\psi = \frac{\partial\psi}{\partial x} + \frac{\partial\psi}{\partial y} + \frac{\partial\psi}{\partial z}$$

$$\nabla^2\psi = \frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2}$$

- It is a 2nd order 3 dimensional wave eqⁿ., representing the 3 dimensional wave motion of an electronic wave in a vol. space (dv) is very close to the nucleus in the form of orbitals like s, p, d, f etc.

Significance:

- When these 3 dimensional is put into solⁿ many solⁿs are found out. Some of them are real & some are imaginary.
- Those solⁿs of ψ which are to be accepted must satisfy the following conditions.

Conditions for ψ:

1) ψ (wave funⁿ) must be finite / single-valued & continuous.

2) $\frac{\partial\psi}{\partial x}, \frac{\partial\psi}{\partial y}, \frac{\partial\psi}{\partial z}$ must be finite / single-valued & continuous. The same should be valid for 2nd order differentials.

- Those accepted sol^{n}s satisfying the above conditions are known as Eigen fun^n. & the corresponding energy values are known as Eigen energy.

Significance of ψ:

- It represents the amplitude of an electronic wave having a 3 dimensional wave motion, exhibiting in orbitals like s,p,d,f etc.
- Various values of ψ (real & imaginary) are known by putting the 3 dimensional Schrondinger's wave eq^n for a particular atomic state into sol^n.
- This wave fun^n known as Eigen fun^n if it is finite, continuous & single valued.

Significance of ψ^2:

- For a light wave it represents the intensity. But for electronic wave it represents the probability of finding max^m electron charge density and some point in a volume space dV very close to the nucleus known as an orbital.

Dt. 6.9.12

Orbital:

- It is the 3 dimensional space very close to nucleus where the probability of finding electron charge density is max^m.
- Mathematically it is given as $\int_{-\infty}^{+\infty} \psi^2 dV = 1$

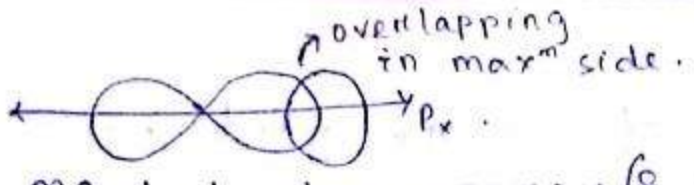
$$\Rightarrow \int_{-\infty}^{+\infty} \psi \psi^* dV = 1$$

ψ - Real value of ψ

ψ^* - Imaginary value of ψ

Significance of getting a real sol^n of the volume integral having both real & imaginary fun^n within the limit of $-\infty$ to $+\infty$ is that the electronic wave propagates/ dissipates even upto ∞. The probability of finding

e.g.



3) A bonding MO is having energy (& stability) much ~~more~~ less compared to that of indivisual atomic orbitals. This is ~~reverse~~ not in case of Antibonding MO.

4) Presence of half filled or unpaired e^-s decides factors like ~~magnitude~~ magnetic behaviour amount of magnetic moment, bond order, stability etc.

5) Overlapping of e^- wave fun^n is decided by a concept known as linear combination of atomic orbitals (LCAO).

Atoms —	A	B
Amplitude of electronic wave fun^n (ψ) —	ψ_A	ψ_B
No. of valance e^- —	1	1

1) In phase (addition) overlapping (bet^n ψ_A & ψ_B):

$$(\psi_A + \psi_B)^2 = \psi_A^2 + \psi_B^2 + 2\psi_A\psi_B = \psi_{AB}^{2b} \quad (b \rightarrow \text{bonding})$$

2) Out of phase (substraction) overlapping:

$$[\psi_A + (-\psi_B)]^2 = [\psi_A - \psi_B]^2 = \psi_{AB}^{2*} \quad (* \rightarrow \text{antibonding})$$

$$\Rightarrow \psi_A^2 + \psi_B^2 - 2\psi_A\psi_B = \psi_{AB}^{2*}$$

Conclusion:
ψ_A^2 & ψ_B^2 represent the probability of binding max^m e^- charge density when the atoms are isolated. But $(\pm 2\psi_A\psi_B)$ represents the probability of binding max^m e^- charge density in a 3D volume space either in case of bonding or antibonding MO. This factor $(\pm 2\psi_A\psi_B)$ is known as overlap integral.

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Importance of overlapping integral:

1) Both the value of overlap integral (I) the extend of bonding & antibonding is known.
2) The value of overlapping integral signifies the no. of bonding M.O. & corresponding no. of antibonding M.O. & anti bonding e^-.

Molecular Orbital Diagram & Electronic Configuration:

1) When e^-'s are being filled up in various bonding & antibonding orbitals the following 3 principles are followed as you do in case of atom.

i) Afbau Principle
ii) Hund's rule of max^m multiplicity
iii) Pauli's exclusion principle.

For homonuclear molecule:

1) For $H_2 - N_2$ (2-14 e^-):

$$\sigma^b_{1s} < \sigma^A_{1s} < \sigma^b_{2s} < \sigma^A_{2s} < (\pi^b_x = \pi^b_y) < \sigma^b_{2p_z}$$

2) For $O_2 - Ne$ (16-20 e^-):

$$\sigma^b_{1s} < \sigma^A_{1s} < \sigma^b_{2s} < \sigma^A_{2s} < \sigma^b_{2p_z} < (\pi^b_x = \pi^b_y) < (\pi^A_x = \pi^A_y) < \sigma^A_{2p_z}$$

- The difference in the above order is because of the fact that upto N_2 the atomic size is very small. So 2s & 2p orbital lie very close to each other. Repulsive interaction bet^n 2s-2s and bet^n 2p & 2p & also 2s & 2p leads to more energy per $2p_z$ also bore $\sigma^b_{2p_z}$ as $2p_z$ orbitals are axially oriented (more repulsion). This is not the case bore O_2 & above, as the atomic size is not that much small.

H_2 :

$B.O. = \frac{1}{2}(N_b - N_a)$

$B.O. \propto \frac{1}{B.L.} \propto$ stability (bond dissociation energy).

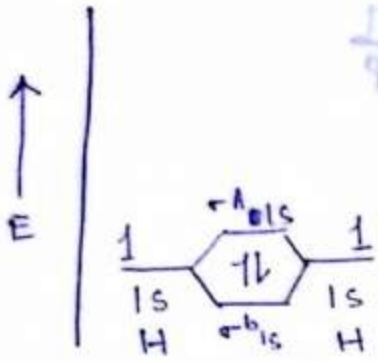
$\sigma^b_{1s^2}$

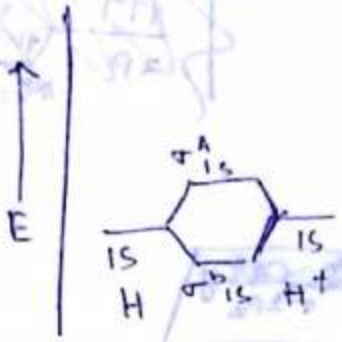
$B.O. = \frac{1}{2}(2-0) = 1$

H_2^+ :

σ^b_{1s}

$B.O. = \frac{1}{2}(1-0) = 0.5$





H_2^- :

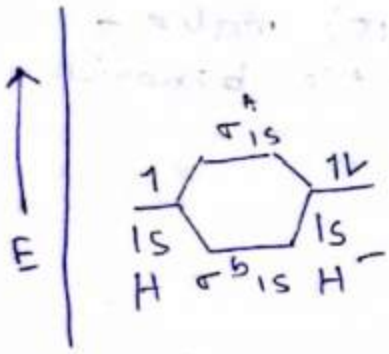
$\sigma^b_{1s^2} \; \sigma^A_{1s}$

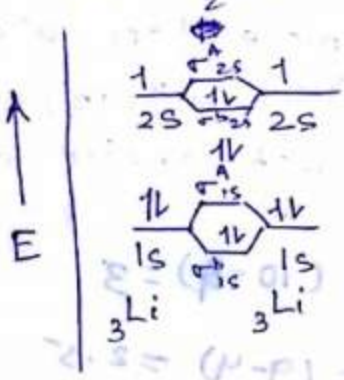
$B.O. = \frac{1}{2}(2-1) = 0.5$

Li_2 : $6e^-$

$\sigma^b_{1s^2} < \sigma^A_{1s^2} < \sigma^b_{2s^2}$

$B.O. = \frac{1}{2}(4-2) = 1$





Q) Make a comparision betn bond order & stability, betn H_2, H_2^+, H_2^- by giving the electronic configuration.

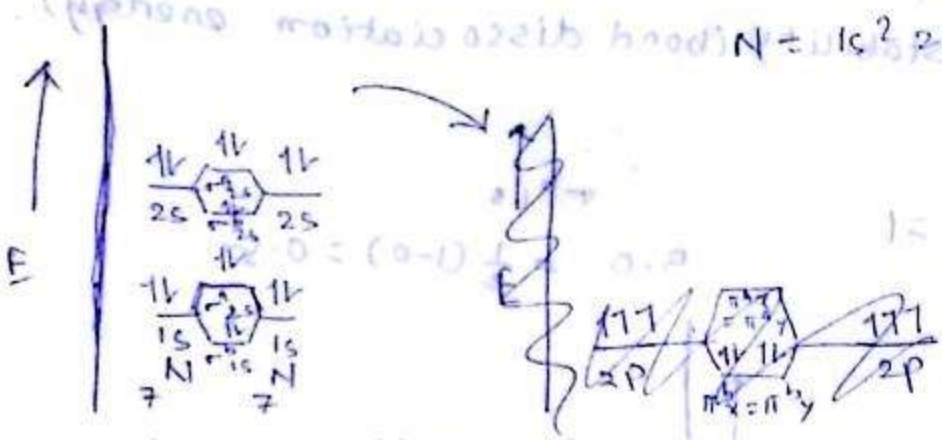
$H_2 > H_2^+ > H_2^-$

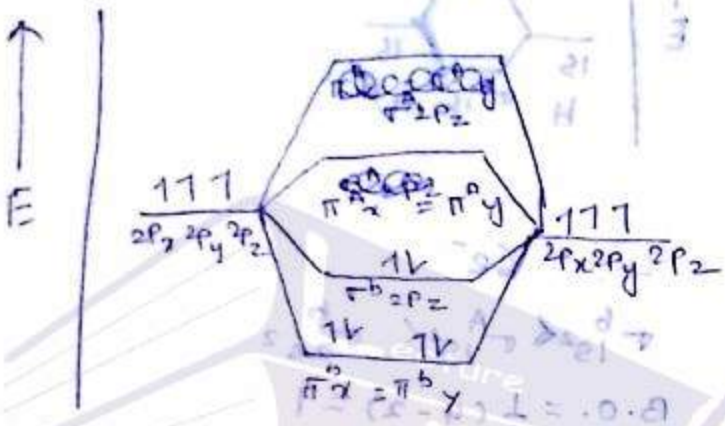
Q) Give a species where we find H_2^+.

N_2:

$N_2 - \sigma^b_{1s^2} < \sigma^A_{1s^2} < \sigma^b_{2s^2} < \sigma^A_{2s} < (\pi^b_x = \pi^b_y)^4 < \sigma^b_{2p_z^2}$

$N = 1s^2\, 2s^2\, 2p^3$





Q) By giving the molecular electronic configuration of $N_2(14)$, $N_2^+(13)$, $N_2^-(15)$ make a comparision bet^n their magnetic behavior & stability.

B.O. of N_2 (14) : $\frac{1}{2}(10-4) = 3$

N_2^+ (13) : $\frac{1}{2}(9-4) = 2.5$

N_2^- (15) : $\frac{1}{2}(10-5) = 2.5$

$N_2 > N_2^+ > N_2^-$

O_2:

$O_8 = 1s^2\, 2s^2\, 2p^4$

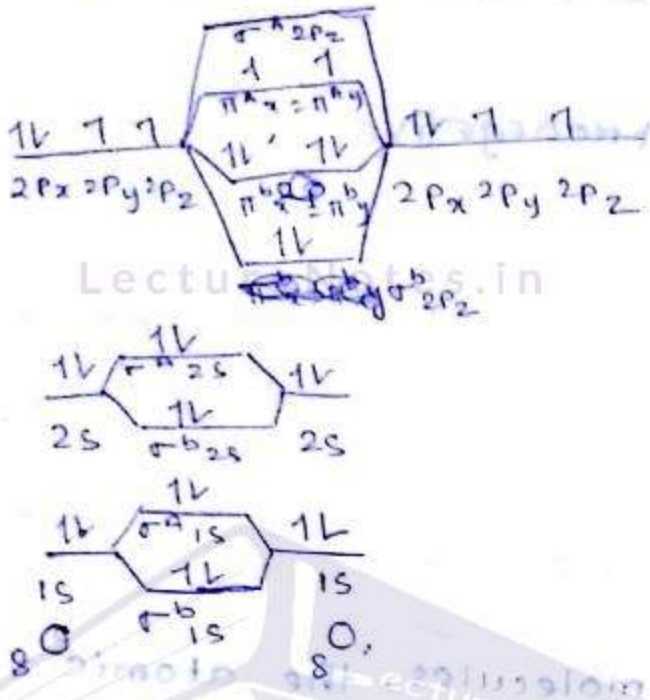
$O_2 = \sigma^b_{1s^2} < \sigma^A_{1s^2} < \sigma^b_{2s^2} < \sigma^A_{2s^2} < \sigma^b_{2p_z^2} < (\pi^b_x = \pi^b_y)^4$

$< (\pi^A_x - \pi^A_y) < \sigma^A_{2p_z}$

Lone pairs in O_2 molecule are

$\sigma^b_{2s}{}^2$ $\sigma^A_{2s}{}^2$

$B.O. = \frac{1}{2}(10-6) = 2$



Q) Writing the e^- configuration of O_2 molecule specify the lone pairs available.

Q) Writing the molecular e^- configuration of O_2, O_2^+, O_2^- & O_2^{2-}. compare their magnetic property & stability.

Q) Find out the bond order and O-O bond length available in the following species.

i) H_2O_2 iii) O_2^+

ii) O_2

Q) Make a comparision of bond stability & magnetic behaviour for He_2, He_2^+, He_2^{2+}

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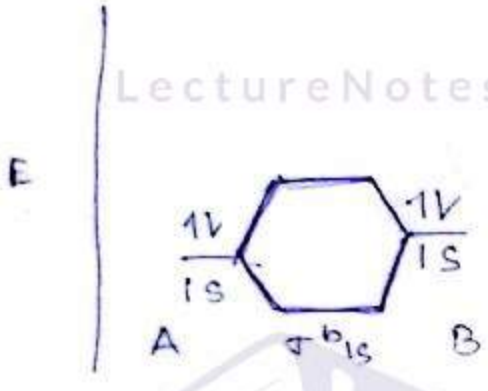
- Electronegetive element contribute more toward antibonding orbital rather than bonding orbital ~~viceversa~~. Similary electrodve element contribute more towards bonding.

Eg A → more electronegetive

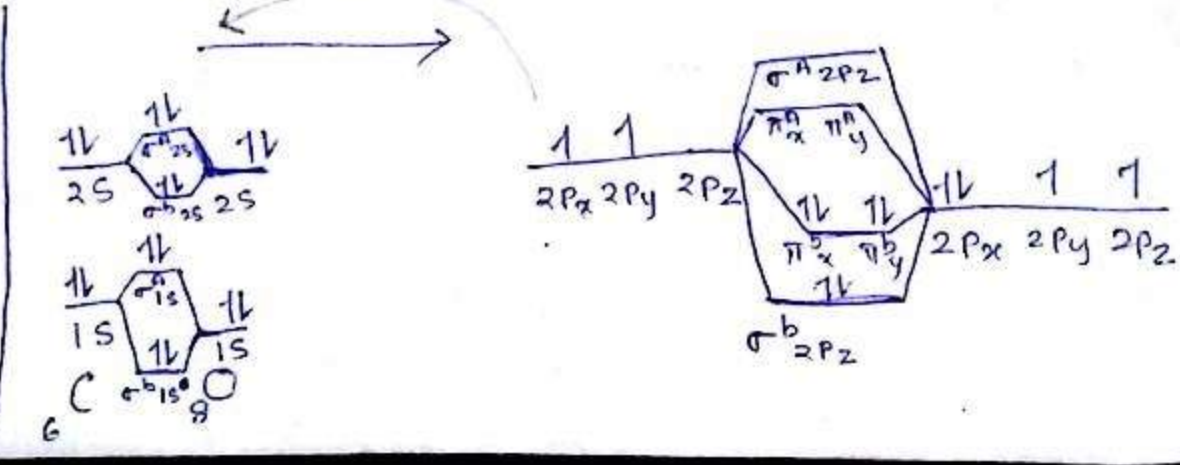


- In heteronuclear molecules, the atomic orbitals of a ~~more~~ less electronegetive element make more contribution to the bonding MO. Whereas the atomic orbital of ~~less~~ more electronegetive element makes more contribution to the antibonding. The indivisual atomic orbitals being at different levels make different amount of contribution either to bonding or antibonding. So we get a distorted str.

CO: (14 electrons)

$\sigma^b_{1s^2} < \sigma^A_{1s^2} < \sigma^b_{2s^2} < \sigma^A_{2s^2} < \sigma^b_{2p_z^2} < (\pi^b_x = \pi^b_y)^4$

B.O. $= \frac{1}{2}(10-4) = 3$ [C≡O]



Reason of $2p_z$ bonding:

- As the energy of $2p_x, 2p_y$ & $2p_z$ are approx. same, so e^- from $2p_y$ go to $2p_z$ orbital of C. Then they form $\sigma^b_{2p_z}$.
- Now again from $2p_x$ an e^- go to $2p_y$ on $2p_y$ & after overlapping remaining element.

- When an e^- lost from antibonding MO. B.O. increases. (If B.O. increases bond length decreases.)

- For CO^+ configuration is written as

$$\sigma^b_{1s} < \sigma^A_{1s} < \sigma^b_{2s} < \sigma^b_{2p_z} < (\pi^b_x = \pi^b_y)^4 < \sigma^A_{2s}$$

To explain the above change in the order, it is suggested that the X-Ray dibbraction study of CO & CO^+ indicates that the bond length of CO is more than CO^+, so to explain the decrease in bond length so to explain the decrease in bond length from CO to CO^+ the bond order should go up, for that the valance e^- must be lost from an antibonding MO.

- CO is diamagnetic.

Q) Make a comparision betn CO, CO^+, CO^- by writing their electronic configuration w.r. to magnetic behaviour & stability.

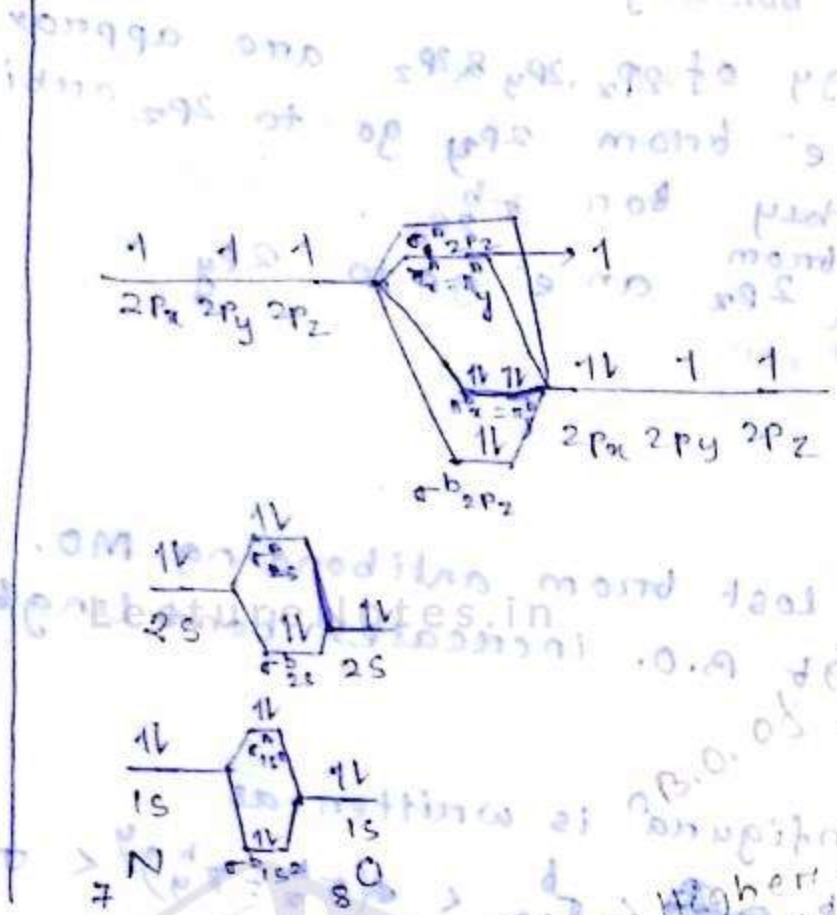
NO: (15-electrons)

$$\sigma^b_{1s^2} < \sigma^A_{1s^2} < \sigma^b_{2s^2} < \sigma^A_{2s^2} < \sigma^b_{2p_z^2} < (\pi^b_x = \pi^b_y)^4 < (\pi^A_x = \pi^A_y)^1$$

$$B.O. = \frac{1}{2}(10-5)$$

$$= 2.5$$

It is paramagnetic.



Q Make a comparision betn NO, NO+, NO− w.r.t. their magnetic behaviour and bond dissociation energy.

Higher the

HF: (10 electrons) H− 1s¹ F− 1s² 2s² 2px² 2py² 2pz¹ (Non-bonding pairs, Lone pairs)

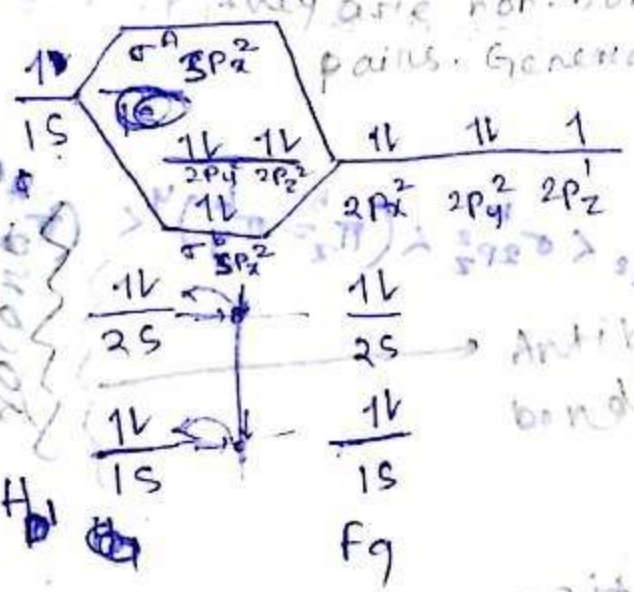
$\sigma^b_{1s^2} < \sigma^A_{1s^2} < \sigma^b_{2s^2} < \sigma^A_{2s^2} < \sigma^b_{2p_z^2}$

$B.O. = \frac{1}{2}(\overset{2}{\cancel{6}} - \overset{0}{\cancel{4}}) = 1$

$1s^2 < 2s^2 < \sigma^b_{sp_x}{}^2 < (2p_y^2 = 2p_z^2) < \sigma^A_{sp_x}$

For molecules $1s^2 < 2s^2 < \sigma^b_{sp_x}{}^2 < (2p_y^2 = 2p_z^2) < \sigma^A_{sp_x}$

1s² & 2s² are not lone pair. They are non-bonding pairs. Generally lone pairs are of valence shell/ electron-rich orbital



Antibonding (σ*1s < σ1s) bond (σ*1s < σ1s)

2) Give the electronic configuration of HCl.

Dt. 26/9/12

Metallic bonding:

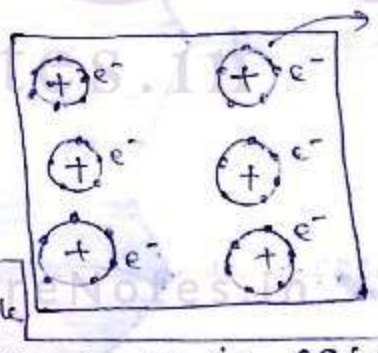
d' block elements - $(n-1)d^{1-10} ns^{1-2}$

f' block elements - $(n-2)f^{1-14} (n-1)d^{1-10} ns^{1-2}$

- The various characteristics of metal like valancy, complex formⁿ, good electrical & thermal conductivity etc. can be explained on the basis of avialability of a good no. of free electrons and vacant orbitals. It is the mobile moment of this free e⁻s betⁿ the valance level and the higher vacant orbitals, which explains all the above characteristics.

Electron-Gas model:

Here the metal surface is thought to have composed of a large no. of +vely charged cations known as Kernels and an equivalent no. of free electrons & it is the coulombic interaction betⁿ these two which makes a strong metallic bonding.



Virtually these cations are nothing but gases. It is easier for isolated gas to ionise to cation because the molecules are more flexible so there is no force on atoms. So it is easier in case of gas.

Molecular Orbital Theory (MOT):

On a metallic surface when the no. of atoms is least (i.e. 3) the valance electrons are placed in the increasing order of bonding MO, non-bonding MO then antibonding MO.

- When conc. of atoms is more then the energy gap betⁿ normal valance level

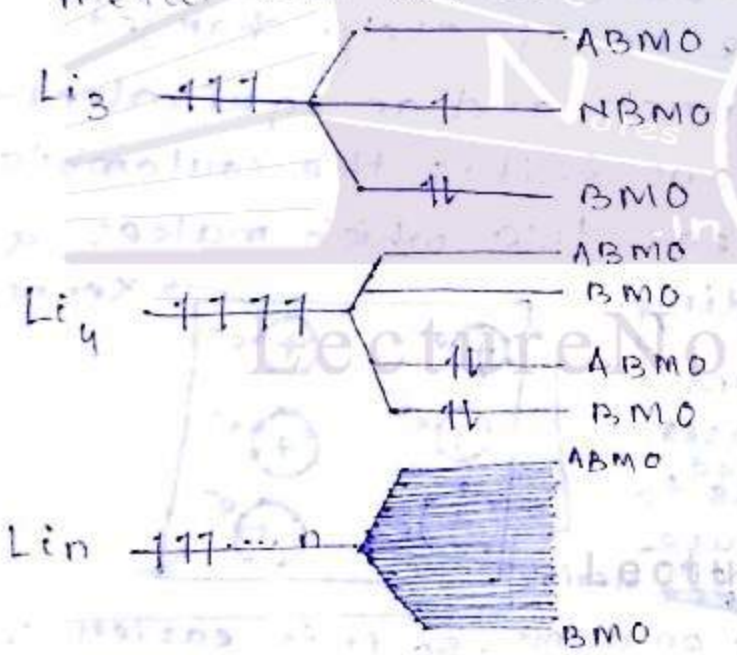
i.e. bonding MO & the higher antibonding MO is bound to be less. This helps in transition of the free e^- or valance e^- becomes much more easier as the energy gap becomes much much less.

- The energy of ground state (BMO) is referred to as valance band energy & that of the high ABMO is refered to as the conduction band energy.

i) If the energy gap betn valance band & conduction is much less, then the metal acts as 100% conductor.

ii) If the energy gap is high then metal acts as insulator.

iii) If energy gap is of avg. value the metal can act as a semiconductor.



Vand defect

PHASE EQUILIBRIUM:

It is an application of thermodynamics which takes into account the various phase changes at definite temp. & press. with a corresponding change in enthalpy.

~~Mathematically~~

Phase Rule:

- It is only applicable to heterogenous system (both physical & chemical) in equilibrium.
- Mathematically it is given as

i) Normal: $F = C - P + 2$

where F = degree of freedom.
C = no. of components
P = no. of phases.
'2' stands for two indepent variables like temp. & press.

(e.g. - H_2O system, Sulphur system)

ii) Condensed (Reduced):

$F = C - P + 1$

'1' stands for only one independent variable (temp.).

(e.g. - Fe-C system, Bi-Cd system, Cu-Zn, Cu-Ag system)

Dt 27/9/12.

Phase diagram:

It is a schematic diagram betn the independent variables like press., temp. or composition, which gives enough information about a phase change in a heterogenous system at equilibrium.

Phase (P): It is an individual part of a heterogenous system at equilibrium, which is physically distinct, mechanichally separable & each one is well separated by a well defined boundary.

Note:

i) Each solid is an indivisual phase.

ii) Gaseous mixture is one phase (e.g. : atmosphere)

iii) Miscible liquids are one phase (e.g. - alcohol + water, water + milk, benzene + cyclohexene etc.).

iv) Immiscible liquids ~~then they~~ are in the no. of ~~liquid~~ phases equal to the no. of liquids.

v) Saturated salt sol^n is in one phase.

vi) Unsaturated salt sol^n is in 2 phases.

1) $CaO(s) + CO_2(g) \longrightarrow CaCO_3(s)$

No. of phase = 3

2) $Zn(s) + H_2SO_4(l) \longrightarrow ZnSO_4(s) + H_2(g)$

No. of phase = 4

3) Partially frozen H_{Ac} (Acetic acid)

No. of phase = 2

4) $Fe(s) + H_2SO_4(l) \longrightarrow Fe_2SO_4(s) + H_2(g)$

No. of phase = 4

<u>Component (C)</u>: It is the least no. of independently variable constituents with the help of which a phase can be known either directly or indirectly with the help of a chemical eq.

1) Simple system (Only phase change):

$$H_2O(s) \rightleftharpoons H_2O(l) \rightleftharpoons H_2O(g)$$

Here component = 1

phase = 3

So $F = C - P + 2$

$= 1 - 3 + 2$

$= 0$

$I_2(s) \rightleftharpoons I_2(l)$

KCl, NaBr, H_2O

$KCl \rightleftharpoons K^+ + Cl^-$

$NaBr \rightleftharpoons Na^+ + Br^-$

$C = S - (R + 1)$

$= 6 - (2 + 1)$

$= 6 - 3 = 3$

2) Indirect (Chemical process):

a) Non-ionic:

$C = S - R$

C → components
S → Indivisual species
R → No. of chemical eq.

e.g. $CaC_{(s)} + CO_{2(g)} \longrightarrow CaCO_{3(s)}$

$C = S - R$
$= 3 - 1$
$= 2$
$P = 3$

b) Ionic:

$C = S - (R+1)$

'1' is added of electrical neutrality.

e.g. - $NaCl_{(s)(l)} - KCl_{(s)(l)} - H_2O_{(l)(l)}$ system.

$Na^+_{(1)}$ $Cl^-_{(5)}$ $K^+_{(6)}$

$NaCl \rightleftharpoons Na^+ + Cl^-$
$KCl \rightleftharpoons K^+ + Cl^-$

$C = S - (R+1)$
$= 6 - (2+1)$
$= 6 - 3 = 3$

$NaCl_{(s)} - KBr_{(s)} - H_2O_{(l)}$ system

Na^+_{4} Cl^-_{5} K^+_{6} Br^-_{7} $NaBr_{8}$ KCl_{9}

$NaCl \rightleftharpoons Na^+ + Cl^-$
$KBr \rightleftharpoons K^+ + Br^-$
$KCl \rightleftharpoons K^+ + Cl^-$
$NaBr \rightleftharpoons Na^+ + Br^-$

$C = S - (R+1)$
$= 9 - (4+1)$
$= 4$

$NaCl - KCl - H_2O$ (100% ionised) system

$NH_{3(g)} - HCl_{(l)} - NH_4Cl_{(s)}$ system

$\log K = \frac{\Delta H}{2.303RT}$ Ellingham

$\Delta G = \Delta H - T\Delta S$
$\Rightarrow 0 = \Delta H - T\Delta S$
$\Rightarrow \Delta H = T\Delta S$

Degree of freedom(F):

It is the least no. of independent variables like temp., press., composition with the help of which a heterogeneous system at equilibrium can be explained completely

- If $F = 0$, system is known as zero variant.
- If $F = 1$, system is known as uni/mono variant.
- If $F = 2$, system is known as bivariant.

Dt. 3/10/12

Note:

1) For any system $P > 1$, $C \geq 1$, $F \geq 0$.
   $F > 3$ & a -ve value never allowed.

2) For any 2 systems having same value of P, $C \propto F$.

3) A system is said to be in complete equilibrium if the system can be visualised or explained from all possible directions.
   e.g. - Triple pt. of water / sulphur system
   Eutetic pt. of alloy system.

4) The system is said to be in metastable equilibrium if the system can be visualised only from one direct.
   e.g. - metastable pt. of water system.

5) In a phase diagram a single phase is always represented by area.

6) A two phase equilibrium is represented by a line.

7) A 3 phase equilibrium is represented by a pt.

Advantages of phase rule:

1) Much informd about the values of P, C & F under a given set of variables.

2) Much informa^n about the equilibrium stage of a heterogenous system involving independent variables like temp & press.

3) Much information about involvement of thermodynamic fun^n like ΔG, ΔH & ΔS, along with the type of process.

Disadvantages:

1) Only restricted to heterogenous system at equilibrium.

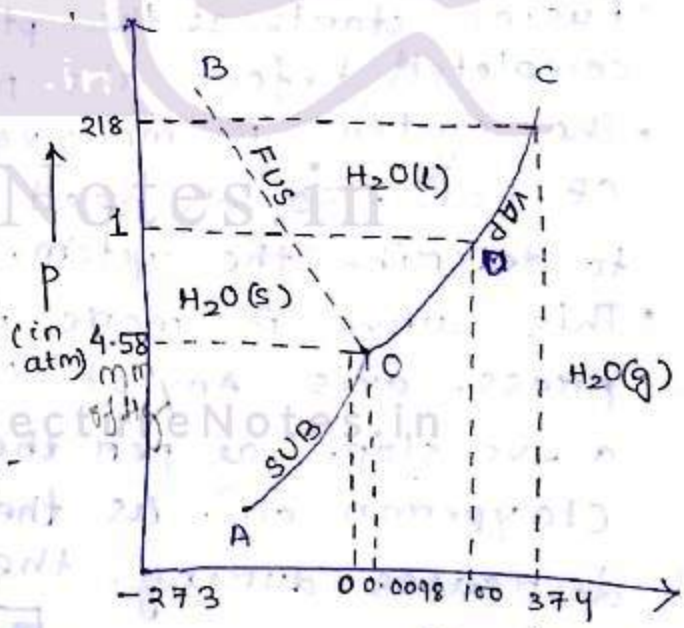
2) It gives only the value of P, C & F but never says about the amount of phases etc.

3) There are some good systems having F > 3 but phase rule is not applicable to it.

ONE-COMPONENT SYSTEM:

1) Water system:

- It is a one component system having all the 3 phases co-existing at the triple point.
- This phase diagram is having 4 curves out of which three are the normal phase transformation & the 4th one is a metastable curve.



- Area within BOC represents water in liquid phase. Area left of AOB represents water in solid phase/ice. Area right of AOC represents water in gaseous phase/water vapour.

OA curve:

- It represents a complete equilibrium bet^n $H_2O(s)$ & $H_2O(g)$. Starting at its sublimation temp.

- The lower point of this curve is -273°C which is reffered to as absolute zero temp. (On absolute zero, all the molecules don't have any motion.) At this no vapour phase exist. So 100% water is solid.
- This curve shows the influence of both temp. & press. on the ~~process~~ rate of sublimaⁿ (+ve effect).
- The sublimation gets completed just before the pt. 'O'.

Ct. 4/10/12

OB curve:

- $H_2O_{(s)} \rightleftharpoons H_2O_{(l)}$ (Fusion)
- This curve shows the effect of press on the melting of ice.
- mp of ice is indirectly proportional to vapour pressure.
- Fusion starts at the pt. 'O' & almost gets completed before the pt. 'B'.
- The system is monovariant, at any pt along OB (F=1). So we need either temp. or press. to describe the system.
- This curve is more inclined towards the press. axis. Any pt. on this curve is having a -ve slope as per the ~~gives~~ Clausious-Clayperan eqⁿ. as the volume of water decreases during the melting of ice.

OC curve:

- It maintains equilibrium betⁿ

$H_2O_{(l)} \rightleftharpoons H_2O_{(v)}$

- The system is mono-variant along this curve as F=1.

Clausious-Clayperan eqⁿ. gives a relationship betⁿ the change in independent variables like temp. & press. with thermodynamical funⁿs like ΔH or ΔS. Mathematically it is

$F = C - P + 2$

$= 1 - 2 + 2 = 1$

given as

$$\frac{dP}{dT} = \frac{\Delta H}{\Delta V} = \frac{\Delta S}{\Delta V}$$

- Boiling starts at pt. 'O' and can go upto pt. M corresponding to a temp. of 100°C & press. of 1 atm, which is the normal BP of water.
- This curve is more tilted towards the temp. axis.
- BP of water ∝ vapour press.
- Any pt. along this curve is having a +ve slope (as per the Clacius - clayperan eq.)
- The upper pt. of this curve corresponds to a temp. of 374°C which is the critical temp. of water ($T_c = 374°C$) & the corresponding press. (218 atm) is known as the critical press. of water.
- Critical temp. is that temp. beyond which no easy liquification is possible.

e.g.- when (V) is put into liquification at its own P_c value but increasing of P_c value, a defined form of (l) comes out - know as supercritical fluid.

- Supercritical CO_2 is helpful in the extract^n of caffeine.

Metastable pt. (OD):

- This is a small deviation from OC curve.
- It represents a metastable equilibrium bet^n

$$H_2O(l) \rightleftharpoons H_2O \text{ (supercooled)}$$

- This ~~system~~ curve is very short lived & unstable because the temp. have a bigger effect on it.
- e.g.- Existance of some amount of water even at -4°C under the ice caps in the north pole.

Why:
Fusion curve of water is having a -ve slope/
The fusion curve of water system is more inclined towards press axis.
As the volume changes so it is

Triple pt. (O):

- It is the end pt. of one process & the begining of another process where the 3 phases co-exist.
- Phase is max^m i.e. 3 & F is minimum i.e. 0.
- This pt. corresponds to a press of 4.58 mm & a temp. of 0.0098°c.
- The system is non-variant/zero variant/invariant as any change w.r. to either temp. or press makes a heavy/big change on this pt. If any change is made with r. to either the two variable one phase vanishes. & the pt. can move along any of this curves.

Physical significance of triple pt.:

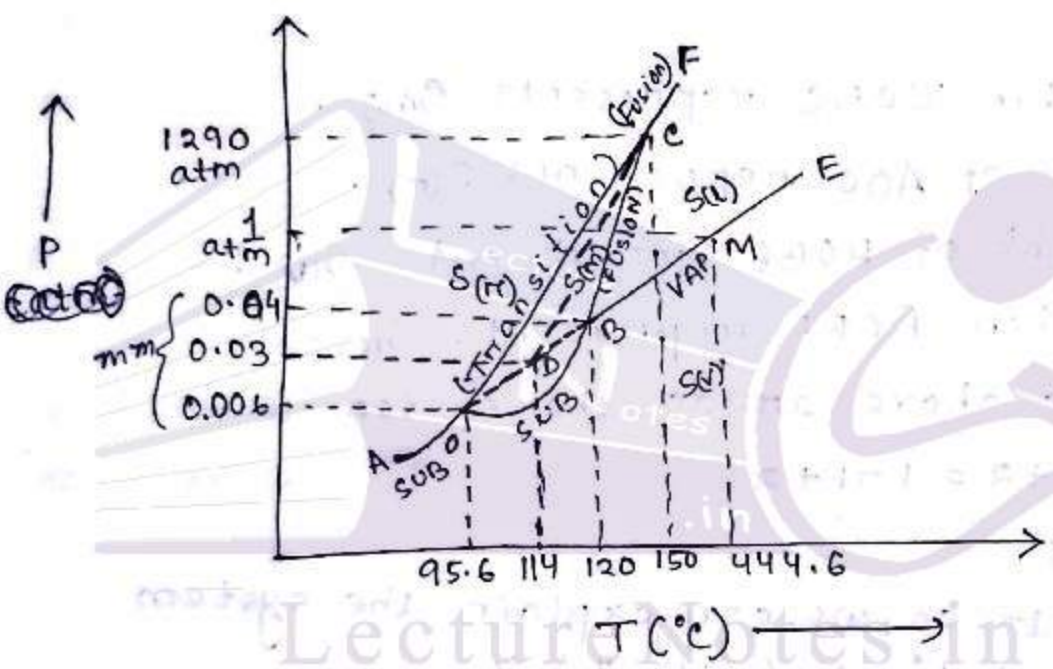
- It gives much information about the importance of independent variables like P&T & max^m phase change.
- It gives information on the physical state of an equilibrium stage, involving max^m phases.
- It gives information about nature of process & importance of thermodynamic properties ΔG, ΔH etc. at this pt.

Lt. 10/10/12

Sulphur System:

- It is a one component system having 4 phases.
- The 4 phases include ~~sulphur~~ $S_{(rhombic)}$, $S_{(monoclinic)}$, $S_{(liquid)}$ & $S_{(vapour)}$.
- $S_{(r)}$ is stable at room temp. where as $S_{(m)}$ is stable at 95.6°C. This 95.6°C temp. is known as the transition temp.

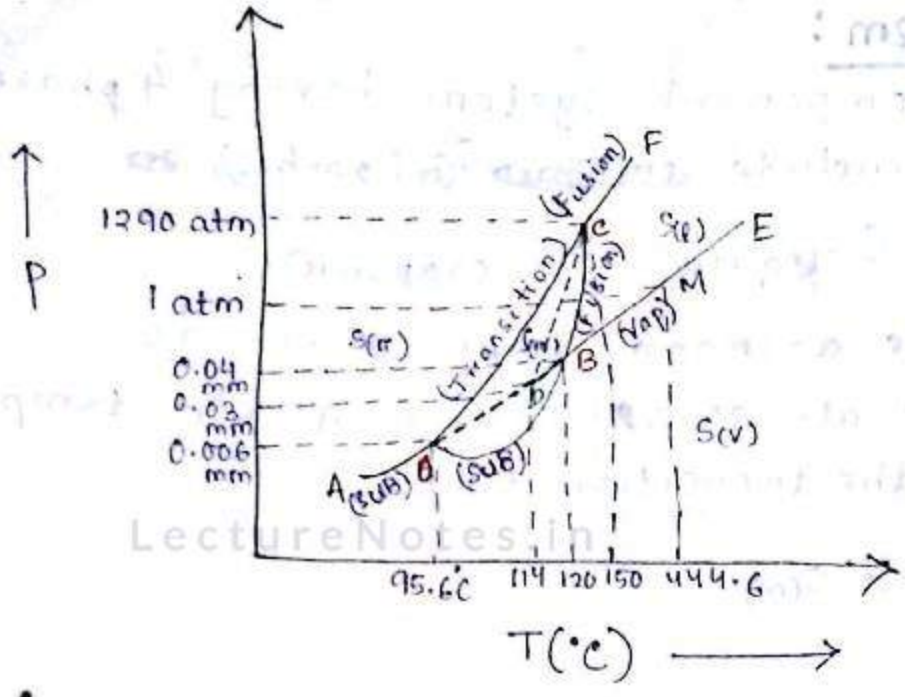
$$S_{(r)} \xrightleftharpoons{95.6^\circ C} S_{(m)}$$



The phase diagram has 6 curves representing transition, vaporisation & fusion. Besides this there are 3 metastable curve. These diagram also contain 3 normal triple pts & one metastable pt.

✓ In this system, no 4 phases can not exist at any time at any pt. Because

$$F = C - P + 2$$
$$= 1 - 4 + 2$$
$$= -1$$ which is not allowed.



Area:

Area within COBC represents $S_{(m)}$.
Area left of AOC represents $S_{(r)}$.
Area right of ACBE represents $S_{(v)}$.
Area within FCBE represents $S_{(l)}$.
In all the above areas, the system is

$F = C - P + 2 = 1 - 1 + 2$

$\Rightarrow (F = 2)$

bivariant so we can explain the system with the help of both T & P.

Curves:

OA: Represents a complete equilibrium bet

$S_{(r)} \rightleftharpoons S_{(v)}$

The sublimation starts at the pt. A goes upto a pt. very close to 'O'. Pt. 'O' corresponds to a temp. of 95.6°C & a press. of 0.006 mm of Hg. The system is monovariant along this curve ($F = C - P + 2 = 1 - 2 + 2 = 1$). This curve is more tilted towards temp. axis.

OB: Represents a complete equilibrium bet

$S_{(m)} \rightleftharpoons S_{(v)}$

It starts from pt. 'O' goes upto a pt. very close to 'B'. The system is monovariant along this curve (F=1). This curve is more inclined towards temp. axis.

BC: Represents a complete equilibrium betn

$$S_{(m)} \rightleftharpoons S_{(l)}.$$

The lower pt. of this curve (B) corresponds to a temp. of 120°C and a press. of 0.04mm of Hg. 120°C is the normal melting pt. of $S_{(m)}$. The system is monovariant along this curve (F=1). This curve is more inclined towards the temp. axis. So the M.P./Fusion pt. of $S_{(m)}$ is directly proportional to Patm.

BE: Represents a complete equilibrium betn

$$S_{(l)} \rightleftharpoons S_{(v)}.$$

Maximum boiling is by a temp. of 444.6°C & press. of 1atm. This temp. is known as normal BP of $S_{(l)}$. It is monovariant (F=1).

OC: Represents a complete transition betn

$$S_{(r)} \rightleftharpoons S_{(m)}.$$

This curve goes upto the pt. 'C' corresponding to a temp. of 150°C & a press. of 1290 atm. The system is monovariant along this curve (F=1). This curve is more tilted towards temp. axis & any pt. along this curve is bound to have a +ve slope as per Clausius-Clapeyron eq. ($S_{(r)}$ is more dense than $S_{(m)}$)

$\rho_{S_{(r)}} = 2.06$, $\rho_{S_{(m)}} = 1.86$

04.11/10/12

CF: Represents complete equilibrium betn

$$S_{(r)} \rightleftharpoons S_{(l)}$$

It is a fusion curve. It starts at a pt. C corresponding to temp. 150°C & press 1290 atm. (which doesn't normally take place). The system is monovariant along this curve (F=1).

Metastable curves:

- These represent the curves OD, BD & CD which are very small deviation from the normal phase change.
- These 3 curves represent either sudden cooling, sudden heating or sudden transin of $S_{(r)}$ to $S_{(m)}$.

OD - sudden _____
BD - sudden _____
CD - sudden _____

Points:

- This phase diagram is having 3 normal triple pts (O, B, C) & one metastable pt. (D).
- 'O' → $S_{(r)} \rightleftharpoons S_{(m)} \rightleftharpoons S_{(v)}$ taking place at a temp. 95.6°C & press. 0.006 mm of Hg. At this pt. the system is said to be non(zero) invariant as F=0 (F = C - P + 2 = 1 - 3 + 2 = 0).
- Any change w.r.to either P or T makes one phase vanish (∵ F≠0).
- 'B' → $S_{(m)} \rightleftharpoons S_{(l)} \rightleftharpoons S_{(v)}$ The system is non variant (F=0). This pt. corresponds to a temp. of 120°C (Normal MP of $S_{(m)}$) & a press of 0.09 mm of Hg.
- 'C' → $S_{(r)} \rightleftharpoons S_{(m)} \rightleftharpoons S_{(l)}$ The system is invariant as F=0. This pt. corresponds to a temp. of 150°C & press. of 1290 atm.

- 'D' → It represents the junction of the 3 metastable curves representing either sudden cooling sudden heating or sudden transition. At this pt. the system is in-variant as F = 0. This pt. corresponds to a temp. of 114°C & a press. of 0.03mm of Hg.

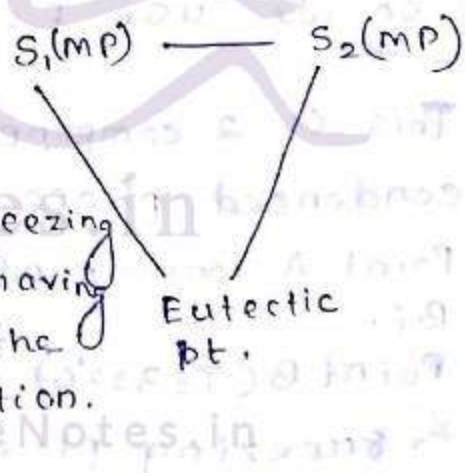
Eutectic System:

It is a heterogenous system having 2 pure solids, not reacting chemically with each other only mixible in their melting phase with each solid having the capacity to reduce the melting pt. or the freezing pt. of another & a time comes where we get a Lowest temp. (Eutectic pt./Eutectic temp.) having a fixed composition. At this pt. P is max^m & F is min^m.

Example: Bi-Cd system having the Eutectic pt. at 140°C with a fixed composition of 60% Bi & 40% Cd.

Characteristics of Eutectic system:

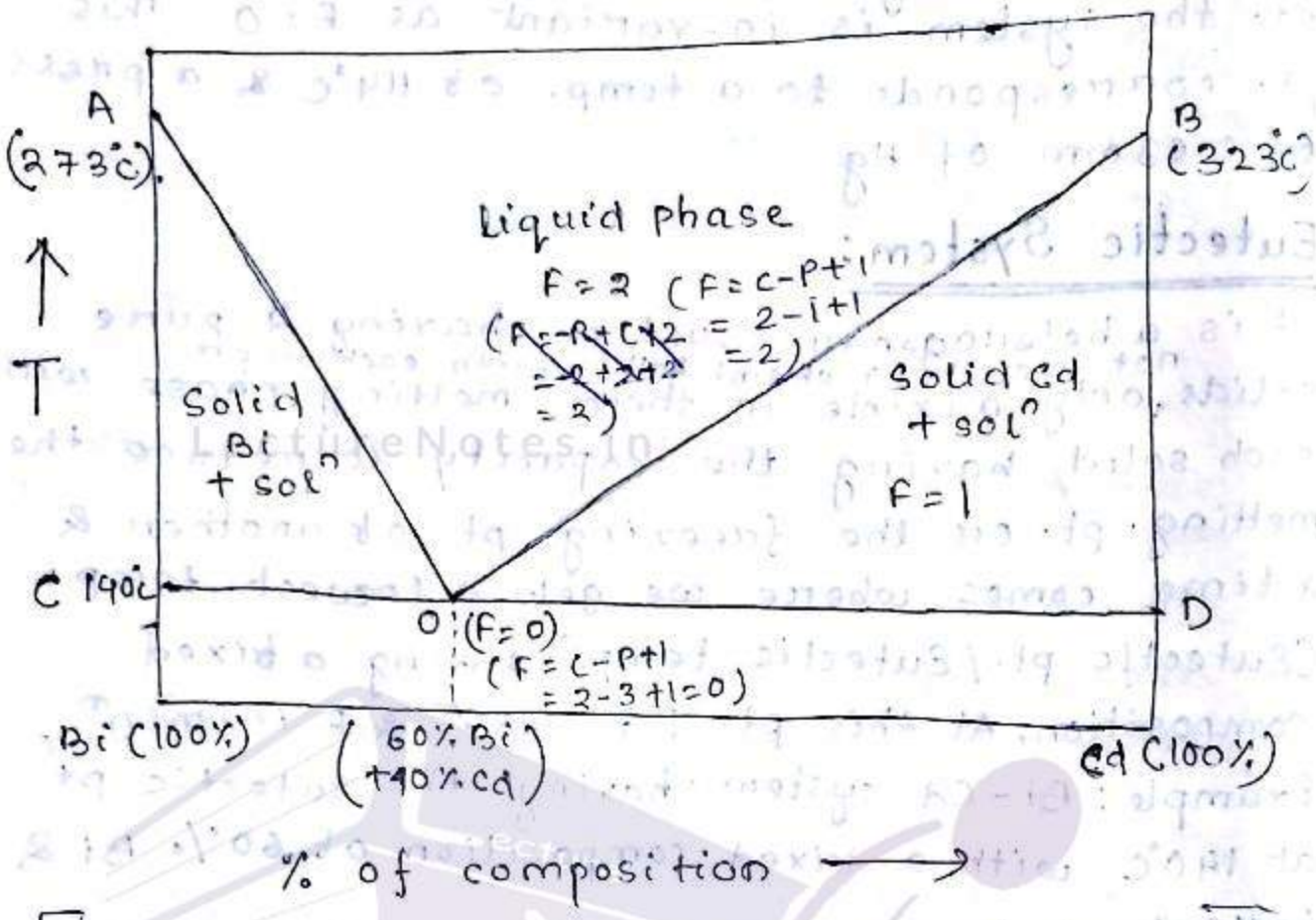
1) 2 immixible solids miscible in melting phase.



2) No chemical reactions.
3) With reduction in MP or Freezing pt. we get an Eutectic pt. having fixed amount of S_1 & S_2 & the rest is their melting solution. (P = 3, F = 0).

Dt. 17/10/12

Bi - Cd system:



As % of composition is not an independent variable so we use F = C-P+1

- This is 2 component system (i.e. Bi & Cd) observing condensed phase rule (i.e. F = C-P+1)
- Point A corresponds to the melting pt. of pure Bi.
- Point B (T = 323°C) corresponds to melting pt. & freezing pt. of pure Cd.
- Each one reduces the freezing pt. of another to reach at a lowest melting pt. or freezing pt. (i.e. pt. 'O').

Areas:

① AOB : Represents the ~~melting~~ liquid phase (or melting phase). The system is bivariant as F = 2 (F = C-P+1 = 2-1+1 = 2).

② BOD : Represents solid Cd crystal along with melting solⁿ of Cd with little amount of Bi. The system is mono-

variant in this area as F = 1 ($F = C - P + 1 = 2 - 2 + 1 = 1$)

③ AOC: Represents solid Bi crystal & a melting sol^n of Bi with little amount of Cd.
The system is monovariant as F = 1 [$F = C - P + 1 = 2 - 2 + 1 = 1$]

Curves:

① AO: Represents reduction in freezing pt. of pure Bi due to addition of Cd. The system is monovariant along this curve. [$F = C - P + 1 = 2 - 2 + 1 = 1$]

② BO: Represents reduction in freezing pt. of pure Cd due to addition of Bi which becomes very faster along BO. The system is monovariant along this curve.

③ CD: It represents a boundary line above which (COD) & below which we find different values of P & F.

Point:

'O': The two freezing pt. curves meet at the pt. 'O' known as the Eutectic pt. or Eutectic temp. It corresponds to a temp. 140°C & a fixed composition of 60% Bi & 40% Cd. P is max^m here i.e. 3 [E] = 60% Bi + 40% Cd + melting sol.

Importance of Eutectic pt.:

- We make a slide change w.r.to either the temp. (140°C) & the composition (60% Bi & 40% Cd) then min^m 1 phase vanishes & the pt. is no-longer said to be the Eutectic temp. or Eutectic pt.
- Above 'O' the value of P changes so also F. & below this pt. two solids crystalise out much faster & finally give back 100% Bi & 100% Cd.

Q) Why an Eutectic mixture is not a compd?

Q) What is the importance of Eutectic composition in a physical system?

Applications:

1) An alloy of Na & K which are liquids at room temp. are used as coolants in nuclear reactors.

2) Eutectic alloy of Pb & Sn & sometimes Ag & Au are used for the purpose of soldering

3) Eutectic mixtures are used as ink in the ink jet printers to avoid any leakage.

4) Eutectic systems containing low melting alloys are used to prepare the safety valves in pressure cookers, automobiles & boilers.

5) Casting alloys like Al-Si & Cast iron (at the composi^n for Austenite - Cementite) eutectic in the Iron-Carbon system.

Peri Eutectic System:

It is a heterogenous system containing 2 pure solids which are mixible in the liquid phase gives one untable compd which break up or decomposes to give one solid in a different phase & a melting sol^n containing a new compd. That new compd is known as peritectic compd. The temp. at which it is avialable (decomposition reaction takes place) is known as peritectic temp. & reaction is known as peritectic reaction.

e.g.- Fe-C system.

$$Fe + C \longrightarrow Fe_xC_y$$

Dt. 31-10-12

Fe-C system:

- It is a two component system having 2 solids Fe (MP- 800°C) and C (a non-metal solid having MP - 3500°C).
- Carbon is soluble in Fe to some extent in solid phase but maximum in melting phase.
- Alloys containing 0.2% of C to 2.14% of C are called steel & those containing 2.14% of C to 6.67% of C are known as cast iron (high carbon steel)
- Alloy with 0.8% of carbon is called Eutectoid steel & with 4.3% of carbon is known as Eutectic cast iron.

α-Ferrite (α-iron) bcc (Mag) $\xrightarrow[\text{CP}]{770°C}$ α-iron (bcc) (Non-mag.) $\xrightarrow[\text{Transition temp. for α-iron}]{912°C}$ γ-iron (Austenite) Non-mag FCC

CP → Curie pt.

FCC → δ-iron (bcc) $\xrightarrow{1578°C}$ Melting solⁿ

Distinction betⁿ Eutectic & Peritectic system:

Eutectic System	Peritectic System
1) No chemical reaction betⁿ two solids S_1 & S_2.	1) Chemical reaction betⁿ two solids S_1 & S_2.
2) Eutectic means lowest melting pt. or freezing pt.	2) Peritectic means nearest melting pt. or freezing pt.
3) Melting solⁿ (S_1+S_2) cooling ↓ ↑ Heating S_1+S_2	3) Melting solⁿ cooling ↓ ↑ Heating S_2 (New solid)
4) Melting pt. or freezing pt. difference is very	4) Huge difference betⁿ Melting or freezing pt.

less. eg.. Bi-Cd system
Bi(273°C), Cd (323°C)

5) Eutectic pt. is lowest with respect to either melting pt. or freezing pt.

e.g. - Fe-C system
Fe (800°C), C (3500°C)

5) Peritectic temp. is mostly the decomposi temp. which is in betn the two melting pt. or freezing pt.

LectureNotes.in

SOLID STATE

Difference betⁿ amorphous solid & crystalline solid:

Amorphous Solid	Crystalline solid
1) Characteristic Geometry:	
* Amorphous solids don't have orderly arrangement i.e. they have very short range order.	* Crystalline solids have definite & regular geometry which extends throughout the crystal. i.e. they have long range order.
2) Melting points:	
* Amorphous solids don't have sharp melting point.	* Crystalline solids have sharp melting point.
3) Isotropy & Anisotropy:	
* Amorphous solids are isotropic i.e. their physical properties such as refractive index, conductivity & mechanical strength have same values in all directions.	* Crystalline solids are anisotropic i.e. their physical properties such as refractive index & conductivity have different values in different directions.
4) Cleavage:	
* An amorphous solid on being cut with a sharp edged tool gives two pieces with irregular surface.	* When cut with a sharp edged tool, crystalline solids give two pieces with plane surface
5) Symmetry:	
* They do not possess symmetry.	* They possess crystal symmetry.

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Classification of crystalline solid:

1) Molecular solid:

Characteristics:

i) They are soft.

ii) Molecular solids have low melting points.

iii) They have low heats of vapourisation & are volatile.

iv) These are bad conductors because of the absence of mobile electrons in them.

Examples - solid CO_2, wax, sulphur, ice, CH_4 & ICI.

2) Ionic solid:

i) They have very high melting & boiling points.

ii) They have high heats of fusion.

iii) Ionic solids are bad conductors in solid state.

iv) They are hard & brittle.

Examples - NaCl, $BaCl_2$, CsCl.

3) Network or Covalent Solids:

i) They are generally hard due to the presence of strong covalent bonds.

ii) They have high heats of fusion and high melting pts due to presence of strong covalent bonds.

iii) Covalent solids are bad conductors of electricity due to absence of mobile electrons in them.

4) Metallic solids:

i) They are malleable & ductile.

ii) They are good conductors of heat and electricity because of the free movement of electrons throughout the crystal.

: BASIC CRYSTAL SYSTEMS :-

Crystal System	Symmetry Elements	Axial lengths of unit cell (a, b & c)	Interaxial angles (α, β & γ)	Examples	Bravis Lattice
Cubic	4 (3-fold) & 3 (4-fold) axis	$a = b = c$	$\alpha = \beta = \gamma = 90°$	Au, Cu, NaCl	P, I, F
Tetragonal	One 4-fold axis.	$a = b \neq c$	$\alpha = \beta = \gamma = 90°$	TiO_2, SnO_2	P, I
Orthorhombic	Three 2-fold axis.	$a \neq b \neq c$	$\alpha = \beta = \gamma = 90°$	KNO_3, $BaSO_4$, $PbCO_3$, $MgCl_2$.	P, I, C, F
Monoclinic	One 2-fold axis.	$a \neq b \neq c$	$\alpha = \beta = 90° \neq \gamma$	$CaSO_4 \cdot 2H_2O$, (Gypsum), $FeSO_4$, Na_2SO_4, $KClO_3$.	P, C
Triclinic	One 1-fold axis.	$a \neq b \neq c$	$\alpha \neq \beta \neq \gamma \neq 90°$	$K_2Cr_2O_7$, $CuSO_4 \cdot 5H_2O$	P
Trigonal	One 3-fold axis	$a = b = c$	$\alpha = \beta = \gamma \neq 90°$	As, Sb, Bi, Calcite	P
Hexagonal	One 6-fold axis	$a = b \neq c$	$\alpha = \beta = 90°$ & $\gamma = 120°$	SiO_2, Zn, Mg, Cd.	P

iii) They have metallic lustre, i.e. their surface appears bright.

iv) Their melting pts depend upon the strength of bonds in them.

v) They have moderate heats of fusion.

Dt. 26/11/12

Problems on pH:

1) Consider an electrochemical cell,

$Pt, H_2(1atm) | H^+(C=?) || KCl(satd.) | Hg_2Cl_2, Hg, Pt.$

The emf of the cell is 0.445 V. Calculate the pH of the solⁿ.

2) Find out the pH of a solⁿ in a quindrone half cell, combined with a standard calomel electrode. The emf of the cell is 0.123 V at 25°C.

3) A galvanic cell was constructed by combining a hydrogen electrode at 25°C (partial press of H_2 = 1 atm) with a Cu electrode in a solⁿ of $CuSO_4$ of 1M conc. at 25°C. Calculate the pH of the solⁿ if standard reduction potential of Cu is 0.34 V. The emf of cell is 0.48 V.

4) Write the Nerst's eqⁿ & calculate the reduction potential for reduction of O_2 at pH = 7.96 partial press. of O_2 is 0.2 atm & E° = 1.229 V.

1)

$$pH = \frac{E_{cell} - 0.2422}{0.0591} = \frac{0.445 - 0.2422}{0.0591}$$

$$= 3.43$$

~~2) $E_{cell} = 0.6994 - 0.0591 pH$~~

~~$\Rightarrow 0.0591 pH = 0.6994 - E_{cell} = 0.6994 - 0.123$~~

~~$\Rightarrow pH = 9.7$~~

2) 2)

$$pH = \frac{0.4572 - E_{cell}}{0.0591} = \frac{0.4572 - 0.123}{0.0591}$$

$$= 5.6$$

~~3) $E_{cell} = E_{cathode} - E_{anode}$~~

~~$= -0.0591\,pH - E^{\circ}_{Cu/Cu^{2+}} + 0.0591 \log \frac{[Cu^{2+}]}{[Cu]}$~~

~~2) $= -0.0591\,pH - 0.03$~~

3) $E_{cell} = E_{Cu} - E_{H_2}$

$\Rightarrow 0.48 = E^{\circ}_{Cu} - (-0.0591\,pH)$

$\Rightarrow 0.48 - 0.34 = 0.0591\,pH$

$\Rightarrow pH = 2.36$

4) $\frac{1}{2}O_2 + 2H^+ + 2e \longrightarrow H_2O$

Applying Nernst's eq.

$$E = E^{\circ} - \frac{0.0591}{2} \log \frac{[H_2O]}{[O_2]^{1/2}[H^+]^2}$$

$$= 1.229 - \frac{0.0591}{2} \log \frac{1}{(0.2)^{1/2}(10^{-7})^2}$$

$= 0.80\,V$

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Solid state:

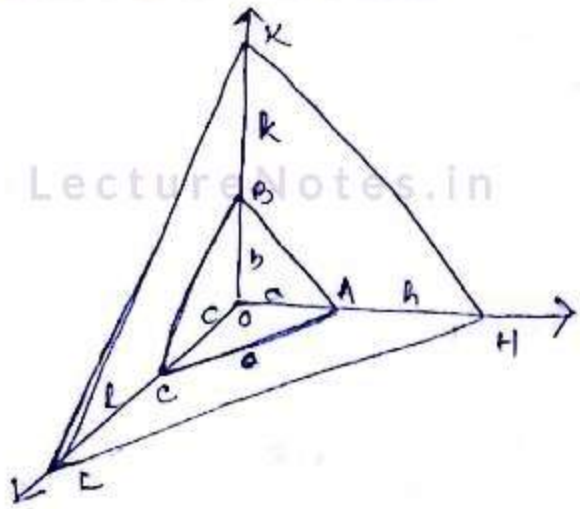
Laws of crystal structure:

1) Law of constancy of interfacial angle.
2) Law of rationality of indices
3) Law of symmetry.

1. Law of constancy of interfacial angle:
According to this law the angle betn corresponding faces of a crystal is constant even though the crystal habits may change.
e.g.- The interfacial angle in all NaCl crystals are same (90°) ~~even if their~~ irrespective of their shape & size.

2. Law of rationality of indices:
According to this law the intercepts of any face of crystal along crystalographic axes are either equal to the unit intercepts (a, b, c) or some simple hole number multiple of them, i.e. n_1a, n_2b, n_3c, where n_1, n_2, n_3 are simple hole numbers & known as Weiss indices.

$h = n_1 a$
$k = n_2 b$
$l = n_3 c$



Miller indices: The Miller indices of a face of a crystal are inversely proportion to the intercepts of that face along different axes.

Methods to convert Weiss indices to Miller indices:

① Weiss indices - (2a, 3b, c)

a	b	c
2	3	1
$\frac{1}{2}$	$\frac{1}{3}$	1
3	2	6

Miller indices - (3 2 6)

② Weiss indices - (2a, -3b, -3c)

a	b	c
2	-3	-3
$\frac{1}{2}$	$-\frac{1}{3}$	$-\frac{1}{3}$
3	-2	-2

Miller indices - $(3\bar{2}\bar{2})$

③ Weiss indices - $(\frac{1}{2}a, \frac{1}{2}b, \infty)$

a	b	c
$\frac{1}{2}$	$\frac{1}{2}$	∞
2	2	0

Miller indices - (2 2 0)

3. Law of symmetry:

According to this law, all the crystals of same substance causes the same element of symmetry. There are 3 elements of symmetry associated with crystal.

i) ~~Axis~~ Plane of symmetry

ii) Axis of symmetry

iii) Centre/point of symmetry.

Crystal lattice:

- It is a highly ordered 3D structure formed by its constituent atoms, ions or molecules.
- If the constituents are considered as pts the regular arrangement of such pts. in space is called space lattice.
- Unit cell: The smallest building unit which when repeated again & agin in 3-dimension results in a space lattic is known as unit cell.

Bravais Lattice:

From the geometrical arrangement of 3D network of pt (Bravais) found that there are 14 different ways in which the similar pts can be arranged. These 14 different ways are known as 14 Bravais lattice which are related to 7 crystal system & subdivided into 4 types:

i) Simple / Primitive (P)
ii) Body centred (I)
iii) Face centred (F)
iv). Base / End centred (C)

Crystal system	Bravais Lattice	Number
Cubic	P, I, F	3
Tetragonal	P, I	2
Orthorhombic	P, I, F, C	4
Rhombohedral	P	1
Hexagonal	P	1
Monoclinic	P, C	2
Triclinic	P	1
	Total	14

LectureNotes.in

Cubic crystal :

Characteristics :

1. No. of atoms per unit cell :-

In SCC – $\frac{1}{8} \times 8 = 1$

In BCC – $\frac{1}{8} \times 8 + 1 = 2$

In FCC – $\frac{1}{8} \times 8 + \frac{1}{2} \times 6 = 4$

2. Co-ordination number :- No. of nearest neighbours in a packing of crystal is known as co-ordination number.

For SCC – 6 (4 in same plane & 2 above & below the plane)

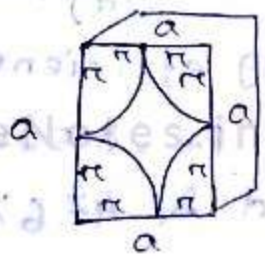
For BCC – 8 (4 above the plane & 4 below the plane.

For FCC – 12 (4 above, 4 below & 4 in same)

3. Atomic radius :- The half of the distance betn centre of 2 immidiate neighbouring atoms in a unit cell is known as atomic radius & the distance betn center of 2 corner atoms in a unit cell is known as length of the cube-edge (a).

For SCC – $a = 2r$

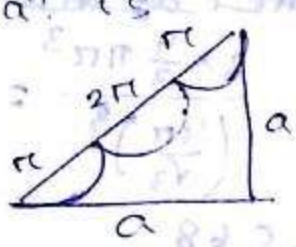
$\Rightarrow \boxed{r = \frac{a}{2}}$



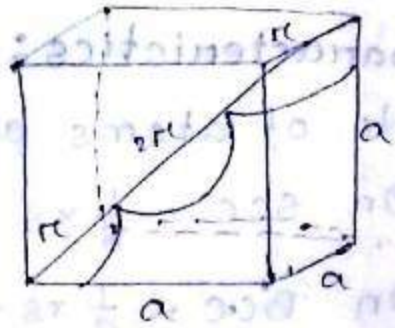
For FCC – 3 atoms along the face diagonal touch each other, the relan is

$(4r)^2 = a^2 + a^2$

$\Rightarrow \boxed{r = \frac{a}{2\sqrt{2}}}$



For BCC - 3 atoms along body diagonal touch each other



$$(4r)^2 = (a^2 + a^2) + a^2$$

$$\Rightarrow \boxed{r = \frac{\sqrt{3}}{4} a}$$

~~Dt 7/11/12~~

Dt 4/12/12

5. PACKING FRACTION OR ATOMIC PAKING FACTION:

It is the ratio of volumes of the atoms present in the unit cell to the volume of unit cell.

i.e.

$$PF = \frac{\text{Volume of the atoms in unit cell}}{\text{Volume of unit cell.}}$$

For SCC:

Volume of atom $= \frac{4}{3}\pi r^3$

volume of unit cell $= a^3 = (2r)^3$

$$PF = \frac{1 \times \frac{4}{3}\pi r^3}{(2r)^3} = \frac{4}{3} \cdot \frac{1}{8}\pi = \frac{\pi}{6} = 0.524$$

Packing efficiency = 52.4 %

From PF = 0.524, we know that 52.4% are packed & 47.6% are void.

For BCC:

~~Volume of atom~~

$$PF = \frac{2 \times \frac{4}{3}\pi r^3}{\left(\frac{4r}{\sqrt{3}}\right)^3} = \frac{2 \times 4}{3} \cdot \frac{3\sqrt{3}\pi}{64} = \frac{3\sqrt{3}\pi}{24} = \frac{\sqrt{3}\pi}{8}$$

$= 0.68$

It means 68% are packed & 32% are void.

For FCC:

$$PF = \frac{4 \times \frac{4}{3}\pi r^3}{(2\sqrt{2}r)^3} = \frac{16\pi}{3 \cdot 8 \cdot 2\sqrt{2}} = \frac{\pi}{3\sqrt{2}} = 0.74$$

It means 74% are packed &

- Among SCC, BCC & FCC, SCC is least stable due to least packing efficiency.

CHARACTERISTICS OF SCC

6) **Radius ratio:**

- Radius ratio is the ratio of radius of cation to radius of anaion.
- By knowning the radius ratio, the co-ordinat number & the structure of solid can be predicted.

$$\text{Radius ratio} = \frac{r_+}{r_-}$$

Radius ratio	CN	Shape
< 0.155	2	Linear
0.155 - 0.225	3	Trigonal
0.255 - 0.414	4	Tetrahedral
0.414 - 0.732	6	Octahedral
0.732 - 0.99	8	BCC
1	12	FCC, HCP

Structure of some compounds:

(i) AX :

1. Rock salt (NaCl)
2. $CsCl_2$ structure
3. ZnS structure
4. Wurtzite structure.

(ii) AX_2:

1. Flourite structure (CaF_2)
2. Rutile structure. (TiO)

Relation betⁿ density of the crystal & the lattice const. or length of the cube edge(a):

Let's consider a cubic crystal having 'n' number of atoms per unit cell & ρ is the density of the crystal. & M is the molecular wt. or atomic wt. of the crystal & N is the Avogadro's number.

Volume of crystal containing "N" atoms $= \frac{M}{\rho}$

for 1 atom $= \frac{M}{\rho} \times \frac{1}{N}$.

Volume of crystal containing "n" atoms per unit cell, $a^3 = \frac{M \times n}{\rho \times N}$

$$\Rightarrow \boxed{\rho = \frac{M \times n}{a^3 \times N}}$$

Q) Cu has a FCC structure and an atomic radius of 1.278 Å unit. & atomic mass of Cu is 63.5 gm/mol. Calculate the density of the crystal.

For FCC: $a = 2\sqrt{2}r$

Given, $\frac{M}{n} = 63.5$ gm/mol

$r = 1.278$ Å

$= 1.278 \times 10^{-10}$ m

$= 1.278 \times 10^{-8}$ cm

$a^3 = (2\sqrt{2}r)^3$

$= 8 \cdot 2\sqrt{2}\left[(1.278 \times 10^{-8})\right]^3$

$= 4.72 \times 10^{-23}$

$$\rho = \frac{M \times n}{a^3 \times N} = \frac{63.5 \times 4}{4.72 \times 10^{-23} \times 6.023 \times 10^{23}}$$

$$= \frac{63.5 \times 4}{4.72 \times 6.023} = 8.9$$

Q) NaCl has FCC structure, $\rho = 2.18\ gm/cc$ calculate distance betn 2 adjacent atom.

$$\rho = \frac{M \times n}{a^3 \times N}$$

$$\Rightarrow 2.18 = \frac{58.5 \times 4}{16\sqrt{2}\, r^3 \times 6.023 \times 10^{23}}$$

$$\Rightarrow r^3 = \frac{58.5 \times 4}{16\sqrt{2} \times 2.18 \times 6.023 \times 10^{23}}$$

$$\Rightarrow r = 1.98 \times 10^{-8}\ cm$$

$$= 1.98 \times 10^{-10}\ m$$

$$= 1.98\ \mathring{A}$$

Distance betn adjacent atoms

$$= 2r$$

$$= 2 \times 1.98 = 3.96\ \mathring{A}$$

Interplanar spacing:

- The distance (d_{hkl}) betn adjacent planes of miller indices hkl is defined as the spacing betn 1st such plane & a parallel plane passing through origin. It is given by

$$\boxed{d_{hkl} = \frac{1}{\sqrt{\frac{h^2}{a^2} + \frac{k^2}{b^2} + \frac{l^2}{c^2}}}}$$

where h, k, l – miller indices
a, b, c – distance parameter.

For cubic crystal, a = b = c, so

$$d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}$$

Q) Determine the interplanar spacing betn 220 plane of a crystal having length of the cube $h = 450$ pm.

Given $h = 2$
$k = 2$
$l = 0$

$a = 450$ pm

$$\therefore d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} = \frac{450}{\sqrt{2.4}} = \frac{450}{2\sqrt{2}}$$

$= 159$ pm.

Bragg's eqn:

$$\boxed{2d\sin\theta = n\lambda}$$

where n - order of reflection
λ - wavelength
θ - Angle of incidence / Glancing angle.
d - Interplanar spacing.

Q) At what glancing angle the 1st order diffraction from 110 plane of KCl can be observed using x-rays of wavelength 150 pm. Given the unit cell dimension is 305 pm.

Given $h = 1$
$k = 1$
$l = 0$

$$\therefore d_{hkl} = \frac{a}{\sqrt{h^2+k^2+l^2}} = \frac{305\text{ pm}}{\sqrt{2}} = 215.6\text{ pm}$$

$$\sin\theta = \frac{n\lambda}{2d} = \frac{1\times 150}{2\times 215.6} = 0.34786$$

$\Rightarrow \theta = 20.3^\circ$

Dt. 6/11/12

CHEMICAL KINETICS

Fast ⟷ Spontaneous ⟷ One way

Ex. - All ionic reaction.

Slow ⟷ Non-spontaneous ⟷ One way

Ex. - All organic reaction.

Moderate ⟷ Non-spontaneous ⟷ One/two way

Ex. -

i) Hydrolysis of ester in acid or alkali medium

ii) Decomposition of $KClO_3$

$$KClO_3 \xrightarrow{MnO_2} KCl + O_2$$

Rate equation / Rate law:

It signifies how the conc. of reactant or product changes w.r.to time.

Rate of reaction:

It is the rate of change of conc. of reactant and product per unit time.

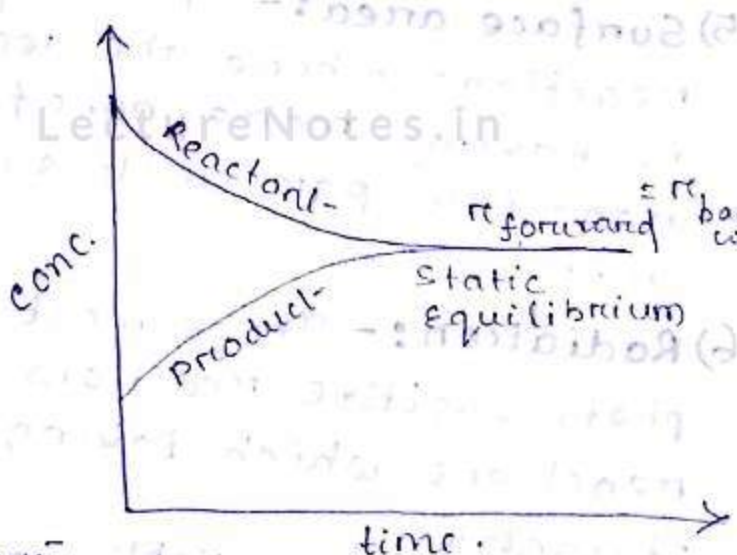
Rate of reaction = Rate constant, when unimolar or unit conc. of reactant is taken. Such type of rate const. is known as specific rate const. or specific velocity constant.

$2A \longrightarrow$ Product

$$\text{rate} = -\frac{1}{2}\frac{d[A]}{dt}$$

$2A + 3B \longrightarrow$ Product

$$\text{rate} = -\frac{1}{2}\frac{d[A]}{dt} = -\frac{1}{3}\frac{d[B]}{dt}$$



$$Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-$$

S 2S

$$K_{sp} = S \times (2S)^2$$

Factors affecting rate of reaction:

1) Type of reactant:- Reactants having ionic bond undergo 1st reactions where as most of the organic reaction having covalent bond undergo slow reaction.

2) Temperature:- More temp. makes more number of molecules to become activated for an effective collision. Normally ~~by~~ increasing temp. by 10°c the rate const. is normally found to be minimum 2 times of original value

$$\frac{T_{10^\circ c}}{T_{0^\circ c}} = \frac{2k_p}{k_p}.$$

3) Catalyst:- Positive catalyst reduces the value of Ea making the reaction fast. Negetive catalyst increases the value of Ea making the reaction slow.

4) Concentration:- More the conc. of reactant more is the no. of activated molecules ready for effective collision making the reaction fast.

5) Surface area:- Most important for surface reactions where the least surface area is having more no. of active molecules, reacting per unit surface area per unit time.

6) Radiation:- It is most essential for photosensitive reactions like photochemical reactions which taking place in presence of light.

e.g. - $H_2 + Cl_2 \xrightarrow{\text{sunlight}} 2HCl$

Halogenation of methane leading to the formation of $CHCl_3$ & CCl_4.

Dt. 7/11/12

ORDER	MOLECULARITY
1) No. of reacting molecules whose conc. changes either in a single step or a slow step of a multi-step process.	1) No. of reacting molecules participating either in a single step or the slowest step of a multistep process.
2) It is an experimental concept.	2) It is a theoritical concept
3) It could be an integer, fraction, includizing 0.	3) It is always a +ve integer. It is upto 3 (max).
~~4) All radioactive~~ 4) Gives an idea about the type of reaction mechanism.	4) Gives no idea about type of mechanism.

Zero order reaction:

– Rate is independent of the initial conc. of reactant.

Rate eq^n. $A \longrightarrow$ product

at $t=0$ a 0

$t=t$ $a-x$ x

$$\frac{dx}{dt} \propto [A]_t^0$$

$$\Rightarrow \int_0^x dx = \int_0^t dt$$

$$\Rightarrow x = kt$$

$$\Rightarrow k = \frac{x}{t}$$

Unit of rate const. = conc. time^{-1}.

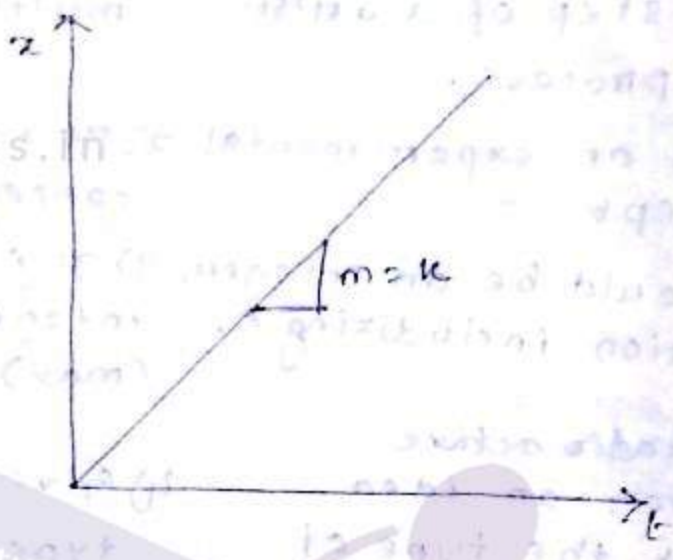
$t_{1/2} = \frac{x}{k} = \frac{a/2}{k} = \frac{a}{2k}$.

$$\boxed{t_{1/2} = \frac{a}{2K}}$$

Graphical representation:

$x = kt$

$y = mx + c$



Examples:

1) Decomposition of phosphene & ammonia on the surface of tungston (W) & Molybdinum (Mo).

2) $H_2 + Cl_2 \xrightarrow[h\nu]{\text{sunlight}} 2HCl$.

3) $2HI \xrightarrow[\Delta]{\text{Gold surface}} H_2 + I_2$

First order reaction:

Rate of reaction is dependant on the rate of change of conc. of 1 reactant though more than 1 may be present.

e.g. - $N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$

$r \propto [N_2O_5]^1$

$\frac{dx}{dt} \propto [N_2O_5]^1 \quad \frac{dA}{dt} \propto [N_2O_5]^1$

$$2KClO_3 \xrightarrow{MnO_2} 2KCl + 3O_2$$

All radio active disintigration are of 1st order but all nuclear reactions are not 1st order.

Rate equation:

$$A \longrightarrow \text{Product}$$

at $t=0$ a $\quad 0$

at $t=t$ $a-x$ $\quad x$

$$\frac{dx}{dt} \propto (a-x)$$

$$\frac{dx}{a-x} = k\,dt$$

1st order rate eq.

$$\Rightarrow \boxed{k = \frac{2.303}{t} \log \frac{a}{a-x}}$$

Unit of k = Time^{-1}.

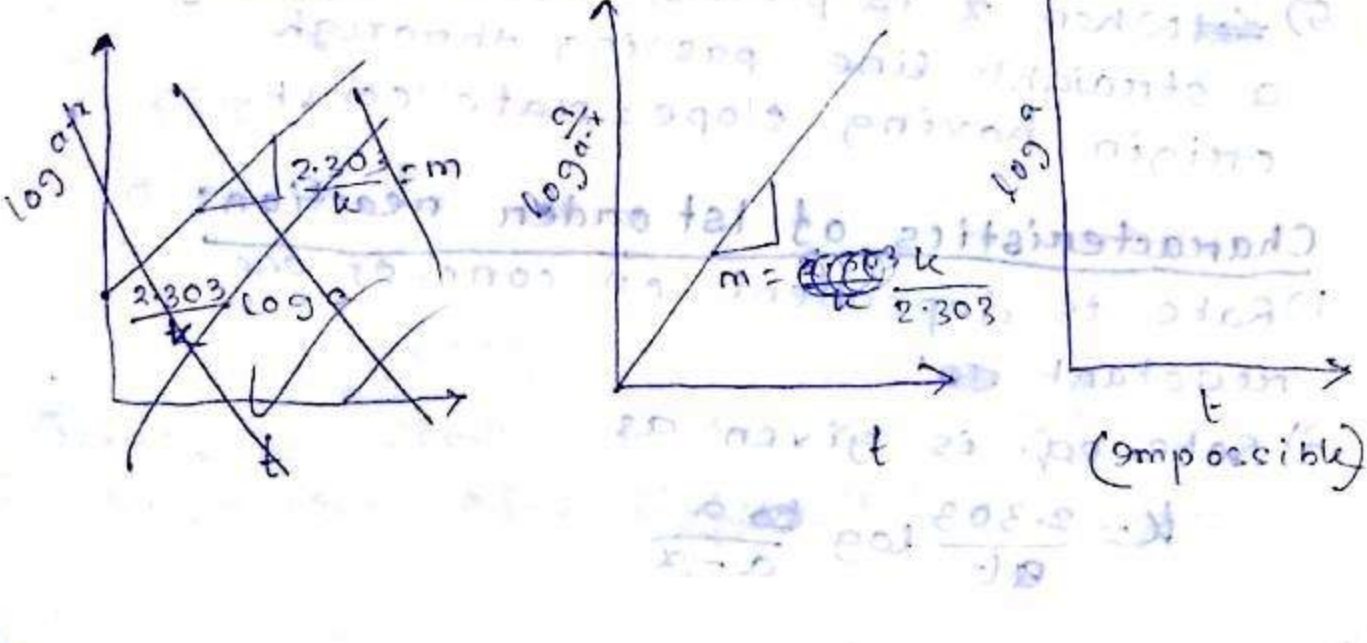
$$k = \frac{2.303}{t_{1/2}} \log \frac{a}{a - a/2}$$

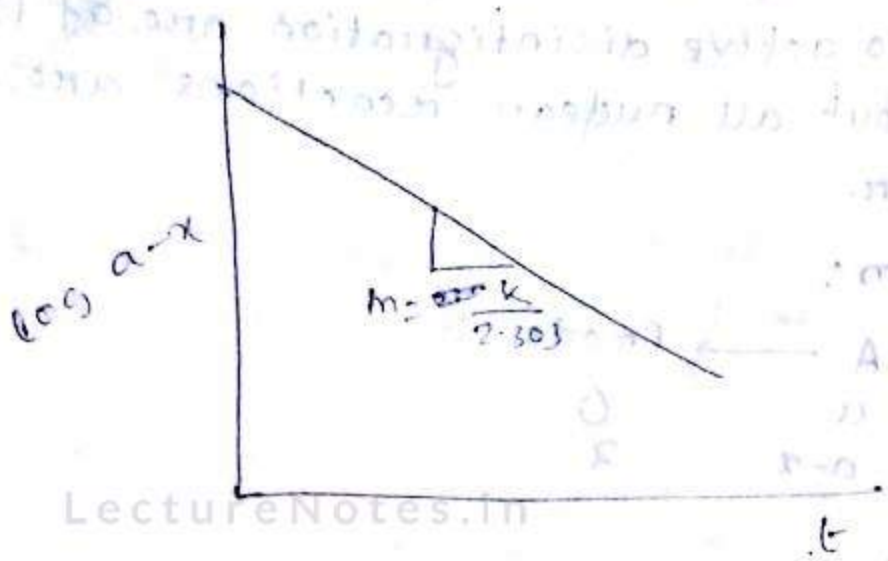
$$\Rightarrow k = \frac{\ln 2}{t_{1/2}}$$

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

Graphical representation:

$\log a - x \propto t$ $\quad \log a \propto t$ $\quad \log \frac{a}{a-x} \propto t$





Why almost all 1st order reactions proceed towards the end?

Characteristics of Zero order reaction:

1) Rate is independent of the intial conc. of reactant.
2) Rate eq. is given as $x = kt$
[x moles of product in time 't = t']
3) $T_{1/2} \propto a$ $\left[T_{1/2} = \frac{a}{2k}\right]$
4) Unit - conc. time^{-1}.
5) When x is plotted against t we get a straight line passing through origin having slope = rate const.

Characteristics of 1st order reaction:

1) Rate is dependent on conc. of one reactant.
2) Rate eq. is given as

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

3) Unit - $time^{-1}$.

4) $T_{1/2}$ is independent of initial conc.

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

5) When $\log \frac{a}{a-x}$ plotted against t we have a slope of $\frac{k}{2.303}$.

Q1. 14/11/12

Q) Spontaneous decomposition of a radioactive nuclei is a 1st order reaction. U_{238} disintegrates with the emission of α particle with a $T_{1/2}$ of 4.5×10^9 years. At $T=0$ 1 mole of U_{238} is present. Calculate the no. of nuclei left after 1 billion (10^9) year. 5.16×10^{23}

$t_{1/2} = 4.5 \times 10^9$ years

$\Rightarrow \frac{0.693}{k} = 4.5 \times 10^9$

$\Rightarrow k = 1.54 \times 10^{-10}$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$\Rightarrow 1.54 \times 10^{-10} = \frac{2.303}{10^9} \log \frac{1}{1-x}$

$\Rightarrow 1.54 \times 10^{-1} = \cancel{2.303 \log} \ln \frac{1}{1-x}$

$\Rightarrow \frac{1}{a-x} = 1.1664$

$\Rightarrow a - x = 0.8573$ mole

$= 0.8573 \times 6.023 \times 10^{23}$ numbers of nuclei

$= 5.16 \times 10^{23}$ no. of nuclei.

Q) Find out expression for time taken for 2/3 fraction of a 1st order process.

$$k = \frac{2.303}{t_{2/3}} \log \frac{a}{a - \frac{2a}{3}}$$

$$= \frac{2.303}{t_{2/3}} \log \frac{3a}{a}$$

$$= \frac{2.303 \log 3}{t_{2/3}}$$

$$\Rightarrow t_{2/3} = \frac{2.303 \log 3}{k}$$

$$\Rightarrow t_{2/3} = \frac{1.098}{k}$$

Q) In the reactⁿ.

$$CH_3COOCH_3(l) \rightleftharpoons C_2H_4(g) + H_2(g) + CO_2(g)$$

Initial press. is found to be 0.4 atm & after 10 min it becomes 0.5 atm. Find out rate const.

0.01335 min^{-1}

	$CH_3COOCH_3(g)$	$\rightleftharpoons$	$C_2H_4(g)$	+	$H_2(g)$	+	$CO_2(g)$
at t=0	a		0		0		0
at t=10 min	a − x		x		x		x

$a = 0.4$

$$a - \cancel{x} + \cancel{x} + x + x = 0.5$$

$$\Rightarrow 2x = 0.5 - 0.4 = 0.1$$

$$\Rightarrow x = \frac{0.1}{2} = 0.05$$

$$k = \frac{2.303}{10} \log \frac{0.4}{0.4 - 0.05}$$

Q) Rate of 1st order process is 0.04 moles s^{-1} at 10 min & 0.03 moles s^{-1} at 20 min. After initiation. Find $T_{1/2}$

25 min.

Q) The rate constants K_1 & K_2 for 2 different reac^{n}s are $k_1 = 10^{16} \cdot e^{-2000/t}$

& $k_2 = 10^{15} \cdot e^{-1000/t}$ respectively.

Find out the temp. at which $k_1 = k_2$.

Ans. $T = 1000/2.303$ K.

Q) By 1st order process, $t_{99x} = x\, t_{1/2}$. Find the value of x. Ans. 10.

Q) A drop of sol^n. having volume 0.05mm contains 3×10^{-6} moles of H^+ ion. If the rate const. of disappearance of H^+ is 1×10^{7} mole lt^{-1} time^{-1}. It takes $x\times10^{-9}$ sec for H^+ to disappear. Find out value of x.

Ans. $x = 6$.

$k = \frac{x}{t}$

Given

$t = x\times10^{-9}$ sec.

& $x \rightarrow$ moles of reactant

0.05 mm contais 3×10^{-6}

1000 mm " $\frac{3\times10^{-6}\times10^{3}}{0.05}$

$\therefore x = \frac{3\times10^{-6}\times10^{3}}{0.05}$

$= 0.06$

$k = \frac{0.06}{x\times10^{-9}}$

$\Rightarrow 10^{7} = \frac{0.06}{x\times10^{-9}}$

$\Rightarrow x = \frac{0.06}{10^{-2}} = 6$.

2nd Order reaction:

Rate is dependent on the 2 reactants either same or different.

Rate eq^n. $2A \longrightarrow$ Product.

	2A		$\longrightarrow$ Product
at $t=0$	a	a	0
$t=t$	$(a-x)$	$(a-x)$	x

$$\frac{dx}{dt} \propto (a-x)^2 \Rightarrow \frac{dx}{dt} = k(a-x)^2$$

$$\Rightarrow \frac{dx}{(a-x)^2} = k\,dt$$

$$\int_0^x \frac{dx}{(a-x)^2} = k\int_0^t dt$$

Let $a-x = z$

$-dx = dz$

for $x=0,\ z=a$

$x=x,\ z=a-x$

$$\Rightarrow \int_a^{a-x} \frac{dz}{z^2} = kt$$

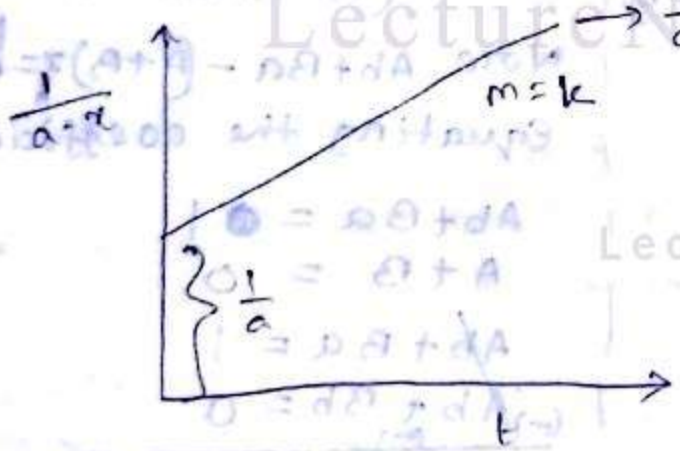
$$\Rightarrow \frac{1}{z}\Big]_a^{a-x} = kt$$

$$\Rightarrow \frac{1}{a-x} - \frac{1}{a} = kt$$

$$\Rightarrow k = \frac{1}{t}\,\frac{x}{a(a-x)}$$

unit of k – $lt\ mol^{-1}\ time^{-1}$

$$\frac{1}{a-x} = kt + \frac{1}{a}$$



Characteristics:

1) Rate is dependent on change in conc. of 2 reactants either same or different

2) Rate eq. is given by

$$k = \frac{1}{t}\,\frac{x}{a(a-x)}$$

3) Unit of Rate const. is mol^{-1} lt time^{-1}.

4) $t_{1/2} = \frac{1}{ka}$

5) When $\frac{1}{a-x} \sim t$ graph is drawn, then it will be a st. line which intersect $\frac{1}{a-x}$ at $\frac{1}{a}$ & slope is $m = k$.

2nd order having 2 different reactants-

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

at $t=0$	a	b	0
$t=t$	$a-x$	$b-x$	x

$$\therefore \frac{dx}{dt} \propto (a-x)(b-x)$$

$$\int_0^x \frac{dx}{(a-x)(b-x)} = k\int_0^t dt$$

$$\Rightarrow \int_0^x \frac{dx}{(b-a)(a-x)} + \int_0^x \frac{dx}{(a-b)(b-x)} = kt$$

$$\Rightarrow -\int_0^x \frac{dx}{a-x} + \int_0^x \frac{dx}{b-x} = kt(a-b)$$

$$\Rightarrow -\ln a-x\Big]_0^x + \ln b-x\Big]_0^x$$

$$= k(a-b)t$$

$$\Rightarrow -[\ln(a-x) - \ln a] + [\ln(b-x) - \ln b]$$

$$= k(a-b)t$$

$$\Rightarrow -\ln\frac{a-x}{a} + \ln\frac{b-x}{b}$$

$$= k(a-b)t$$

$$\Rightarrow \ln 1 - \ln\frac{x}{a} - \ln 1 + \ln\frac{x}{b}$$

$$= k(a-b)t \Rightarrow \ln\frac{x}{b}\cdot\frac{a}{x} = (a-b)kt$$

Put-

$$\frac{1}{(a-x)(b-x)} = \frac{A}{a-x} + \frac{B}{b-x}$$

$$= \frac{Ab - Ax + Ba - Bx}{(a-x)(b-x)}$$

$$= \frac{Ab + Ba - (A+B)x}{(a-x)(b-x)}$$

Now $Ab + Ba - (A+B)x = 1$

Equating the coefficie

$$Ab + Ba = 1$$
$$A + B = 0$$

$$Ab + Ba = 1$$
$$(-)\ Ab + Bb = 0$$
$$(-)$$
$$B(a-b) = 1$$

$$\Rightarrow B = \frac{1}{a-b}$$

$$\therefore A = \frac{-1}{a-b} = \frac{1}{b-a}$$

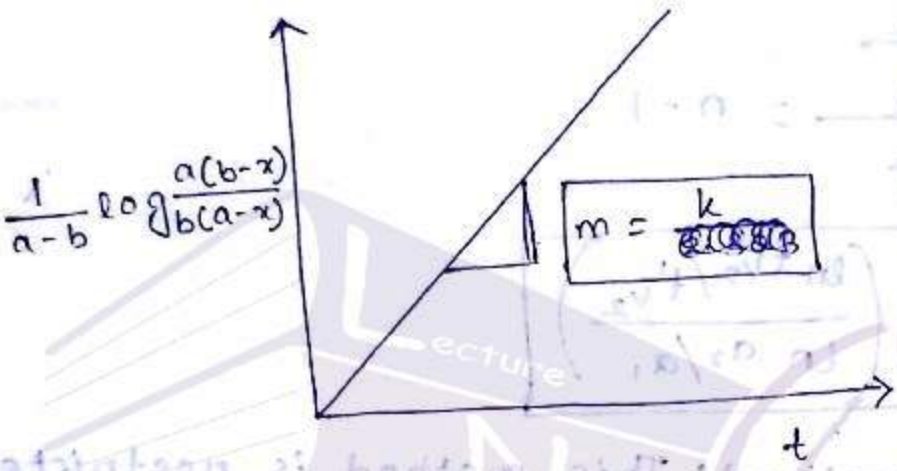
$\Rightarrow \ln \frac{a}{b} = k(a-b)t$

$\Rightarrow \frac{1}{a-b} \ln \frac{b(a-x)}{a(b-x)} = kt$

$$\Rightarrow \boxed{\frac{1}{a-b} \ln \frac{a(b-x)}{b(a-x)} = kt}$$

Dt. 15/11/12

Graphical representation:



Method of determination of order:

1) Method of integration: The various values of factors like initial conc., conc. after certain type the time period \\\\\\ are put in various rate eq^s in different time intervals. If the values of the rate const. are found to be nearly same, the type of rate eq^n gives the order of reaction.

2) Graphical method: The various data given are put in the graphical formulation of that reaction. The nature of the plot & the value of the slope gives the order of reaction.

3) Half life ($t_{1/2}$) method:

$$\underset{a}{A} \xrightarrow{t_{1/2}} \underset{a/2}{\overset{a_1}{C}} \xrightarrow{t_{1/2}} \underset{a/4}{\overset{a_2}{B}} \text{(Product)}$$

$r_1 = k[C_1]^n \quad r_2 = k[C_2]^n$

$$\therefore \frac{r_1}{r_2} = \left[\frac{C_1}{C_2}\right]^n$$

$$\Rightarrow \log \frac{r_1}{r_2} = n \log \frac{C_1}{C_2}$$

$$\Rightarrow n = \frac{\log r_1/r_2}{\log C_1/C_2}$$

$$\Rightarrow \boxed{n = \frac{\log r_1 - \log r_2}{\log C_1 - \log C_2}}$$

Dt. 20-11-12

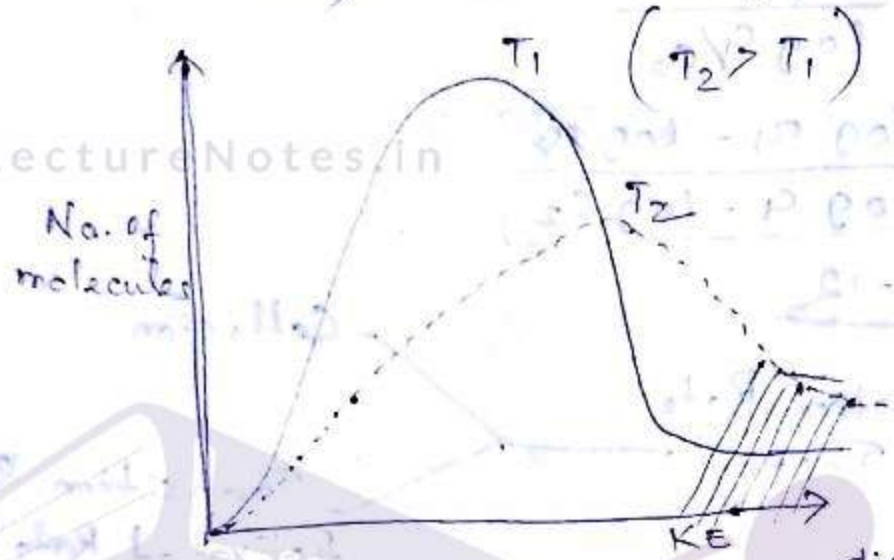
Reaction Rate Theory
- Collision
- Transition State/ Activated Rate Theory.

Collision Theory:

1. Only restricted to simple homogenous gaseous reactants.
2. When reacting molecules approach there take place a large no. of collisions.
3. All collisions are not effective.
4. for an effective collision the reacting molecules should satisfy the following conditions:
   (i) Max^m. no. of molecules should possess an energy more than a min^m. energy known as threshold energy (E_{Th}).
   (ii) The reacting molecules should have a compatible (mutual acceptable) shape or geometrical orientation in space.
5. When the reacting molecules initially causes the min^m. threshold energy, the reaction becomes faster and spontaneous (exothermic). Otherwise if max^m.

molecules don't have the energy in the range of the threshold value, extra energy in the form of activation energy is supplied from outside. Such reactions are very slow at the begining and non-spontaneous (endothermic).

$E_a = E_{Th} - E_{mol}$



- As per Maxwell Boltzmann's ~~distinguition~~ distribution law as per molecular velocity and molecular energy it is clear that all the molecules don't possess the same type of velocity ~~for~~ for same ~~kind of vele~~ amount of KE even at a particular temp.

- 3 kinds of molecular velocity are found out in case of simple gaseous molecule. But with increase in temp. more molecules becomes activated with increase in molecular velocity and KE (Very clear from the graph).

Arrhenious eq.:

It gives a relation between rate constant of a reaction with the amount of activation energy

$$\boxed{K = Ae^{-E_a/RT}}$$

Where A → Arrhenious const./factor.
This Arrhenious const./factor is the number of colliding molecules present per c.c per Sec.

$$\boxed{A = \sqrt{2}\,\pi n \sigma^2 v_{avg}^2}$$

Where n = total no. of reacting molecule
σ = diameter of reacting molecule

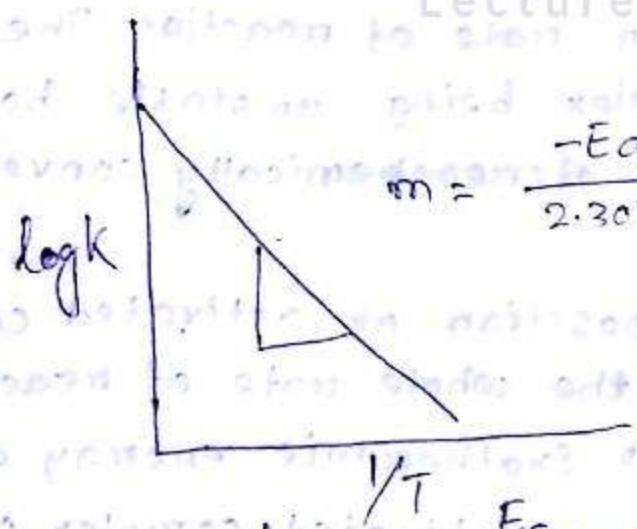
Collision number (Z):

- It is the number of effective collisions taking place per cc per Sec.
- for simple bimolecular collision,

$$Z = \frac{A}{2}$$

- $\left(\frac{-E_a}{R}\right)$ is the fraction of molecules having associated with an activation energy Ea.

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



$$m = \frac{-E_a}{2.303R}$$

$$\log K_1 = \log A - \frac{E_a}{2.303RT_1}$$

$$\log K_2 = \log A - \frac{E_a}{2.303RT_2}$$

$$\boxed{\log \frac{K_2}{K_1} = \frac{E_a}{2.303R}\left(\frac{T_2 - T_1}{T_1 T_2}\right)}$$

Disadvantages of collision theory:

1. Only restricted to simple homogenous gaseous reaction, but fails for high complex reactions.
2. It puts more emphasis on the energy factor, but never says anything on the steric-chemical aspect.
3. It considers the energy of the system as kinetic but the energy is rotation, vibrational, translational and to some extent molecular.
4. It doesnot give any idea about type of reaction mechanism.

Dt: 22/11/12

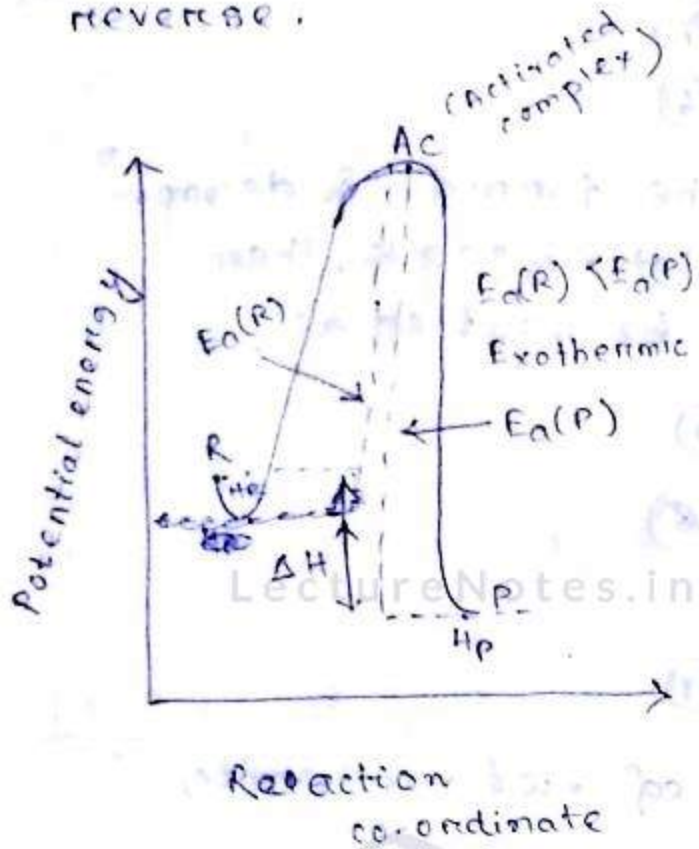
Transition state Theory/Activated Rate Theory:

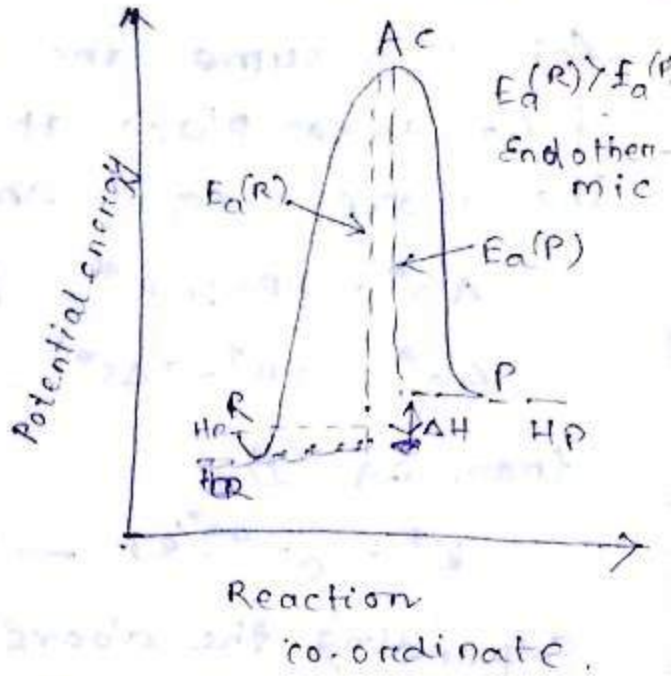
1) This theory takes care of all simple and complex reaction where reactants are directly or indirectly converted to product. Reactants are first converted to activated complex with particular rate of reaction. The activated complex being unstable both energetically & stereochemically converted into products.

2) Rate of decomposition of activated complex to product is the whole rate of reaction.

3) In the case of Exothermic energy difference betn reactant and activated complex is less. So the reacn is faster & spontaneous. In case of Endothermic reacn, the case is just

reverse.





Equation:

$$\overset{R}{A + B-C} \underset{}{\overset{k^*}{\rightleftharpoons}} \overset{AC}{(A \cdots B \cdots C)} \xrightarrow{k_c} \overset{P}{A-B + C}$$

$$k^* = \frac{[ABC]}{[A][BC]} \quad \text{— (1)}$$

Rate of decomposi of activated complex $= \frac{d[AB][C]}{dt} = k_c[AB\cdots C]$ — (2)

Putting the value of conc. of [ABC] from eq. (1) in eq. (2), we get,

$$\text{Rate} = k_c k^* [A][BC] \quad \text{— (3)}$$

As the formaⁿ & decomposition of the AC involves a good no. of effective collisions, these 2 rate consts can be related with the help of statistical mechanics.

$$k_c = \frac{RT}{Nh} k^* \quad \text{— (4)}$$

From Vant-hoff's eq. applicable to state of equilibrium,

$$\Delta G^\circ = -RT \ln k^* \quad \text{— (5)}$$

A/c to Gibb-Helmoltz's eq.,

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 \quad \text{--- (6)}$$

Let us assume the the formaⁿ & decompⁿ of Ac takes place at 1atm & 298 K. Then the above 2 eq.s can be written as,

$$\Delta G^* = -RT\ln k^* \quad \text{--- (7)}$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad \text{--- (8)}$$

from eq. (7)

$$k^* = e^{-\Delta G^*/RT} \quad \text{--- (9)}$$

Expanding the above eq., we can write,

$$k^* = e^{-\frac{\Delta H^*}{RT}} \cdot e^{\frac{\Delta S^*}{R}} \quad \text{--- (10)}$$

Putting value of k^* from (10) to (4), we have,

$$\boxed{\begin{aligned} k_c &= \frac{RT}{Nh} \times e^{-\Delta G^*/RT} \\ &= \frac{RT}{Nh} \times e^{-\frac{\Delta H^*}{RT}} \cdot e^{\frac{\Delta S^*}{R}} \end{aligned}}$$

We know, $k = Ae^{-Ea/RT}$

Q) What is the relation betⁿ Ea & ΔH at normal temp?

2) ~~When~~ What is the relaⁿ betⁿ Ea & ΔH when no gaseous ~~state~~ phase allowed?

$\Delta S = 0$

3) If Ea for a certain biological reaction is 50kJ/mole. By what factor the rate of reaction increases when a human body temp. increases from 37°C (normal) to 40°C (fever). factor $= \frac{k_2}{k_1} = 1.2$

$$\log \frac{k_2}{k_1} = \frac{50,000}{2.303 \times 8.314}\left(\frac{313 - 310}{313 \times 310}\right)$$

$$= 0.080$$

$$\Rightarrow \frac{k_2}{k_1} = 1.2.$$

Dt. 27/11/12

CATALYSIS :

- A catalyst is a chemical entity which influences the rate of a chemical reaction either by increasing or decreasing the energy difference betⁿ the reactant & the activated complex.
- The catalyst would be of following 3 types:
  i) Positive catalyst
  ii) Negetive catalyst.
  iii) Auto catalyst.

Positive catalyst:

It decreases the Ea making the process faster.

e.g. - i) $N_2 + H_2 \underset{\text{Finely divided}}{\overset{Fe}{\rightleftharpoons}} 2NH_3$

ii) $KClO_3 \xrightarrow{MnO_2} KCl + O_2$

iii) ~~H_2SO_4~~ $SO_2 + O_2 + H_2O \xrightarrow{NO(g)} H_2SO_4$

Negetive catalyst:

It increases the Ea value & thus making the reaction slow.

e.g.- i) $CH_3CHO \xrightarrow{\text{Glycerol}} CH_4 + O_2$.

ii) Use of TEL (Tetraethyllead i.e. $(C_2H_5)_4Pb$) in the decomposition of gasoline.

Auto catalyst:

Here one of the products of the reaction act as auto catalyst.

e.g.- i) Reduction of $KMnO_4$ by oxalic ā. in presence of H_2SO_4; produces enough of Mn^{2+} which acts as an auto catalyst.

$KMnO_4 + H_2C_2O_4 + 8H^+ \longrightarrow Mn^{2+} + CO_2 + 4H_2O$.

ii) Hydrolysis of ester like ethylacetate

produces one of organic ā acetic ā which acts as an autocatalyst.

$$CH_3COOC_2H_5 + H_2O \longrightarrow \underbrace{CH_3COOH}_{\text{Auto catalyst.}} + C_2H_5OH.$$

Promoter:

It is a chemical entity which increases the catalytic activity of a +ve catalyst.

e.g.-

i) Use of few pieces of Mo to enhance the catalytic activity of finely divided Fe used for the formation of NH_3 by Haber's process.

$$N_2 + H_2 \underset{Mo}{\overset{Fe}{\rightleftharpoons}} 2NH_3$$

ii) Oxides like Al_2O_3, V_2O_5 & ThO_2 enhance the catalytic activity of finely devided Fe.

iii) Cu & Te enhance the catalytic activity of Ni during the hydrogenetion of oil.

iv) As_2O_3 & ThO_2 also catalyse the catalytic effect of Cu & Fe.

Characteristics of catalyst:

1) A catalyst is very selective.

2) A catalyst is always taken in very small amount.

3) A catalyst in a definite shape like in a finely devided form is more active as the surface area is max^m.

4) A catalyst may undergo a physical change during the process. e.g.- In the decomposi^n

$KClO_3$, MnO_2 is taken in granular form but after the reaction it comes out in powder form.

5) Catalyst is always temp. sensitive continuing for each catalyst there is an optimum temp. where its action is max^m. Most of the +ve catalyst have optimum temp. very close to 35°C.

6) A catalyst never alters the state of equilibrium

Catalytic poisioning:

It is a process in which the catalytic activity of a catalyst decreases in the presence of either a chemical or non-chemical entity (catalytic poison).

e.g. - Use of starch indicator.

- It is of 2 types

i) Temporary type

ii) Permanent type.

Temporary: The catalytic poision preoccupies the active sites of catalytic surface with the help of some physical forces like Vanderwaal's forces of attraction or London's forces of attraction. This can be avoided by increasing the temp. or by use of physical/mechanical methods like scratching or ~~scr~~ scrubing.

Permanent: Here the catalytic poision enters the active site of catalyst surface by strong chemical force like covalent bond. The coating of the poison is very

hard which can only be eliminated by use of sp. chemical treatement & depending on type of poision.

e.g.-

1) Presence of CO poisons the catalytic activity of finely divided Fe in the manufacture of NH_3 in Habar's process as CO molecules preoccupy the active sites of finely divided Fe & form stable compds like $Fe(CO)_5$

2) As_2O_3 acts as a catalytic poision during the manufacture of H_2SO_4 from SO_2, O_2 & H_2O by poisoning the activity of NO.

Dt. 5/12/12

Theory of catalysis:

Homogenous:

Reactants, products & catalysts are in one phase.

e.g. - i) $SO_{2(g)} + O_{2(g)} + H_2O_{(vap)} \xrightarrow{NO_{(g)}} H_2SO_{4(g)}$

ii) Hydrolysis of ester.

$CH_3COOC_2H_{5(l)} + H_2O_{(l)} \xrightarrow{H_2SO_{4(l)}} CH_3COOH_{(l)} + C_2H_5OH_{(l)}$

Heterogenous:

Reactants, products & catalysts are in different phases. e.g.

i) $N_2(g) + H_2(g) \underset{Fe}{\overset{\text{Finely divided}}{\rightleftharpoons}} NH_3(g)$

ii) $2KClO_3(s) \xrightarrow{MnO_2(s)} KCl(s) + O_2(g)$

Homogenous catalysis:

The following theory explains the mechanism behind the catalysis process.

1) Unstable compd formation Theory/Chemical Theory

A catalyst reacts with only one reactant (if present), otherwise it will react with another active reactant to give an unstable compd. The unstable compd either decomposes or react with the second reactant to give a stable product & the catalyst is out.

e.g.- i) $SO_2(g) + O_2(g) \xrightarrow{NO(g)} SO_3(g)$

Step-1 $O_2 + 2NO \longrightarrow 2NO_2^*$

step-2 $[NO_2^* + SO_2 \longrightarrow SO_3 + NO] \times 2$

$2SO_2 + O_2 \longrightarrow 2SO_3$

ii) Fredel-Craft reaction.

a) Alkylation:

$C_6H_6 + CH_3Cl \xrightarrow{AlCl_3} C_6H_5CH_3 + HCl$ (Toluene)

b) Acylation:

$C_6H_6 + CH_3COCl \xrightarrow{AlCl_3} C_6H_5COCH_3 + HCl$. (Acetophenone)

Heterogenous catalysis:

The following 2 theories explain the process of heterogenous catalysis.

1) Unstable compd formation Theory/Chemical Theory:

The catalyst reacts with ~~wit~~ one of the reactants to give an unstable compd, which reacts with the second reactant to give the stable product & catalyst is back.

e.g. -

i) $KClO_3(s) \xrightarrow{MnO_2(s)} KCl(s) + O_2(g)$

Step-1 $[KClO_3 + MnO_2 \longrightarrow KMnO_4 + \frac{1}{2}Cl_2 + O_2]$

Step-2 $[2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2]$

Step-3 $K_2MnO_4 + Cl_2 \longrightarrow KCl + O_2 + MnO_2$

$$2KClO_3 \longrightarrow 2KCl + 3O_2$$

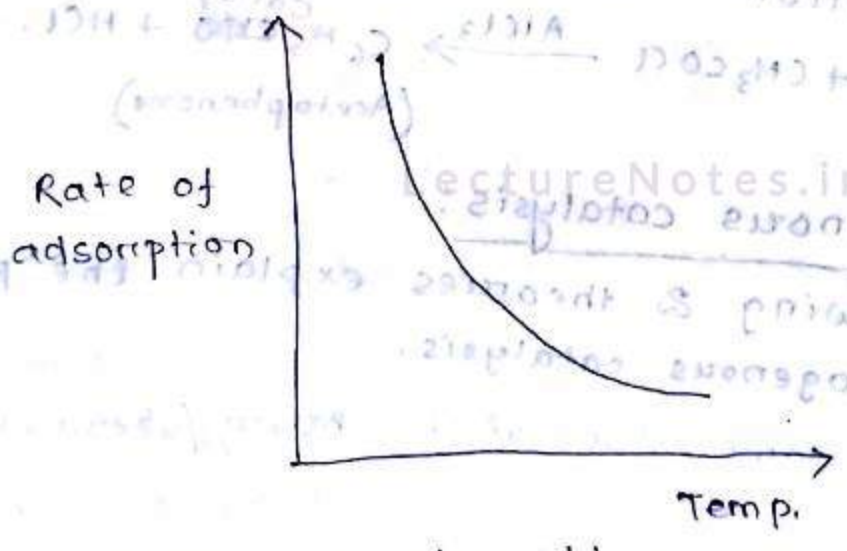
ii) Elimination of ethyl alcohol in presence of conc. H_2SO_4 to give an ether.

$$\underset{\text{(Ethyl alcohol)}}{2C_2H_5OH} \xrightarrow[-H_2O]{H^+} \underset{\text{(Diethyl ether)}}{C_2H_5-O-C_2H_5}$$

2) Adsorption Theory:

a) Physical adsorption: It is only possible due to the formation of physical forces like vanderwaal's forces betn the surface of catalyst & reactants.

- It is inversely proportional to temp.



- Molar rate of adsorption is in the range of 0-10 kcal/mol.
- This process is reversible.
- This process is not reactant specific.

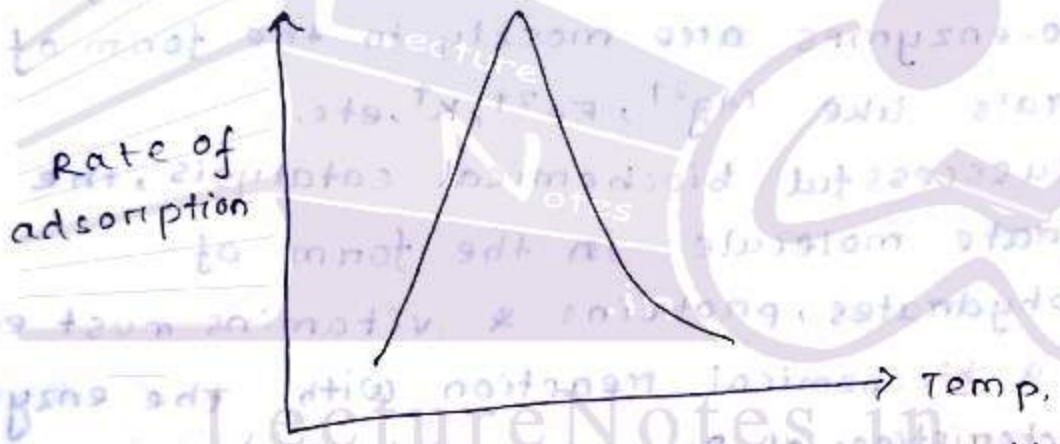
e.g.-

i) Adsorption of any gas on the surface of activated charcoal.

b) Chemical adsorption: It is possible due to the formation of strong chemical bonds betn catalyst surface & reactant.

- The molar heat of adsorption is in the range of 10-100kcal/mol.

- The rate of chemical adsorption is directly proportional to the temp. upto a maxm pt., then it falls with rise in temp. This is because of the avialability of sufficient amount of activation energy in the reaction medium.



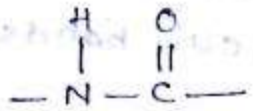
- This process is reactant specific and not reversible.

e.g.-

i) Hydrogenetion of unsaturated compds like alkenes & alkynes to the co-responding alkane in the presence of metals like Ni, Pt, Pd etc.

Biocatalysis :

Biocatalysis is a complex organic molecule containing mostly peptide linkage,



such biochemical catalyst are also known as enzymes having different stereochemical configuration.

The known biochemical catalysts are:

i) Zymase
ii) Invertase
iii) Maltase
iv) Diatase.

- The catalytic reaction are sometimes promoted by certain promotoers known as co-enzymes.
- The co-enzymes are mostly in the form of minerals like Mg^{2+}, Fe^{2+}, K^{+}, etc.
- For sussccessful biochemical catalysis, the substrate molecule in the form of carbohydrates, proteins & vitamins must enter into a biochemical reaction with the enzyme

Characteristics of Bio-catalyst:

i) They are very much specific.
ii) They are temp. & pH ~~specific~~ sensitive.
iii) They do not alter the state of equilibrium

Examples:

i) Hydrolysis of sucrose ($C_{12}H_{22}O_{11}$) in presence of invertase.

$$\underset{\text{sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{G}{C_6H_{12}O_6} + \underset{F}{C_6H_{12}O_6}$$

ii) Fermentation / Decomposition of Glucose in presence of zymase.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + CO_2 .$$

iii) Hydrolysis of starch

$$\underset{\text{starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diatase}} \underset{\text{maltose}}{nC_{12}H_{22}O_{11}}$$

iv) Hydrolysis of maltose in presence of maltose to give glucose.

$$\underset{\text{maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{maltase}} \underset{\text{Glucose.}}{2C_6H_{12}O_6}$$

1) For reaction $2HI \longrightarrow H_2 + I_2$, the value of K is 1.2×10^{-3} $dm^3 mol^{-1} sec^{-1}$ at 700K and 1.5×10^{-2} $dm^3 mol^{-1} sec^{-1}$ at 600K. Determine the value of Ea and the frequency factor.

2) A graph betn $\log K \sim 1/T$ is a straight line with $OX = 5$, $\tan\theta = 1/2.303$. Find out the value of Ea.

3) In a reaction $A \rightarrow B$, the state of reacn increases two times on increase the conc. of reactant 4 times find out the order (n=0.5)

4) On the top of a mountain, where atmospheric press. is 535 mm of Hg pure water shows a boiling pt. of 360K. And it takes 3×10^2 min to boil at the top of the mountain. As against 3 min taken, to boil the egg at 370K. Find x if the ratio of the 2 rate constant is 10^x $\left(\frac{k_{370}}{k_{360}} = 10^2\right)$ Ans - x = 2.

5) For general eq.: $A + B \rightleftharpoons C + D$, the sp. rate const. is $K_{for} = 2\times10^{-3}$ $mol^{-1} lt sec^{-1}$ at a certain temp. Reactions pass with equimolar amount of A & B. Reading at equilibrium it is observed

that the amount of A is twice that of C. Find out the sp. rate const. for the backward reaction (Ans- $8\times10^{-3}\,m^{-1}\,L\,sec^{-1}$)

$$k_{for} = \frac{2.303}{t}\log\frac{[C][D]}{[A][B]} = \frac{2.303}{t}\log\frac{[C][D]}{[A]^2}$$

$$k_{back} = \frac{2.303}{t}\log\frac{[A][B]}{[C][D]}$$

At equilibrium,

$$k_{for} = k_{back}$$

$$\Rightarrow 2\times10^{-3} = \frac{2.303}{t}\log\frac{2[C][B]}{[C][D]}$$

$$= \frac{2.303}{t}\log\frac{2[B]}{[D]}$$

$$C + D \rightarrow A + B$$

$$a-x \quad a-x \qquad 2(a) \quad y$$

$$(a-x)(a-x) = 2(a) + y$$

$$\Rightarrow \cancel{a^2} - 2x = \cancel{2a} + y$$

$$\Rightarrow -2x = y$$

$$\Rightarrow$$

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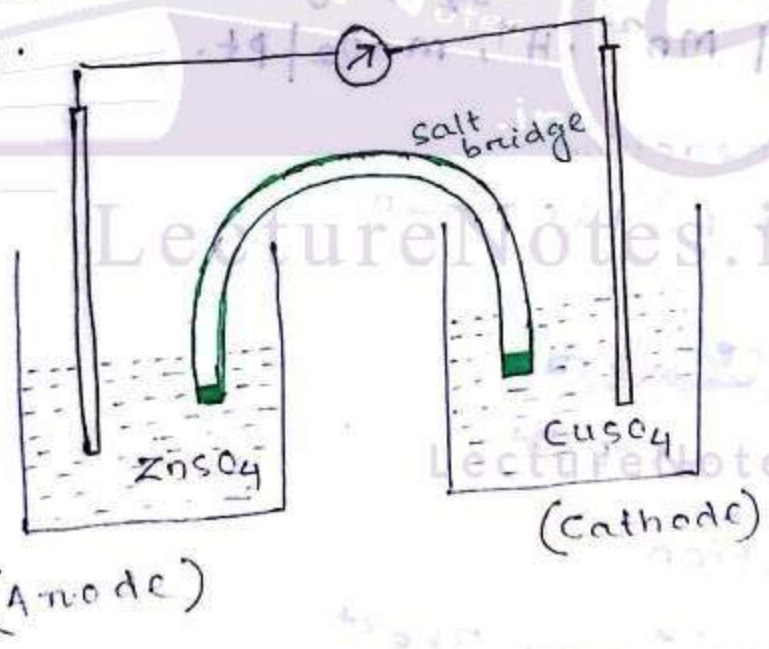
ELECTROCHEMISTRY

Electrolytic cell:
The device in which electric current is used for electrolysis. i.e. electrical energy is responsible for chemical decomposition.

Galvanic cell:
- It is a device in which chemical energy is used to produce electrical energy.

~~Electrochemical cell~~
- The device in which chemical energy is converted to electrical energy or the device in which electrical energy is produced due to indirect redox reaction known as Galvanic cell / Voltaic cell.
- In a Galvanic cell the decrease in free energy of a chemical reaction appears as electrical energy.



Salt bridge:
- It is an inverted 'U' shaped tube containing inert electrolyte like KCl or KNO_3 with some agar-agar or gelatin.
- The two ends of the tube are fitted with porous plug.

Function of salt bridge:

1) It completes the circuit.
2) It maintains electrical neutrality of two sol^n.
3) It takes care of liquid junction potential if any.

- By IUPAC convention, the direc^n of current is opposite to that of electron.

Construction:

Q1. 9/10/12

Write the half cell reac^n & net cell reactions of the following electrochemical cells.

1) $Fe | Fe^{2+} || Fe^{2+} - Fe^{3+} | Pt$.
2) $Pt | K_3[Fe(CN)_6]\ K_4[Fe(CN)_6] || CrCl_3 | Cr$
3) $Zn | ZnO_2^{2-}, OH^- || Hg_2O | Hg$.
4) $Cu | Cu^{2+} || Mn^{2+}, H^+, MnO_2 | Pt$.

1) Half cell reaction.

Anode:

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

Cathode:

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

Net reaction

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

2) Anode:

$$[Fe(CN)_6]^{4-} \longrightarrow [Fe(CN)_6]^{3-} + e$$

Cathode:

$$Cr^{3+} + 3e \longrightarrow Cr$$

Net reaction

$$3[Fe(CN)_6]^{4-} + Cr^{3+} \longrightarrow 3[Fe(CN)_6]^{3-} + Cr$$

3) Anode :

$$Zn + 4OH^- \longrightarrow ZnO_2^{2-} + 2H_2O + 2e$$

Method -1

1) $Zn \longrightarrow ZnO_2^{2-}$

2) $Zn + 2H_2O \longrightarrow ZnO_2^{2-}$ [for O balance]

3) $Zn + 2H_2O + 4OH^- \longrightarrow ZnO_2^{2-} + 4H_2O + 2e$ [To balance extra $4H_2O$]

$\Rightarrow Zn + 4OH^- \longrightarrow ZnO_2^{2-} + 2H_2O + 2e$

cathod :

$$Hg_2O \longrightarrow 2Hg^+ + \frac{1}{2}O_2$$

$$2Hg^+ + 2e^- \longrightarrow 2Hg$$

$$Hg_2O + 2e^- \longrightarrow 2Hg + \frac{1}{2}O_2$$

Net :

$$Zn + Hg_2O + 4OH^- \longrightarrow ZnO_2^{2-} + 2H_2O + 2Hg + \frac{1}{2}O_2$$

4) Anode :

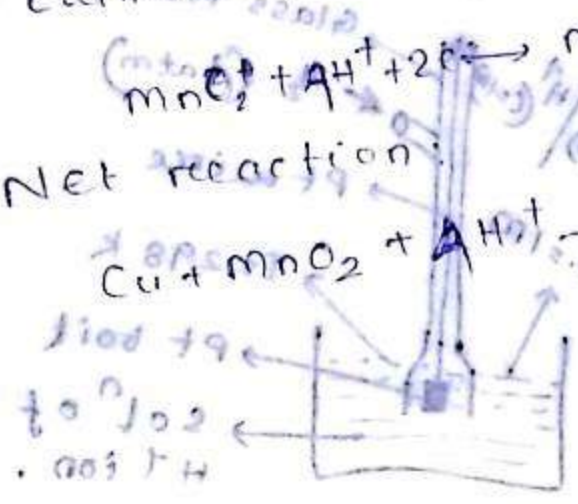
$$Cu \longrightarrow Cu^{2+} + 2e$$

cathode :

$$MnO_2 + 4H^+ + 2e \longrightarrow Mn^{2+} + 2H_2O$$

Net reaction :

$$Cu + MnO_2 + 4H^+ \longrightarrow Cu^{2+} + Mn^{2+} + 2H_2O.$$



Electrode potential:

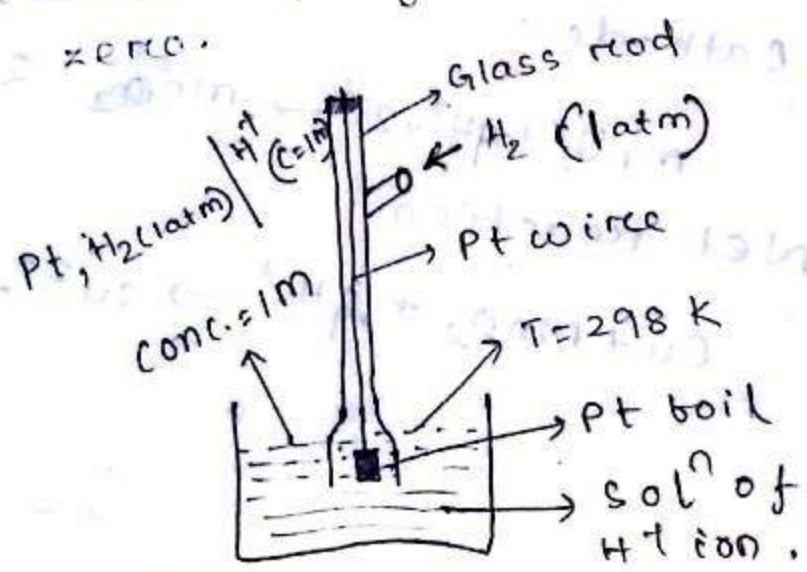
- The tendency of an electrode to loose or gain e^- when it is in contact with its ion is known as electrode potential or single electrode potential.
- The electrode potential is termed as oxidation potential if oxidaⁿ takes place in the half cell. Similarly the electrode potential is termed as reductⁿ potential if reducⁿ takes place in the half cell.
- Both oxidation & reduction potential have same value having opposite sign.

Standard electrode potential (E^0):

The potential of an electrode in solⁿ of its ion of 1 molar conc. maintained at 298 K. For gaseous electrode the press: must be 1 atm.

Measurement of electrode potential:

- It is impossible to determine the absolute value of electrode potential because neither oxidation nor reduction takes place independently. However the difference can be measured potentiometrically by taking one of the electrode as the reference electrode.
- A/c to IUPAC convention, normal hydrogen electrode or standard hydrogen electrode is taken as zero.



Electrochemical series :

When the elements or the electrodes are arrangent in the increasing order of standard reduction potential or decreasing order of standard oxidation potential, then this arrangment is known as electro-chemical series.

Write 3 applications of Electrochemical series with example.

1) Calculating cell potential -

E°_{cell} = [Reduct^n potential of the reduction half cell] - [Reduct^n potential of the oxidation half cell]

= [Oxida^n potential of the oxidat^n half cell] - [Oxida^n potential of the reduction half cell]

e.g. -

Let $E^\circ_{Zn^{2+}/Zn} = -0.76V$ } - Reduct^n potential

$E^\circ_{Ag/Ag^+} = -0.79V$ } - Oxida^n potential

E°_{cell} = [Reduc^n potential of Ag electrode] - [Reduc^n potential of Zn electrode]

$= 0.79 - (-0.76)$

$= 0.79 + 0.76 = 1.55V$

2) Predicting anode & cathode -

An electrode with higher oxidation potential or lower reduction potential is called anode. Similarly an electrode with lower oxidation potential or higher reduction potential is called cathode.

e.g. - The standard reduc^n potential of Zn = -0.76V & the standard reduc^n potential of Cu = +0.335V. The Cu is cathode & Zn is anode.

3) Determination of equilibrium const for a reacⁿ

$$E^\circ_{cell} = \frac{0.0591}{n} \log K_c \text{ (at 298K)}$$

4) Predicting the reactivity of elements:

An element whose oxidaⁿ potential is more is said to be more reactive & an element whose oxidaⁿ potential is less is said to be less reactive. A more reactive metal can displace less reactive metals from the solⁿ of their salts.

e.g. The oxidation potential of Zn is more than that of Cu. So Zn can displace Cu from $CuSO_4$ solⁿ.

~~Dt 11/10/19~~ 5) Feasibility:

~~Effect of~~

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Dt. 16/10/12

Effect of electrolytic conc. on electrode potential

[Derivation of Nernst Equation]

Consider a general redux reaction

$$M^{n+} + ne \longrightarrow M(s)$$

Applying law of mass-action,

$$Q = \frac{[M(s)]}{[M^{n+}]}$$

$$Q = \frac{1}{[M^{n+}]} \quad \text{—— (1)}$$

Since in an electrochemical cell that decrease in free energy appears as electrical energy,

$$-\Delta G = nFE \quad \text{—— (2)}$$

$$-\Delta G^{\circ} = nFE^{\circ} \quad \text{—— (3)}$$

where n = No. of e^- involved in ~~rect~~ half cell reaⁿ.

F = Faraday's const.

A/c to Vanthoff's reaction isotherm,

$$\Delta G = \Delta G_0 + RT \ln Q$$

$$\Rightarrow -nFE = -nFE^{\circ} + RT \ln \frac{1}{[M^{n+}]}$$

$$\Rightarrow E = E^{\circ} - \frac{RT}{nF} 2.303 \log \frac{1}{[M^{n+}]}$$

$$\Rightarrow \boxed{E = E^{\circ} - \frac{2.303RT}{nF} \log \frac{1}{[M^{n+}]}}$$

This is Nernst eqⁿ for reduction reaction.

The Nernst eqⁿ for oxidation potential is

$$\boxed{E = E^{\circ} - \frac{2.303RT}{nF} \log [M^{n+}]}$$

At 25°C,

$$\boxed{E = E^{\circ} - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}}$$

$$E = E^\circ - \frac{0.0591}{n} \log [M^{n+}]$$

Q) Calculate the electrode potential of Zn in $ZnSO_4$ sol^n of 0.1M conc. which is 95% ionised. Given $E^\circ_{Zn^{2+}/Zn} = -0.76V$.

$$E = E^\circ - \frac{0.0591}{n} \log \frac{1}{[M^{n+}]}$$

$$[Zn^{2+}] = 0.1 \times \frac{95}{100} = 0.095$$

$$E = E^\circ - \frac{0.0591}{2} \log\left(\frac{1}{0.095}\right)$$

$$= -0.79$$

Cell potential or EMF (E_{cell}):

In an electrochemical cell there are two half cells & one half cells at higher electrode potential than the other half cell. Due to this potential difference electrons flow from one halfcell of higher oxidation potential to other half cell of lower oxidation potential. This difference bet^n electrode potential is known as cell potential or EMF of cell & can be defined as the force which causes the flow of electrons. The emf of a cell can be calculated

$$E_{cell} = E_{cathode} - E_{anode} \quad \left[\text{For reduction potential}\right]$$
$$= E_R - E_L$$

$$E_{cell} = E_{anode} - E_{cathode} \quad \left[\text{For oxidation potential}\right]$$
$$= E_L - E_R$$

Nernst Eq^n. for EMF:

$$aA + bB \rightleftharpoons mM + nN$$

Applying law of mass-action,

$$Q = \frac{[M]^m [N]^n}{[A]^a [B]^b} \quad \text{—— (1)}$$

Since in an electrochemical cell the decrease in free energy appears as electrical energy.

$$-\Delta G = nFE_{cell} \quad \text{—— (2)}$$

$$-\Delta G^0 = nFE^0_{cell} \quad \text{—— (3)}$$

where n - no. of e^-s in net cell.

A/c to vanthoff's reaction isotherm,

$$\Delta G = \Delta G^0 + RT\ln Q$$

$$\Rightarrow -nFE_{cell} = -nFE^0_{cell} + RT\ln\frac{[M]^m [N]^n}{[A]^a [B]^b}$$

$$\Rightarrow \boxed{E_{cell} = E^0_{cell} - \frac{2.303RT}{nF}\log\frac{[M]^m [N]^n}{[A]^a [B]^b}}$$

$$\Rightarrow \boxed{E_{cell} = E^0_{cell} - \frac{0.0591}{n}\log\frac{[M]^m [N]^n}{[A]^a [B]^b}}$$

Q) Calculate EMF of following cell at 25°c.

$$Cu/Cu^{2+}(0.01M) \,||\, Ag^+(0.1M)/Ag$$

Given $E^0_{Cu^{2+}/Cu} = 0.34V$

$E^0_{Ag^+/Ag} = 0.80V$.

$$Cu(s) \longrightarrow Cu^{2+} + 2e$$

$$\left[Ag^+ + e \longrightarrow Ag^{(s)}\right] \times 2$$

$$Cu(s) + 2Ag^+ \longrightarrow Cu^{2+} + 2Ag(s)$$

$$E^0_{cell} = 0.8 - 0.34 = 0.46$$

$$E^\circ_{cell} = 0.46 - \frac{0.0591}{2} \log \frac{[Cu^{2+}]}{[Ag^+]^2}$$

$$= 0.46 - \frac{0.0591}{2} \log \left[\frac{0.01}{0.01}\right]$$

$$= 0.46\,V$$

Relation betⁿ equilibrium const. & standard EMF of a cell:

$$\Delta G^\circ = -nFE^\circ_{cell} \quad \text{—} (1)$$

$$\Delta G^\circ = -RT \ln K \quad \text{—} (2)$$

$$RT \ln K = nFE^\circ_{cell}$$

$$\Rightarrow \boxed{\log K = \frac{nF}{2.303RT} E^\circ_{cell}}$$

At 25°C. $\boxed{\log K = \frac{n}{0.0591} E^\circ_{cell}}$

Dt. 18/10/12

5) Calculate the reduction potential of Cu at 25°C in a solⁿ of pH = 14. Given the solubility product of $Cu(OH)_2$ is 1×10^{-19} & the standard reduction potential of Cu is 0.34 V.

$$K_{sp}[Cu(OH)_2] = [Cu^{2+}][OH^-]^2$$

Given pH = 14

$$[H^+] = 10^{-14}$$

$$[H^+][OH^-] = 10^{-14}$$

$$\Rightarrow [OH^-] = 1$$

$$K_{sp}[Cu(OH)_2] = [Cu^{2+}][OH^-]^2$$

$$\Rightarrow 1 \times 10^{-19} = [Cu^{2+}]$$

$$E = E^\circ - \frac{0.0591}{2} \log \frac{1}{[Cu^{2+}]} = 0.34 - 0.56$$

$$= -0.22\,V$$

Q) Calculate the electrode potential of Ag in a sol^n i.e. saturated with AgI & has an unit iodide conc. The $K_{sp}(AgI) = 8.3 \times 10^{-17}$ & $E^\circ_{Ag^+/Ag} = 0.799V$.

$[I^-] = 1$

$K_{sp}[AgI] = [Ag^+] \cdot [I^-]$

$\Rightarrow 8.3 \times 10^{-17} = [Ag^+]$

$\therefore E = E_0 - \frac{0.0591}{1} \log \frac{1}{[Ag^+]}$

$= 0.799 - 0.0591 \times 16.08$

$= -0.151V$.

Q) Calculate the standard electrode potential of M^{3+}/M electrode in following electrochemical cell.

$Pt, M|M^{3+}(0.0018M) || Ag^+(0.01M)|Ag(s)$.

emf $= 0.42V$

& $E^\circ_{Ag^+/Ag} = 0.80V$.

$$\cancel{E = E^{\circ}_{M^{3+}/M} - \frac{0.0591}{3} \log \frac{1}{[M^{3+}]}}$$

$$\cancel{\Rightarrow 0.6818 = E^{\circ}_{M^{3+}/M} - \frac{0.0591}{3} \log \frac{1}{0.0018}}$$

$\Rightarrow$

Anode: $M \longrightarrow M^{3+} + 3e$

Cathode: $[Ag^{+} + e \longrightarrow Ag] \times 3$

$$M + 3Ag^{+} \longrightarrow M^{3+} + 3Ag$$

A/c to Nernst eq.,

$$E_{cell} = E^{\circ}_{cell} - \frac{0.0591}{3} \log \frac{[M^{3+}]}{[Ag^{+}]^{3}}$$

$$\Rightarrow 0.42 = E^{\circ}_{cell} - \frac{0.0591}{3} \log \frac{0.0018}{[0.01]^{3}}$$

$$\Rightarrow 0.42 = E^{\circ}_{cell} - \frac{0.0591}{3} \log (18 \times 10^{2})$$

$$\Rightarrow E^{\circ}_{cell} = 0.42 - 0.064$$

$$= 0.484\ V$$

$$E^{\circ}_{cell} = E^{\circ}_{Ag^{+}/Ag} - E^{\circ}_{M^{3+}/M}$$

$$\Rightarrow 0.484 = 0.80 - E^{\circ}_{M^{3+}/M}$$

$$\Rightarrow E^{\circ}_{M^{3+}/M} = 0.316\ V.$$

Q) Calculate the ratio of $[Pb^{2+}]/[Sn^{2+}]$ at which the cell reac^{n} will be reversed at 25°C. Given the standard reduc^{n} potential of Pb & Sn are $E^{\circ}_{Sn^{2+}/Sn} = -0.136\ V$

$$E^{\circ}_{Pb^{2+}/Pb} = -0.126\ V.$$

$$Sn(s) + Pb^{2+} \longrightarrow Sn^{2+} + Pb$$

$E^\circ_{cell} = E_{cathode} - E_{anode}$

$= -0.126 + 0.136$

$= 0.01\,V$

$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[Sn^{2+}]}{[Pb^{2+}]}$

At equilibrium $E_{cell} = 0$

so

$0 = 0.01 - \frac{0.0591}{2} \log \frac{[Sn^{2+}]}{[Pb^{2+}]}$

$\Rightarrow \cancel{\log \frac{[Sn^{2+}]}{[Pb^{2+}]} = \frac{0.01 \times 2}{0.0591}}$

$\Rightarrow \cancel{\log \frac{[Pb^{2+}]}{[Pb^{2+}]} = 0.3384}$

$\Rightarrow \cancel{\frac{[Sn^{2+}]}{[Pb^{2+}]} =}$

$\Rightarrow -0.01 = \frac{0.0591}{2} \log \frac{[Pb^{2+}]}{[Sn^{2+}]}$

$\Rightarrow \log \frac{[Pb^{2+}]}{[Sn^{2+}]} = -0.3384$

$\Rightarrow \ln \frac{[Pb^{2+}]}{[Sn^{2+}]} = -0.3384 \times 2.303$

$= -0.779$

$\Rightarrow \frac{[Pb^{2+}]}{[Sn^{2+}]} = 0.458$

$\therefore$ As long as $\frac{[Pb^{2+}]}{[Sn^{2+}]} = 0.458$, E_{cell}. ~~To reverse~~

ratio must be

Dt. 1.11.12

1) Calculate the equilibrium const. of the reaction

$$Zn + 2Ag^+ \rightleftharpoons Zn^{2+} + 2Ag$$

occurs in a ZnAg cell at 25°C, when conc. of Zn^{2+} ion is 0.1M & conc. of Ag^+ is 10m & the emf of the cell is 1.62V.

$$E_{cell} = E^\circ_{cell} - \frac{0.0591}{n} \log \frac{[M]^m [N]^n}{[A]^a [B]^b}$$

$$\Rightarrow 1.62 = \frac{0.0591 \log K}{n} - \frac{0.0591}{n} \log \frac{[Zn^{2+}][Ag]^2}{[Zn][Ag^+]^2}$$

$$\Rightarrow 1.62 = \frac{0.0591}{2}\left[\log K - \log \frac{0.1}{100}\right]$$

$$\Rightarrow \frac{1.62 \times 2}{0.0591} = \log K + 3$$

$$\Rightarrow \log K = 51.822$$

$$\Rightarrow K = 10^{51.822} = 6.63 \times 10^{51}$$

2) Consider the electrochemical cell,

$Fe | Fe^{2+} (0.1m) || Cd^{2+} (0.001m) | Cd$ in which

$E^\circ_{Cd^{2+}|Cd} = -0.40V$ $\quad E^\circ_{Fe^{2+}|Fe} = -0.448V$

Write cell reaction & calculate the equilibrium const. of that at 25°C.

Anode : $Fe \longrightarrow Fe^{2+} + 2e$

Cathode : $Cd^{2+} + 2e \longrightarrow Cd$

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

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= -0.40 + 0.448$$

$$= 0.048V$$

$$\log K = \frac{n}{0.0591} E^\circ_{cell} = \frac{2 \times 0.048}{0.0591}$$

$$\Rightarrow K = 10^{\left(\frac{2 \times 0.048}{0.0591}\right)}$$

$$\Rightarrow K = 43.108$$

3) Consider an electrochemical cell

$Mg | Mg^{2+}(aq) || Ag^{+}(aq) | Ag$

$E^{\circ}_{Mg^{2+}|Mg} = -2.37V$ $\quad E^{\circ}_{Ag^{+}|Ag} = 0.80V$

Calculate the equilibrium const. & max^m work that can be done during the operation of cell at 25°C.

$E^{\circ}_{cell} = E^{\circ}_{cathode} - E^{\circ}_{anode}$

$= 0.80 + 2.37$

$= 3.17V$

$\log K = \frac{nE^{\circ}_{cell}}{0.0591} = \frac{2 \times 3.17}{0.0591}$

$\Rightarrow \log K = 107.27$

$\Rightarrow K = 10^{107.27}$

$= 10^{107} \cdot 10^{0.27}$

$= 1.862 \times 10^{107}$.

Max^m work $= nFE^{\circ}_{cell}$

$= 2 \times 96500 \times 3.17$

$= 611810 J = 611.81 kJ$

4(b) The emf of the cell, ~~Ag(s)|AgI(sat)~~

$Ag(s) | AgI(sat), KI(0.05M) || AgNO_3(0.05M) | Ag$ is 0.788V. Calculate the solubility product of AgI.

It is a conc. cell, where current produced due to difference in conc. of common ion (Ag^+).

$E_{Left} = E^{\circ} - \frac{0.0591}{1} \log \frac{1}{[Ag^+]_{LHS}}$

$E_{Right} = E^{\circ} - \frac{0.0591}{1} \log \frac{1}{[Ag^+]_{RHS}}$

$E_{cell} = E_{Right} - E_{Left}$

$= \cancel{E^{\circ}} - 0.0591 \log \frac{1}{[Ag^+]_{RHS}} - \cancel{E^{\circ}} + 0.0591 \log \frac{1}{[Ag^+]_{LHS}}$

$= 0.0591 \left(\log \frac{1}{[Ag^+]_{LHS}} - \log \frac{1}{[Ag^+]_{RHS}} \right)$

$= 0.0591 \left(\log \frac{[Ag^+]_{RHS}}{[Ag^+]_{LHS}} \right)$

$$\Rightarrow 0.788 = 0.0591 \log \frac{0.05}{[Ag^+]_{LHS}}$$

$$\Rightarrow \frac{0.788}{0.0591} = \log \frac{0.05}{[Ag^+]_{LHS}}$$

$$\Rightarrow \frac{0.05}{[Ag^+]_{LHS}} = 10^{\left(\frac{0.788}{0.0591}\right)} = 2.15 \times 10^{13}$$

$$\Rightarrow [Ag^+]_{LHS} = 2.325 \times 10^{-15}$$

$$[I^-] = 0.05$$

$\therefore$ Ksp of $AgI = [Ag^+][I^-]$

$$= 2.325 \times 10^{-15} \times 0.05$$

$$= 1.163 \times 10^{-16}$$

$$\boxed{E_{cell} = \frac{0.0591}{n} \log \frac{C_R}{C_L} \quad \text{[For conc. cell]}}$$

Relation betⁿ Electrical energy & enthalpy of a cell reaction:

A/c to Gibb - ~~Helmoltz~~ Helmoltz eqⁿ,

$$\Delta G = \Delta H + T \left[\frac{\partial(\Delta G)}{\partial T}\right]_P \quad \text{--- (1)}$$

But $\Delta G = -nFE_{cell}$

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -nF\left(\frac{\partial E_{cell}}{\partial T}\right)_P \quad \text{--- (2)}$$

Putting eqⁿ (2) in (1), we get

$$\Delta G = \Delta H - TnF\left(\frac{\partial E_{cell}}{\partial T}\right)_P$$

$$\Rightarrow -nFE_{cell} = \Delta H - TnF\left(\frac{\partial E_{cell}}{\partial T}\right)_P$$

$$\Rightarrow \boxed{E_{cell} = \frac{-\Delta H}{nF} + T\left(\frac{\partial E_{cell}}{\partial T}\right)_P}$$

$\left(\frac{\partial E_{cell}}{\partial T}\right)_P \longrightarrow$ temp. coefficient of emf.

Case - 1

If $\left(\frac{\partial E_{cell}}{\partial T}\right)_P = 0$, then the electrical energy will be equal to enthalpy of cell.

Case - 2

If $\left(\frac{\partial E_{cell}}{\partial T}\right)_P > 0$, then the emf of the cell increases with increase in temp. & the additional amount of energy will be supplied from surrounding to system. If this is not done, then temp. of system fall during working.

Case - 3

If $\left(\frac{\partial E_{cell}}{\partial T}\right)_P < 0$ then electrical energy will be less than enthalpy of reaction.

From Gibb-Helmoltz eq^n:

$$\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -\Delta S$$

But $\left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -nF\left(\frac{\partial E_{cell}}{\partial T}\right)_P$

$$\therefore \boxed{\Delta S = nF\left(\frac{\partial E_{cell}}{\partial T}\right)_P}$$

& $\boxed{\Delta G = \Delta H - T\Delta S}$

Dt. 5/11/12

1) Consider an electrochemical cell,

$Cd, CdCl_2 \cdot 2.5H_2O \| AgCl | Ag$ in which the cell reac^n is

$$Cd + 2AgCl \longrightarrow CdCl_2 \cdot 2.5H_2O + 2Ag$$

If the emf of the cell is 0.6915 V at 0°C & 0.6753 V at 25°C, calculate ΔG, ΔH & ΔS at 25°C.

$$\cancel{E_{cell} = \frac{-\Delta H}{nF} + T\left(\frac{\partial E_{cell}}{\partial T}\right)_P}$$

$$\cancel{0.6753 = \frac{-\Delta H}{2 \times 96500} + 298\left(\frac{0.6915 + 0.6753}{}\right.}$$

$$\Delta G = -nFE_{cell}$$
$$= -2 \times 96500 \times 0.6753$$
$$= -130332.9\ J$$
$$= \cancel{-130.33} -130.33\ kJ$$

Temp. coeff^{ic} of emf $= \dfrac{E_{25} - E_0}{298 - 273}$

$$= \frac{0.6753 - 0.6915}{25}$$
$$= -6.48 \times 10^{-4}$$

$$\Delta S = nF\left(\frac{\partial E_{cell}}{\partial T}\right)_P$$
$$= -2 \times 96500 \times 6.48 \times 10^{-4}$$
$$= -125.064\ J$$

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

$\Rightarrow -130332.9 = \Delta H + 298 \times 125.064$

$\Rightarrow \Delta H = -130332.9 - 298 \times 125.064$
$$= -167601.972\ J$$
$$= -167.601\ kJ$$

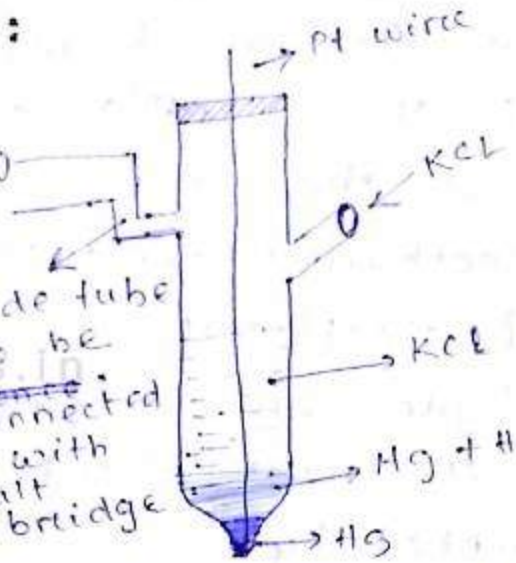
Determination of pH by emf measurement:

Some common reference electrodes:

1) Normal Hydrogen electrode

2) Calomel Electrode:

It consist of a glass tube containing Hg at the bottom over which a paste of $Hg + Hg_2Cl_2$ is placed. A Pt wire is inserted for electrical contact. The tube is filled with KCl sol^n.



- The potential of calomel electrode varies with conc. of KCl sol^n

Conc. of KCl	E° value
0.1N	0.3335 V
1N	0.2810 V
saturated	0.2422 V

- Representation is $Pt, Hg | Hg_2Cl_2 | KCl$ (saturated/1N/0.1N).

Determination of pH by emf measurement:

1) By using Hydrogen electrode:

The potential of hydrogen electrode involved in the reaction

$$H^+ + e \longrightarrow \frac{1}{2} H_2(g)$$

is given by

$$E_{H_2} = E^\circ_{H_2} - \frac{0.0591}{1} \log \frac{1}{[H^+]}$$

$\Rightarrow E_{H_2} = 0 - 0.0591 pH$

$\Rightarrow \boxed{E_{H_2} = -0.0591 pH}$

Thus, the potential of hydrogen electrode depends on the pH of sol^n so in order to determine the pH this half cell is combined with another reference electrode say calomel electrode.

- When hydrogen electrode is combined with calomel electrode then the net cell is represented by

$$\underbrace{Pt, H_2(1atm) | H^+ (c=?)}_{anode} \| \underbrace{KCl(satd) | Hg_2Cl_2, Hg, Pt}_{cathode}$$

Emf of cell = $E_{cell} = E_{cathode} - E_{anode}$

$= E_{calomel} - E_{H_2}$

$= 0.2422 - (-0.0591 pH)$

$\Rightarrow \boxed{pH = \frac{E_{cell} - 0.2422}{0.0591}}$

Dt. 8/11/12

Limitations:

1) It is very difficult to set up hydrogen electrode
2) It is easily affected / poisoned by compds Hg, As, Sb and oxidising agent like Fe^{3+} ion, MnO_4^- etc.
3) It can't be used in a sol^n containing many metal ions.

2) By using Glass electrode:

When two sol^{n}s of different pH values are separated by a glass membrane, then there exist a potential difference which varies.

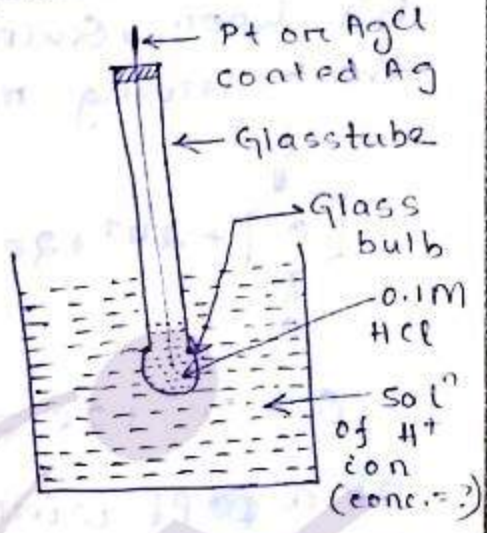
with conc. of H^+ ion or pH value. For a particular type of glass the potential established is given by,

$$E_G = E^\circ_G - 0.0591 \log \frac{1}{[H^+]}$$

$$\Rightarrow E_G = E^\circ_G - 0.0591 pH$$

In order to determine the pH of solution glass electrode is combined with a reference electrode say calomel electrode.

- It consist of a glass tube connected with a glass bulb containing Pt or AgCl coated Ag in 0.1M HCl sol^n. Glass bulb is dipped in a sol^n of $[H^+]$ ion whose concentration has to be determined.



Representation of electrode:

Ag, AgCl, 0.1M HCl, glass / sol^n of H^+ ion (c = ?)

- When glass electrode is combined with calomel electrode, the complete electrode can be written as

Ag, AgCl, 0.1M HCl, glass | sol^n of H^+ ion || KCl (satd) | Hg_2Cl_2, Hg, Pt.

Emf of cell is given by,

$$E_{cell} = E_{calomel} - E_G$$
$$= 0.2422 - E^\circ_G + 0.0591 pH$$

$$\Rightarrow pH = \frac{E_{cell} - 0.2422 + E^\circ_G}{0.0591}$$

Advantages:

1) It is very very easy to set up & the equilibrium is rapidly attained.
2) It is not easily affected or poisoned.

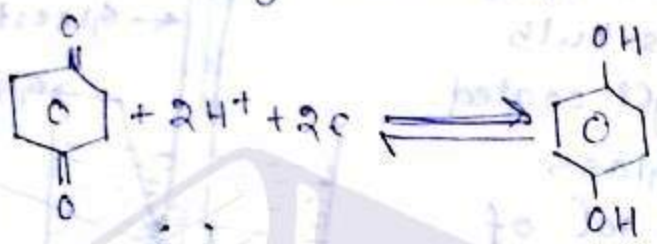
Limitations:

1) It can't be used in highly alkaline sol^n. (pH > 10). Because in alkaline sol^n the cations present affect the glass interface.

2) Although the glass ~~resistance~~ is very ~~high~~ thin but its resistance is very high which can't be measured by ordinary potentiometer.

3) Quinhydrone electrode:

We know, Quinone & Hydroquinone involve the following reaction,



$$Q + 2H^+ + 2e \rightleftharpoons QH_2$$

If a Pt wire is inserted containing Q & QH_2 then the potential established is given by

$$E_Q = E_Q^0 - \frac{0.0591}{2} \log \frac{[QH_2]}{[Q][H^+]^2}$$

$$\Rightarrow E_Q = E_Q^0 - \frac{0.0591}{2} \log \frac{[QH_2]}{[Q]} - \frac{0.0591}{2} \log \frac{1}{[H^+]^2}$$

If Q & QH_2 are taken in equimolar proportion, then

$$E_Q = E_Q^0 - \frac{0.0591}{2} \times 2 \log \frac{1}{[H^+]}$$

$$\Rightarrow E_Q = E_Q^0 - 0.0591\, pH$$

$$\Rightarrow \boxed{E_Q = 0.6994 - 0.0591\, pH}$$

In order to determine the pH, quinhydrone electrode is combined with reference electrode say calomel electrode. Complete cell can be written as

$$Pt, Hg, Hg_2Cl_2 | KCl(satd.) \| H^+ sol^n, QH_2, Q | Pt.$$

(c = ?)

Emf of cell can be written as

$$E_{cell} = E_Q - E_{calomel}$$

$$= 0.6994 - 0.0591pH - 0.2422$$

$$\Rightarrow E_{cell} = 0.4572 - 0.0591pH$$

$$\Rightarrow \boxed{pH = \frac{0.4572 - E_{cell}}{0.0591}}$$

Limitations:

1) This electrode can't be used in alkaline solution because in alkaline sol^n. Hydroquinone ionises appriciably & also get oxidised.

Dt. 12/11/12

BATTERY:

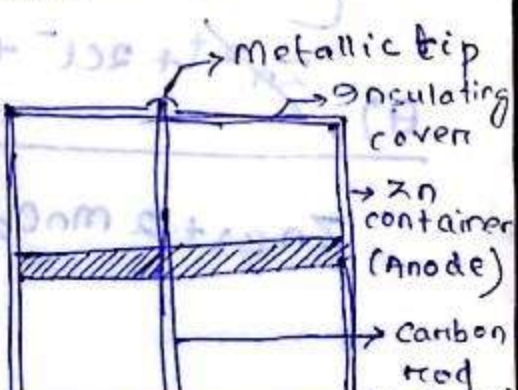
It is a device which stores chemical energy for the later release of electricity or it is an electrochemical cell or several electrochemical cells connected in series which can be used as source of direct electric current at const. voltage.

Classification:

1) **Primary cell / Battery**: The battery in which cell reaction can't be reversed by passing electrical current from external source, i.e. when most of the reactants converted into products the cell becomes dead.

e.g.- Dry cell or Laclanche cell.

Dry cell or Laclanche cell:



It consist of a Zn container which acts as anode & carbon rod which acts as cathode. The electrolyte is a mixture of MnO_2

NH_4Cl & ZnO_2 to which a little amount of starch is added to make a paste & avoid the leakage of electrolyte.

At anode – $Zn(s) \longrightarrow Zn^{2+}_{(aq)} + 2e$

At cathode – It involves following steps.

Step-1:- MnO_2 is reduced to Mn_2O_3 in alkaline medium.

$$2MnO_2 + H_2O + 2e \longrightarrow Mn_2O_3 + 2OH^-$$

Step-2:- OH^- ions produced combines with NH_4^+ (from NH_4Cl) to form ammonia.

$$NH_4^+ + OH^- \longrightarrow NH_3 + H_2O$$

Step-3:- Formation of ammonia may disrupt flow of electric current. So in order to balance the effect of ammonia $ZnCl_2$ is added which forms complex with ammonia.

$$Zn^{2+} + 2Cl^- + 2NH_3 \longrightarrow [Zn(NH_3)_2]Cl_2$$

Diaminezinc(II) chloride.

Net cell reaction –

$$Zn(s) \longrightarrow \cancel{Zn^{2+}_{(aq)}} + \cancel{2e}$$

$$2MnO_2 + H_2O + \cancel{2e} \longrightarrow Mn_2O_3 + \cancel{2OH^-}$$

$$[NH_4^+ + \cancel{OH^-} \longrightarrow \cancel{NH_3} + H_2O] \times 2$$

$$\cancel{Zn^{2+}} + 2Cl^- + \cancel{2NH_3} \longrightarrow [Zn(NH_3)_2]Cl_2$$

(H).

$$Zn(s) + 2MnO_2 + 2NH_4^+ + 2Cl^- \longrightarrow Mn_2O_3 + 2H_2O + [Zn(NH_3)_2]Cl_2 + E$$

(Electrical energy)

The emf of cell = 1.5V.

Drawbacks:

1) Since the electrolytic medium is acidic so Zn dissolves in acidic medium to produce Zn^{2+}. As a result the cell deteriates or run down slowly even it is not used before.

2) When current is drawn rapidly some products are deposited at the electrode, which cause a drop in voltage.

Application: Flash light.

Alkaline Battery: It is an improved form of dry cell in which NH_4Cl is replaced by KOH.

Cell reaction:

At anode: $Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^-$

$Zn^{2+} + 2OH^- \longrightarrow Zn(OH)_2$

At cathode: $2MnO_2 + H_2O + 2e^- \longrightarrow Mn_2O_3 + 2OH^-$

Net cell reaction: $Zn(s) + 2MnO_2 + H_2O \longrightarrow Zn(OH)_2 + Mn_2O_3$.

2) Secondary cell/Battery: The battery in which the cell reaction can be reversed by acting or passing electric energy from external source i.e. the secondary battery can be used in large number of cycle of charging or discharging process.

e.g. - Lead acid storage cell.

Lead acid storage cell:

- A storage cell is the cell which can act as both electrolytic & voltaic cell.
- When act as voltaic cell, it produces electric current & being discharged & when recharged operates as electrolytic cell.

Construction: It consist of Pb & PbO_2 electrodes on a paste of PbO_2 pressed over a grid of lead. In a lead-acidic storage cell, a number of Pb & PbO_2 electrodes are connected & these are separated from each other by an separator. The entire combination is dipped in 20-21% of H_2SO_4.

- One combination of Pb & PbO_2 in 21% of H_2SO_4 can produce 2V.

Dt. 20/11/12

Cell reaction:

1) Discharging (operates as a voltaic cell):

At anode: $Pb \longrightarrow Pb^{2+} + 2e$

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

At cathode: $PbO_2 + 4H^+ + 2e \longrightarrow Pb^{2+} + 2H_2O$

$Pb^{2+} + SO_4^{2-} \longrightarrow PbSO_4$

$$Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O + EE \text{ (Electrical energy)}$$

2) Charging (operates as electrolytic cell):

At anode: $PbSO_4 \longrightarrow Pb^{2+} + SO_4^{2-}$

$Pb^{2+} + 2H_2O \longrightarrow PbO_2 + 4H^+ + 2e$

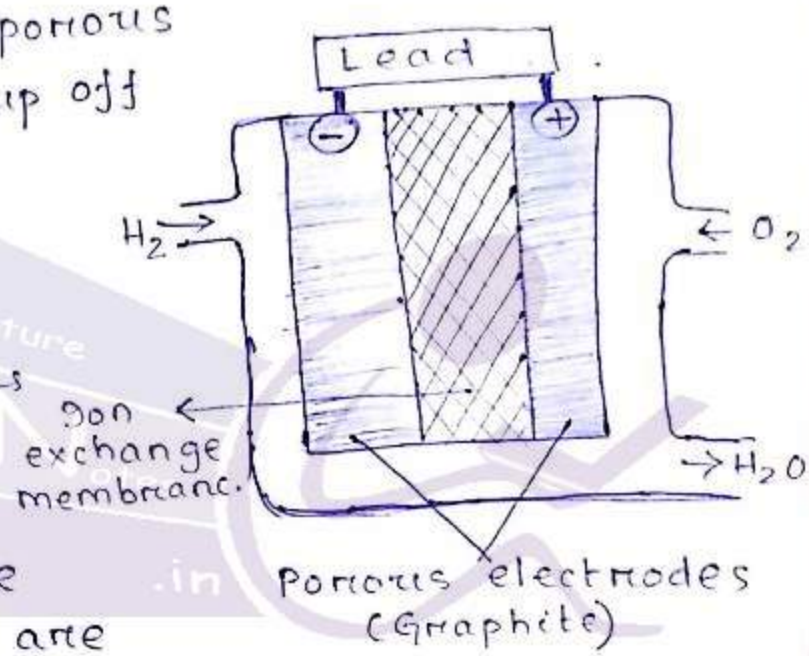
At cathode: $PbSO_4 \longrightarrow Pb^{2+} + SO_4^{2-}$

$Pb^{2+} + 2e \longrightarrow Pb$

$$2PbSO_4 + 2H_2O + EE \longrightarrow Pb + PbO_2 + 4H^+ + 2SO_4^{2-}$$

FUEL CELL:

- The device in which chemical energy is directly converted to electrical energy or the device in which electrical energy is produced without the combustion of a gas that can be oxidise.
- In a fuel cell, the reactants, products & the electrolytes are continuously passed through the battery.
  e.g.- Hydrogen- Oxygen battery.
- It consist of two porous electrodes made up off Graphait, coated with a catalyst like Ag, Pt or Au.



- These two electrodes are separated by an ion exchange membrane & these electrodes are dipped in aq. sol. of NaOH or KOH.
- The electrodes used in this fuel cell ~~and~~ should have the following characteristics.
  i) Good conductor
  ii) Good electron source/sink
  iii) Good catalyst
  iv) Should not be consumed /det~~erior~~riated by the action of heat, light, electrolyte or cell reaction.

Cell reaction:

At anode: $H_2 \longrightarrow \cancel{2H^+} + \cancel{2e}$] × 2

$\cancel{2H^+} + \cancel{2OH^-} \longrightarrow 2H_2O$

At cathode: $O_2 + 2H_2O + \cancel{4e} \longrightarrow \cancel{4OH^-}$

$2H_2 + O_2 \longrightarrow 2H_2O + EE$

- It is used as an auxilary energy source in space vehicles & sumerines, because H_2O produced during cell reaction can be used for drinking.

LectureNotes.in

Dt. 2[illegible].8.12

- The properties depend on mass - Extensive property
- The thermodynamic properties which depend on mass ~~of~~/quantity ~~are~~ of the substance are called extensive property.
  e.g. - mass, energy, enthalpy, ~~internal energy~~, free energy, entropy.
- The thermodynamic properties that don't depend on quantity of the substance - Intensive property.
  e.g. - Density, refractive index, internal energy, surface tension, MP, BP.
- A thermodynamic property said to be state fun^n which depend on final & initial state & not on path.
  e.g. - Enthalpy, Entropy, Gibbs free energy.
- Process which is infinitesimally slowly so that at every stage system & environment are in same stage is called reversible process.
- Workdone by the system is +ve for system & +ve for surrounding. Workdone on the system is +ve for system & -ve for surrounding.
- $W = PdV$

Workdone during isothermal expansion of an ideal gas,

$$W = -\int_{V_1}^{V_2} PdV = -\int_{V_1}^{V_2} \frac{nRT}{V} dV$$

$$= -nRT \ln \frac{V_2}{V_1}$$

$$= -2.303\, nRT \log \frac{V_2}{V_1}$$

$$= -2.303\, nRT \log P_1/P_2$$

- For irreversible process

$$W = -P_{ext.}(V_2 - V_1)$$

- Internal energy (U/E): Total energy stored in system. It is a state fun^n & an intensive property

Dt. 27.8.12

Internal energy:

$$\Delta E = E_f - E_i$$

$$\Delta E = \Sigma E_{products} - \Sigma E_{reactants}$$

- Generally ΔE is calculated by heat gain or lose at const. volume.

$$\Delta E = q_V$$

- Again. ΔH or change in enthalpy in terms of heat evolved or heat absorbed at const. press.

$$\Delta H = q_P$$

Ist Law of thermodynamics:

Mathematically, $\boxed{\Delta E = q + (\pm W)}$

Ethalpy (H): Total heat content of system at const. press.

- According to Ist law of thermodynamics,

$$\Delta E = q + W \quad \text{--- (1)}$$

If w is done by system, then $W = -P\Delta V$

$$\therefore \Delta E = q - P\Delta V \Rightarrow q = \Delta E + P\Delta V \quad \text{--- (2)}$$

- If the process is carried out at const. volume, then $\Delta V = 0$.

So $\boxed{q_V = \Delta E}$

Thus, the change in internal energy is an quantity of heat evolved or absorbed at const. volume.

- If the process is carried out at const. press. then

$$q_p = \Delta E + P\Delta V$$

By absorbing q_p amount of heat let the Internal Energy changes from E_1 to E_2 & volume changes from V_1 to V_2.

$$q_p = (E_2 - E_1) + P(V_2 - V_1)$$

$$\Rightarrow q_p = (E_2 + PV_2) - (E_1 + PV_1) \quad \text{--- (3)}$$

Since E, P & V are state functions, so the term E+PV is also a state function which is known as enthalpy of the system. So, enthalpy of a system is thermodynamic state fun^n; defined as the sum of internal energy & product of press. & volume.

i.e. $\boxed{H = E + PV}$

$$\Delta H = H_f - H_i$$

$$\Delta H = \Sigma H_{products} - \Sigma H_{reactants}$$

- Enthalpy is an extensive property, state fun^n & its absolute value can't be determined

For initial state $H_1 = E_1 + PV_1$

For final state $H_2 = E_2 + PV_2$

From eq^n (3) $q_p = H_2 - H_1$

$$\Rightarrow \boxed{q_p = \Delta H}$$

Thus, change in enthalpy is the amount of heat evolved or absorved at const. press.

Heat capacity (C):

- It is the amount of heat required to increase the temp. from lower to higher temp. divided by temp. difference.

Mathematically, $\boxed{C = \frac{q}{T_2 - T_1}}$

If process is carried out at const. volume, then $q_v = q_v = \Delta E$

$\therefore \boxed{C_v = \frac{\Delta E}{\Delta T}}$ [For finite change].

$\boxed{C_v = \left[\frac{\partial E}{\partial T}\right]_{V=const.}}$ [For infinitsimally small change.]

- Similarly if the process is carried out at const. press., then $q = q_p = \Delta H$

$\therefore \boxed{C_p = \frac{\Delta H}{\Delta T}}$ [For finite change]

$\boxed{C_p = \left[\frac{\partial H}{\partial T}\right]_{P=const.}}$ [For infinitsimally small change]

$\boxed{\frac{C_p}{C_v} = \gamma}$ & $\boxed{C_p - C_v = R}$

Q) Calculate the workdone when 2 mole of an ideal gas expand isothermally & reversibly from 10L to 20L at 298K.

$W = -2.303\, nRT \log \frac{V_2}{V_1}$

$= -2.303 \times 2 \times 8.314 \times 298 \times \log 2$

$= -2.303 \times 2 \times 8.314 \times 298 \times 0.3010$

$= -3434.92\ J.$

- Neutralisation may be defined as the combinaⁿ of $H^+(aq)$ & $OH^-(aq)$ ions to produce water.
- Ions of strong electrolyte have no tendency to combine.
- Ions of weak electrolyte have a tendency to combine.
- A substance which gives oxygen ~~and~~ or removes hydrogen is called oxidising agent.
- A substance which gives hydrogen or removes oxygen is called reducing agent.
- A/c to electronic concept, a chemical reaction in which there occurs transference of electrons from one substance (atom, ion or molecules) to another substance is called an oxidation-reduction reaction or a redox reaction.
- Oxidation is the process which involves loss of e^- by an atom, ion or molecule whereas reduction is a process involving gain of electrons by an atom, ion or molecule.
- Equivalent mass - The eq. mass of a substance is that much wt. of it which is chemically equivalent of 1 gm atom of hydrogen, ½ gm atom of oxygen or 1gm atom of chlorine.
- Relationship betⁿ molecular mass & eq. mass

$$\boxed{\text{Molecular mass} = \text{Eq. mass} \times n}$$

where n = number of electrons gained or lost per formula mass of oxidant or reductant.

~~Name of oxidant~~ ~~$KMnO_4$~~ ~~Molecular wt~~ ~~Eq wt~~

(OR) number of gm atoms of H or ½ gm atoms of oxygen or 1gm atoms of Cl.

Name of oxidants	n	molecular wt.	Equivalent wt.
$KMnO_4$	5	$39+55+4\times16$ $= 94+64$ $= 158$	$\frac{158}{5} = 31.6$
$K_2Cr_2O_7$	6	$2\times39+2\times54+7\times16$ $= 78+108+112$ $= 298$	$\frac{298}{6} = 49.$

Name of reductants	n	molecular wt.	Equivalent wt.
Oxalic $\bar{a}$ $(H_2C_2O_4 \cdot 2H_2O)$	2	$2\times1+24+64+36$ $= 126$	$\frac{126}{2} = 63$
Sod. oxalate $(Na_2C_2O_4)$	2	$23\times2+24+64$ $= 88+46$ $= 134$	$\frac{134}{2} = 67$
Sod. thiosulphate $(Na_2S_2O_3 \cdot 5H_2O)$	1	$2\times23+2\times32+48+5\times18$ $= 46+64+48+90$ $= 248$	$\frac{248}{1} = 248$

- Equivalent mass $= \frac{\text{Strength in gm/lt}}{\text{Normality}}$
- Oxidation state of an element in a compd is its oxidation number per atom of the element.
- Formality - It is defined as the number of gram formula wt. of the substance present in 1 lt of solution.

Formality $= \frac{\text{No. of gm formula mass}}{\text{Volume of sol}^n \text{ in lt}}$

- Molality - It is the number of gram moles of the substance dissolved in thousand gms of the solvent. Molality is not affected by change in temp.

$$\text{Molality} = \frac{\text{Mass of substance (gm)}}{\text{Molecular mass (gm)}} \times \frac{1000}{\text{mass of the solvent (gm)}}$$

- Molarity - No. of moles of the solute dissolved in one lt sol^n.

$$\text{Molarity} = \frac{\text{Mass of substance}}{\text{Molecular mass}} \times \frac{1000}{V(ml)}$$

- Normality - ~~The no. of eq.~~ It is defined as no. of eq. or gm eq. of solute present in 1 lt solution.

$$\text{Normality} = \frac{\text{No. of gm eq.}}{\text{Volume of sol}^n \text{ in ml}} \times 1000$$

$$= \frac{\text{Mass of substance}}{\text{Eq. mass}} \times \frac{1000}{V}.$$

- pH - pH of a solution is defined as the (-ve) logarithm of hydrogen ion conc. in moles/lt.
- A calorie is a quantity of heat required to raise the temp. of one gm of water through 1°C.
- Enthalpy: It is defined as the total energy content of the system at const. press. It is also defined as the sum of the internal energy and product of press. & volume.

$$\Delta H = \Delta U + \Delta nRT$$

- 1 lt atm = 101.13 J , $R = 8.314\ JK^{-1}mol^{-1}$
- Thermochemical reaction: The reactions which take place with the evolution or absorption of heat energy are called thermo-chemical reactions.
- Enthalpy of reaction: The total amount of heat energy evolved or absorbed when the number of moles of reactants react completely to give the products as given in the balanced eq. is known as heat of reaction.

Mathematically, $\Delta H_{reaction} = \Delta H_{product} - \Delta H_{reactant}$.

- Enthalpy of formation: The enthalpy change when

- Standard enthalpy of formation: The enthalpy change when one mole of a substance is formed from its constituent elements in their standard state at 1 atm press. & 298K. temp.
- The enthalpy change when 1 mole of a substance undergoes complete combustion is called as Enthalpy of combustion.
- Enthalpy of Neutralisation: The change in enthalpy when one gram equivalent of an acid is neutralised by a base or vice-versa in dil. solution.
- $\Delta H^\circ_{sublimation} = \Delta H^\circ_{fusion} + \Delta H^\circ_{vapourisation}$.
- The av. amount of energy per mole required to break one type of bonds in a molecule to free atoms or radicals are called bond energy. (OR) It is the amount of energy released when one mole of a particular bond is formed from and respective atoms or radicals.
- Entropy: The property of a substance which measures the disorder or randomness in a system (or) entropy is the net disorderness present in a system.
- Gibb's free energy: Free energy is defined as the amount of energy avialable from a system at a particular set of conditions that can be put into useful work.

ΔG is -ve → Process is spontaneous

ΔG is 0 → Process is in equilibrium

ΔG is +ve → Process is non-spontaneous but reverse process may be spontaneous.

Dt. 28.8.12

Q) 5 moles of an ideal gas expands isothermally & reversible from 10 atm to 2 atm at 300K. What is the largest mass which can be lifted to a height of 1m due to this expansion?

$W = -2.303 \times 5 \times 8.314 \times 300 \times \log 5$

$= -20,074.9 J$

$\Rightarrow mgh = |-20,074.9|$

$\Rightarrow m \times 9.8 \times 1 = 20,074.9$

$\Rightarrow m = 2048.46 kg.$

Work done in adiabatic expansion:

A/c to 1st law of thermodynamics

$\Delta E = q + W$

For adiabatic process, $q = 0$

$\Delta E = W$

Again $C_v = \frac{\Delta E}{\Delta T} \Rightarrow \Delta E = C_v \Delta T$

$\therefore \boxed{\Delta E = W = C_v \Delta T}$

For n moles, $\boxed{\Delta E = W = n C_v \Delta T}$

Final temp. & final press. in reversible & irreversible adiabatic expansion:

Reversible expansion:

A/c to 1st law of thermodynamics,

$\Delta E = q + W$ —— (1)

For adiabatic process $q = 0$

So $\Delta E = W$

Let 'p' is the external press. against which the expansion is taking place and 'ΔV' is the change in volume.

Then workdone by system,

$W = \Delta E = -P\Delta V$ —— (2)

Again, $\Delta E = C_v \Delta T$ — (3)

From (2) & (3),

$C_v \Delta T = -P\Delta V$

For infinitesimal small change,

$C_v\, dT = -P\, dV$

$= \frac{-RT}{V} dV$

$\Rightarrow C_v \frac{dT}{T} = -R \frac{dV}{V}$

Integrating the above eqn betn temp. T_1 & T_2 & corresponding volume V_1 & V_2, we get

$$C_v \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1}$$

$\Rightarrow \ln \frac{T_2}{T_1} = -\frac{R}{C_v} \ln \frac{V_2}{V_1}$

$\Rightarrow \ln \frac{T_2}{T_1} = \frac{C_p - C_v}{C_v} \ln \left(\frac{V_2}{V_1}\right)^{-1}$

$\Rightarrow \ln \frac{T_2}{T_1} = (\gamma - 1) \ln \left(\frac{V_1}{V_2}\right)$

$\Rightarrow \frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma - 1}$

$\Rightarrow T_1 V_1^{\gamma-1} = T_2 V_2^{\gamma-1}$

$\Rightarrow \boxed{TV^{\gamma-1} = \text{const.}}$

For ideal gas,

$P_1 V_1 = RT_1$, $P_2 V_2 = R \cdot T_2$

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

$\Rightarrow \frac{P_2 V_2}{P_1 V_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$

$\Rightarrow P_2 V_2^{\gamma} = P_1 V_1^{\gamma}$

$\Rightarrow \boxed{PV^{\gamma} = \text{const.}}$

Irreversible expansion:

Case-1 (Free expansion):

- In free expansion the ext. press. is equal to zero, so the work done $W = P_{ext.} \Delta V = 0$

  & $\Delta E = W = 0$.

- Since internal energy is a fun. of temp., so $\Delta T = 0$. So $\Delta H = C_p \Delta T = 0$.

Case-2 (Intermediate expansion):

- Let $P_{ext.}$ is the external press. against which the expansion is taking place from initial volume V_1 to V_2, so the work done by system

$$W = -P_{ext.}(V_2 - V_1)$$

For adiabatic process $\Delta E = W = C_v (T_2 - T_1)$

$$\therefore C_v (T_2 - T_1) = -P_{ext.}(V_2 - V_1)$$

$$\Rightarrow C_v (T_2 - T_1) = P_{ext.}(V_1 - V_2)$$

$$\Rightarrow C_v (T_2 - T_1) = P_{ext.}\left(\frac{RT_1}{P_1} - \frac{RT_2}{P_2}\right) = P_{ext.} \cdot R\left(\frac{T_1P_2 - P_1T_2}{P_1P_2}\right)$$

$$\Rightarrow C_v (T_2 - T_1) = R \cdot P_{ext.}\left(\frac{T_1P_2 - T_2P_1}{P_1P_2}\right).$$

Q) A certain volume of dry air at NTP is expanded reversibly to 3 times of its volume (i) isothermally, ii) adiabatically. Calculate final temp. & press. in each case assuming the ideal behaviour. For dry air $\gamma = 1.4$ at NTP.

i) For isothermal process,

$$P_1V_1 = P_2V_2$$

$$\Rightarrow 1 \times V = P_2 \times 3V$$

$$\Rightarrow P_2 = \frac{1}{3}\text{ atm} = 0.333\text{ atm}$$

$T_2 = T_1$ (as it is an isothermal process)

$= 273K$

For adiabatic process,

$PV^{\gamma} = \text{const.}$

$\Rightarrow P_1V_1^{\gamma} = P_2V_2^{\gamma}$

$\Rightarrow \frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma} = (3)^{1.4}$

$\Rightarrow \frac{1}{P_2} = \frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$

$\Rightarrow \frac{1}{P_2} = (3)^{1.4}$

$\Rightarrow P_2 = \frac{1}{3^{1.4}}$

$\frac{T_1}{T_2} = \left(\frac{V_2}{V_1}\right)^{\gamma-1}$

$\Rightarrow \frac{273}{T_2} = (3)^{2/5}$

$\Rightarrow T_2 = 176\ K.$

(OR) $\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2}$

$\Rightarrow \frac{1 \times V}{273} = \frac{P_2 \times 3V}{176}$

$\Rightarrow P_2 = \frac{176}{273 \times 3}$

$= 0.214\,atm$

6) One mole of an ideal monoatomic gas at 27°C, expands reversibly & adiabatically from volume of 10lt to 20lt. calculate q, ΔE & W. Assuming ideal behaviour & $C_v = \frac{3}{2}R$.

$C_v \ln \frac{T_2}{T_1} = R \ln \frac{V_1}{V_2}$

$\Rightarrow \frac{3}{2}R \ln \frac{T_2}{300} = R \ln \frac{10}{20}$

$\Rightarrow \ln \left(\frac{T_2}{T_1}\right)^{3/2} = \ln\left(\frac{1}{2}\right)$

$\Rightarrow \left(\frac{T_2}{300}\right)^{3/2} = \frac{1}{2}$

$\Rightarrow \frac{T_2}{300} = \left(\frac{1}{2}\right)^{2/3}$

$\Rightarrow T_2 = 300 \times \left(\frac{1}{2}\right)^{2/3} = 189\ K.$

As adiabatic process, $q = 0$

$\Delta E = W = C_v(T_2 - T_1)$

$= W = \frac{3}{2} \times R \times (189 - 300)$

$= -1384.2$

Q) 2 moles of ideal gas at NTP compressed adiabatically & reversiblely to occupy volume of $4.48\ dm^3$, calculate W, ΔE, T_{Final} & P_{Final} by assuming $C_v = 12.45\ J\ K^{-1}\ mol^{-1}$ & $\gamma = 1.667$.

$V_{initial} = 22.4 \times 2 = 44.8\ lt$

$V_{final} = 4.48\ dm^3 \cong 4.48\ lt$

We know $PV^{\gamma} = const.$

$$\Rightarrow \frac{P_1}{P_2} = \left(\frac{V_2}{V_1}\right)^{\gamma}$$

$$\Rightarrow \frac{1}{P_2} = \left(\frac{4.48}{44.8}\right)^{1.667} \Rightarrow P_2 = \left(\frac{448}{10} \times \frac{100}{448}\right)^{1.667}$$

$$\Rightarrow P_2 = 46.45\ atm$$

Combined gas eq.:

$$\frac{P_1V_1}{T_1} = \frac{P_2V_2}{T_2} \Rightarrow \frac{1 \times 44.8}{273} = \frac{46.45 \times 4.48}{T_2}$$

$$\Rightarrow T_2 = \frac{46.45 \times 4.48 \times 273}{44.8} = 1268K.$$

$$\Delta E = W = nC_v\Delta T$$

$$= 2 \times 12.45 \times (1268 - 273)$$

$$= 24775.5\ J.$$

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If the enthalpy of formaⁿ of ethlene is -800 kJ/mol

$$2C + 2H_2 \rightarrow C_2H_4 \quad \Delta H = -800 kJ/mol.$$

Enthalpy of formⁿ of acetic ā.

$$2C + 2H_2 + O_2 \longrightarrow CH_3COOH \quad \Delta H = -500 kJ/mol$$

Enthalpy of combustion of acetic ā.

$$CH_3COOH + 2O_2 \longrightarrow 2CO_2 + 2H_2O$$

- In case of calorific value we use 1gm of substance but in case of combustion we use 1 mole of substance.
- $\frac{\text{Enthalpy of combustion}}{\text{Molecular wt.}}$ = Calorific value.
- If a fuel has more calorific value then it is a very good quality of fuel.
- Enthalpy of neutralisation: The enthalpy change when 1gm eq. of acid react with 1gm. eq. of base in presence of dil. aq. solⁿ.
- Experimentally it is know that $\Delta H_n = 57.1$ kJ/gmeq.
- Neutralisation - It is the reacⁿ betⁿ acid & base to destroy their characteristics. Generally neutralisation requires gm eq. mass.
- In too much conc. solⁿ there will not full dissociation of reactants.

Q) 100 ml of 0.1 N H_2SO_4 is mixed with 200 ml of 0.1N NaOH. What will be the enthalpy of neutralisation?

No. of gm eq. of H_2SO_4 = $\frac{N \times V}{1000}$

$= \frac{0.1 \times 100}{1000} = 0.01$ gm eq.

No. of gm eq. of NaOH = $\frac{0.1 \times 200}{1000} = 0.02$ gm eq.

$\Delta H_n = -57.1 \times 0.01$ [∵ ΔH_n for 1gm eq. of strong acid & base = -57.1 kJ]

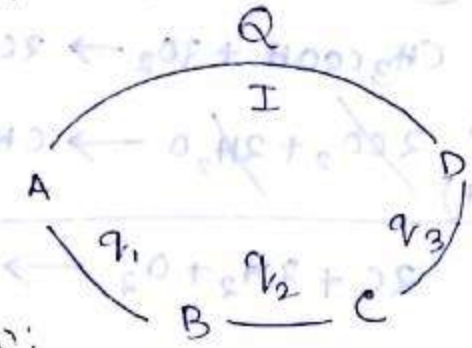
$= -571$ J

Hess's law: The enthalpy change of a reaction is same whether the reaction is carried out in one step or in several steps.

$Q' = q_1 + q_2 + q_3$

A/c to Hess's law

$Q = Q'$.



Theoritical proof of Hess's law:

Suppose $Q \neq Q'$, Let us consider $Q > Q'$.

So, if we move from A → D by path I & return from D-A by path II then Q-Q' amount heat is produced. i.e. by completing 1 cyclic process Q-Q' amount of heat can be produced which is a contradiction to 1st law of thermodynamics.

Thus $Q \not> Q'$. Similarly we can prove $Q \not< Q'$

So $Q = Q'$.

Application of Hess's law:

1) To calculate different types of enthalpies of reaction:

2) Calculate the enthalpy of formation of acetic acid from the following data:

Enthalpies of formation of CO_2 & H_2O are -94.48 & -68.4 kcal/mol & the enthalpy of combustion of acetic acid is 207.9 kcal/mol. $\Delta H = -117.86$ kcal/mol

Given eq. are:

$C + O_2 \longrightarrow CO_2$ $\quad \Delta H = -94.48$ kcal/mol

$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O$ $\quad \Delta H = -68.4$ kcal/mol

$CH_3COOH + 2O_2 \longrightarrow 2CO_2 + 2H_2O$ $\quad \Delta H = -207.9$ kcal/mol

Required eq.:

$2C + 2H_2 + O_2 \longrightarrow CH_3COOH$.

$[C + O_2 \longrightarrow CO_2] \times 2 \quad \Delta H = -94.48 \times 2$

$[H_2 + \frac{1}{2}O_2 \longrightarrow H_2O] \times 2 \quad \Delta H = -68.4 \times 2$

$CH_3COOH + 3O_2 \rightarrow 2CO_2 + 2H_2O \quad \Delta H = -207.9$ kcal/mole

$\Rightarrow 2CO_2 + 2H_2O \longrightarrow CH_3COOH + 2O_2 \quad \Delta H = 207.9$ kcal/mol

(+)

$2C + 2H_2 + O_2 \longrightarrow CH_3COOH \quad \Delta H = -117.86$ kcal/mol.

Q) Calculate the enthalpy of formation of ethyl alcohol from the following data:

i) $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l) \quad \Delta H = -1368.2$ kJ

ii) $C(s) + O_2(g) \longrightarrow CO_2(g) \quad \Delta H = -393$ kJ

iii) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) \quad \Delta H = -286.6$ kJ

Required eq^n.

$2C + 3H_2 + \frac{1}{2}O_2 \longrightarrow C_2H_5OH$

$[H_2 + \frac{1}{2}O_2 \longrightarrow H_2O] \times 3 \quad \Delta H = -286.6 \times 3$ kJ

$[C + O_2 \longrightarrow CO_2] \times 2 \quad \Delta H = -393 \times 2$ kJ

$2CO_2 + 3H_2O \longrightarrow C_2H_5OH + 3O_2 \quad \Delta H = 1368.2$ kJ

(+)

$3H_2 + 2C + (\frac{3}{2} + 1 - 3)O_2 \longrightarrow C_2H_5OH \quad \Delta H =$

$[H_2O \rightarrow H_2 + \frac{1}{2}O_2] \times 3 \quad \Delta H = +286.6 \times 3$ kJ

$[CO_2 \longrightarrow C + O_2] \times 2 \quad \Delta H = 393 \times 2$ kJ

$C_2H_5OH + 3O_2 \longrightarrow 2CO_2 + 3H_2O \quad \Delta H = -1368.2$ kJ

(+)

$C_2H_5OH \longrightarrow 3H_2 + 2C + (\frac{3}{2} + 2 - 3)O_2 \quad \Delta H = 277.6$ kJ

$\Rightarrow 3H_2 + 2C + \frac{1}{2}O_2 \longrightarrow C_2H_5OH \quad \Delta H = -277.6$ kJ

Q) Calculate the heat of formation of benzene given that the standard heat of combustion of benzene is -3266 kJ and standard heats of formation of CO_2 (g) and H_2O (l) are -393.1 kJ and -286 kJ respectively.

Required eqn.

$$6C + 3H_2 \longrightarrow C_6H_6.$$

Given eqns

$$C_6H_6 + \frac{15}{2}O_2 \longrightarrow 6CO_2 + 3H_2O \qquad \Delta H = -3266\,kJ \quad (1)$$

$$C + O_2 \longrightarrow CO_2 \qquad \Delta H = -393.1\,kJ \quad (2)$$

$$H_2 + \frac{1}{2}O_2 \longrightarrow H_2O \qquad \Delta H = -286\,kJ \quad (3)$$

Eqn. (2) × 6 + Eqn. (3) × 3 − Eqn. (1)

$$6C + \left(6 + \frac{3}{2} - \frac{15}{2}\right)O_2 + 3H_2 \longrightarrow C_6H_6 \qquad \Delta H = 49.4\,kJ.$$

Q) Calculate the enthalpy of formation of SO_3 at 298 K using the following reactions & enthalpies:

$$S_8(s) + 8O_2(g) \rightarrow 8SO_2(g) \qquad \Delta H^\circ = -2775\,kJ$$

$$2SO_2(g) + O_2(g) \rightarrow 2SO_3(g) \qquad \Delta H^\circ = -198\,kJ$$

Required eqn.

$$\frac{1}{8}S_8 + \frac{3}{2}O_2 \longrightarrow SO_3$$

$$\left[S_8 + 8O_2 \longrightarrow 8SO_2\right] \times \frac{1}{8} \qquad \Delta H^\circ = -2775 \times \frac{1}{8}\,kJ$$

$$\left[2SO_2 + O_2 \longrightarrow 2SO_3\right] \times \frac{1}{2} \qquad \Delta H^\circ = -198 \times \frac{1}{2}\,kJ$$

(+)

$$\frac{1}{8}S_8 + \frac{3}{2}O_2 \longrightarrow SO_3 \qquad \Delta H_f = -445.87\,kJ$$

Q) The heat of formation of methane, CO_2 and H_2O at 25°C are -18.1, -94.2 and -68.3 kcal respectively. Calculate the heat of reaction.

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l).$$

Given eq^ns:

$C + 2H_2 \rightarrow CH_4$ $\Delta H = -18.1$ kcal

$C + O_2 \rightarrow CO_2$ $\Delta H = -94.2$ kcal

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ $\Delta H = -68.3$ kcal

$CH_4 \rightarrow \cancel{C} + 2\cancel{H_2}$ $\Delta H = 18.1$ kcal

$\cancel{C} + O_2 \rightarrow CO_2$ $\Delta H = -94.2$ kcal

$[\cancel{H_2} + \frac{1}{2}O_2 \rightarrow H_2O] \times 2$ $\Delta H = -68.3 \times 2$ kcal

(+)

$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$ $\Delta H = -212.7$ kcal.

Dt. 4.9.12

Q) Calculate the enthalpy of formation of sucrose if the enthalpies of combustion of sucrose is 5200.7 kJ & enthalpies of formation of CO_2 & H_2O are -394.5 & -285.8 kJ/mol respectively.

Required eq^n:

$12C + 11H_2 + \frac{11}{2}O_2 \rightarrow C_{12}H_{22}O_{11}$

Given eq^n:

$C_{12}H_{22}O_{11} + 12O_2 \rightarrow 12CO_2 + 11H_2O$ (1) $\Delta H = -5200.7$ kJ

$C + O_2 \rightarrow CO_2$ (2) $\Delta H = -394.5$ kJ

$H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ (3) $\Delta H = -285.8$ kJ

Eq^n (2) × 12 + Eq^n (3) × 11 − Eq^n (1)

$12C + 12\cancel{O_2} \rightarrow 12\cancel{CO_2}$ $\Delta H = -394.5 \times 12$ kJ

$11H_2 + \frac{11}{2}O_2 \rightarrow 11\cancel{H_2O}$ $\Delta H = -285.8 \times 11$ kJ

(+) $11\cancel{H_2O} + 12\cancel{CO_2} \rightarrow 12\cancel{O_2} + C_{12}H_{22}O_{11}$ $\Delta H = 5200.7$ kJ

$12C + 11H_2 + \frac{11}{2}O_2 \rightarrow C_{12}H_{22}O_{11}$ $\Delta H = -2677.1$ kJ

3) 6 marks

Born-Haber cycle:

- It is a cyclic process by which the lattice energy of a crystaline solid ~~solute~~ can be calculated indirectly using other thermodynamic properties ~~values/quantities~~ (e.g. Enthalpy of formation, $\Delta H_c, H_f$ etc)

~~Amount of energy released~~ when one of & this process is based on Hess's law.

- The amount of energy released / required to form a compd/crystaline compd from its constitute anion & cation at their gaseous state is known as Lattice energy.

Let us calculate lattice energy of a crystal solid MX:

MX(s) can be prepaired by 2 ways.

1) Direct process -

M(s) combines with $\frac{1}{2}X_2(g)$ to form MX(s) and the amount of energy released is known as enthalpy of formation.

$$M(s) + \frac{1}{2}X_2(g) \longrightarrow MX(s) + \Delta H_f$$

2) Indirect process -

Step-1

Conversion of M(s) to M(g) & the amount of energy required equal to enthalpy of sublimation.

$$M(s) \xrightarrow{\Delta H_{sublimation}} M(g)$$

Step-2

Dissociation of $\frac{1}{2}$ moles of $X_2(g)$ to X(g) and the amount of energy required is equal to $\frac{1}{2}$ of enthalpy of dissociation.

$$\frac{1}{2}X_2(g) \xrightarrow{\Delta H_{dissociation}} X(g)$$

Step-3

Ionisation of ~~metal gas to~~ M(g) to $M^+(g)$ & the

amount of energy required is called as ionisation energy.

$$M(g) + IE \longrightarrow M^+(g) + e^-$$

Step-4

Ionisation of $X(g)$ to $X^-(g)$ and the amount of energy released is known as electron affinity or electron gain enthalpy.

$$X(g) + e^- \longrightarrow X^-(g) + E.A.$$

Step-5

Combination of $M^+(g)$ with $X^-(g)$ to form $MX(s)$ and the amount of energy released equal to Lattice energy.

$$M^+(g) + X^-(g) \longrightarrow MX(s) + L.E.$$

The entire process can be represented as

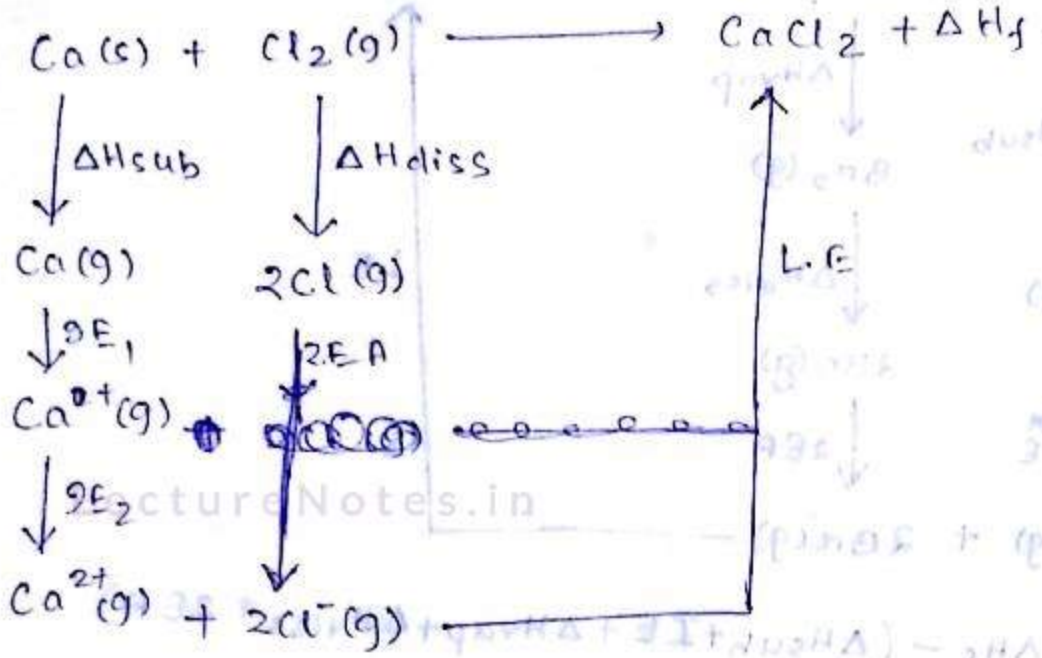
$$\begin{array}{ccccc}
M(s) & + & \frac{1}{2}X_2 & \longrightarrow & MX(s) + \Delta H_f \\
\downarrow \Delta H_{sub} & & \downarrow \frac{1}{2}\Delta H_{dissociation} & & \uparrow L.E. \\
M(g) & & X(g) & & \\
\downarrow IE & & \downarrow E.A. & & \\
M^+(g) & + & X^-(g) & & \longrightarrow MX(s)
\end{array}$$

Applying Hess's law, the total energy change in the direct process should be equal to sum of the enthalpies of indirect process.

$$\Delta H_f = \Delta H_{sub} + \frac{1}{2}\Delta H_{dissociation} + IE + EA + L.E$$

$$\Rightarrow \boxed{LE = \Delta H_f - \left(\Delta H_{sub} + \frac{1}{2}\Delta H_{dissociation} + IE + EA\right)}$$

Q) What will be the chart for formⁿ of $CaCl_2$.



Q) Calculate LE of $CaCl_2$ if enthalpy of sublimⁿ of Ca is 121 kJ/mol, dissociation enthalpy of Cl is 242.8 kJ/mol, ionisation energy of Ca to Ca^{2+} is 2422 kJ/mol, E.A. of Cl_2 355 kJ/mol, Enthalpy of formⁿ of $CaCl_2$ −795 kJ/mol.

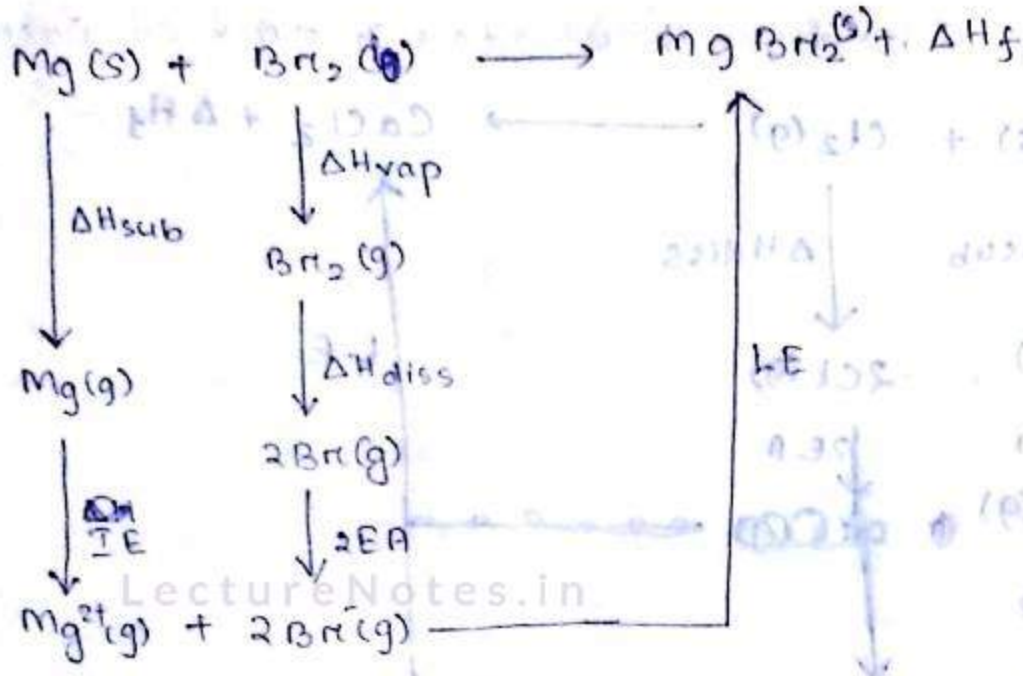
~~LE = (−795 − (121 + 2422 + 242.8 + 2 × 355))~~

$LE = \Delta H_f - (\Delta H_{sub} + \Delta H_{diss} + IE_1 + IE_2 + 2EA)$

$= -795 - (121 + 2422 + 242.8 - 2 \times 355)$

$= -2870.8$ kJ/mol

Q) If ΔH_f of $MgBr_2$ is −524 kJ/mol, ΔH_{sub} of Mg = 2187 kJ/mol, $\Delta H_{vap.}$ of Br = 31 kJ/mol, ΔH_{diss} of Br = 193 kJ/mol, & EA of Br = −331 kJ/mol, IE of Mg to Mg^{2+} = 148 kJ/mol. LE = −2421 kJ/mol.



$LE = \Delta H_f - (\Delta H_{sub} + IE + \Delta H_{vap} + \Delta H_{diss} + 2EA)$

$= -524 - (2187 + 148 + 31 + 193 - 662)$

$= -2421$ kJ/mol

Dt 11.9.12

3) Bond Energy:

- The amount of energy required to break ~~down~~ 1 mole of a bond of a specific type betn 2 atoms in gaseous state is called bond energy.
- In case of diatomic molecules containing 1 type of bond, the bond energy is equal to the bond dissociaⁿ energy of the molecule. Whereas in polyatomic molecules containing more than 1 type of bonds, the bond energy is calculated as the avg. of all the bonds of a particular type present in the molecule.
- By knowing the bond energies of different types of bonds present in the reactants & products of a chemical reaction, the enthalpy of the reaction can be calculated as $\Delta H = \Sigma BE$ of reactants $- \Sigma BE$ of products.

Q) Calculate enthalpy of formation of NH_3 from following BE data.

N-H = 389 kJ , H-H = 435 kJ , N≡N = 945.36 kJ

$$N_2 + 3H_2 \longrightarrow 2NH_3$$

$$\frac{1}{2}N_2 + \frac{3}{2}H_2 \longrightarrow NH_3 \qquad \Delta H_f = ?$$

$$\frac{1}{2}N\equiv N + \frac{3}{2}\,H-H \longrightarrow H-\underset{H}{\overset{H}{N}}$$

$$\frac{1}{2}(945.36) + \frac{3}{2}(435) - 3\times 389 = \Delta H_f$$

$$\Rightarrow \Delta H_f = -41.82\ kJ$$

Q) Calculate the enthalpy of combustion of ethelene, from following BE data,

C=C = 619 kJ , C-H = 414 kJ , O=O = 499 kJ,

C-O = 724 kJ , O-H = 460 kJ .

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

$$\begin{matrix} H \\ H \end{matrix}\!\!>C=C<\!\!\begin{matrix} H \\ H \end{matrix} + 3(O=O) \rightarrow 2\left(\underset{O}{\overset{|}{C}}-O\right) + 2(H-O-H)$$

$$\Delta H_f = 4(C-H) + (C=C) + 3(O=O) - 4(C-O) - 4(H-O)$$

$$= 4\times 414 + 619 + 3\times 499 - 4\times 724 - 4\times 460$$

$$= -964\ kJ$$

Variation of enthalpy with temp. (Kirchoff's equation):

Let us consider a general reaction,

$$aA + bB \longrightarrow mM + nN.$$

$$\Delta H = (m H_M + n H_N) - (a H_A + b H_B)$$

Diff. w.r.to temp. at const. press.

$$\left.\frac{\partial(\Delta H)}{\partial T}\right]_{P=const.} = \left[m\left(\frac{\partial H_M}{\partial T}\right)_P + n\left(\frac{\partial H_N}{\partial T}\right)_P\right] - \left[a\left(\frac{\partial H_A}{\partial T}\right)_P + b\left(\frac{\partial H_B}{\partial T}\right)_P\right]$$

$$= (mC_{p_M} + nC_{p_N}) - (aC_{p_A} + bC_{p_B})$$

$$\Rightarrow \left[\frac{\partial(\Delta H)}{\partial T}\right]_p = \Delta C_p \quad \text{——— (1)}$$

Similarly $\left[\frac{\partial(\Delta E)}{\partial T}\right]_V = \Delta C_V$ — (2)

Eq. (1) is known as differential form of Kirchoff's eq.

Now $d(\Delta H) = \Delta C_p dT$ — (3)

→ If the temp. range is small & it assumes that heat capacity is independent of temp then integral of eq. (3) bet temp. T_1 & T_2 & corresponding enthalpies ΔH_1 & ΔH_2, we get-

$$\int_{\Delta H_1}^{\Delta H_2} d(\Delta H) = \Delta C_p \int_{T_1}^{T_2} dT$$

$$\Rightarrow \boxed{\Delta H = \Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)} \quad \text{——— (4)}$$

- If the temp. range is not small then the assumption that heat capacities are independent of temp. is not valid, so we have to express C_p as a fun^n of temp. & it is convenient to express C_p as a power series in T.

i.e. $C_p = \alpha + \beta T + \gamma T^2 + \ldots$

where $\alpha, \beta, \gamma \ldots$ are constants for a given species.

$$\Delta C_p = \Delta\alpha + \Delta\beta T + \Delta\gamma T^2 + \ldots$$

Putting this value in eq^n (3) & integrating we get

$$\boxed{\Delta H = \Delta H_2 - \Delta H_1 = \Delta\alpha(T_2 - T_1) + \Delta\beta\left(\frac{T_2^2 - T_1^2}{2}\right) + \Delta\gamma\left(\frac{T_2^3 - T_1^3}{3}\right) + \ldots}$$

Eqn. (4) & (5) are known as integrated form of Kirchoff's eqn.

Q) The enthalpy of the reaction for formn of NH_3 according to the reacn

$N_2 + 3H_2 \longrightarrow 2NH_3$ is -91.94 kJ at 27°C.

What will be the enthalpy of the reaction at 50°C by assuming heat capacities are independent of temp.

Given Cp of N_2, H_2 & NH_3 are 28.45, 28.32, 37.07 J respectively.

$\Delta C_p = 2 \times 37.07 - 28.45 - 28.32 \times 3$

$= -39.27$ J

$\Delta H_2 - \Delta H_1 = \Delta C_p (T_2 - T_1)$

$\Rightarrow \Delta H_2 + 91.94 \times 10^3 = (-39.27)(50 - 27)$

$\Rightarrow \Delta H_2 = (-39.27)(50-27) - 91.94 \times 10^3$

$= -92.84$ kJ

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Date:- 13.9.12

Entropy:-

- It is a thermodynamic state function defined as the degree of disorderness or randomness of a system.
- It is an extensive property.
- The absolute value of entropy cannot be determined however, the change of entropy (ΔS) $\Delta S = S_2 - S_1$

for a chemical reaction:

$$\Delta S = \Sigma S_{products} - \Sigma S_{reactants}$$

Mathematical defination of entropy:-

Entropy change of a system is defined as the integral of all the terms involving heat change devided by the absolute temperature during each infinitsimal small change of process carried out reversibly at a temp. T.

i.e.

$$ds = \frac{1}{T}\int dq_{rev.}$$

$$\Rightarrow \boxed{\Delta S = \frac{q_{rev.}}{T}}$$

If heat is absorved then ΔS is +ve and if heat is lost ΔS is -ve.

Entropy change in reversible & irreversible process

Case-1 (Reversible process):

Let q amount of heat is absorbed by the system at a temp. T.

$$\Delta S_{system} = +\frac{q}{T}$$

$$\Delta S_{surrounding} = -\frac{q}{T}$$

$$\boxed{\Delta s \text{ total} = 0}$$

for reversible process total entropy is zero.

Case-2 (Irreversible process):

Let the system is at higher temp. T_1 and surrounding is at lower temp. T_2.

$$\Delta S \text{ system} = -\frac{q}{T_1}$$

$$\Delta S \text{ surrounding} = +\frac{q}{T_2}$$

$$\boxed{\Delta s \text{ total} = -\frac{q}{T_1} + \frac{q}{T_2} = q\left(\frac{T_1 - T_2}{T_1 T_2}\right)}$$

Spontanity in terms of entropy change:

For isolated system, there is ~~no exchange~~ exchange of energy or matter between the system and the surrounding. Therefore the condition of spontanity is

$\Delta s > 0 \Rightarrow$ Spontaneous

$\Delta s < 0 \Rightarrow$ Non-spontaneous

$\Delta s = 0 \Rightarrow$ Equilibrium.

* At equilibrium entropy becomes maximum and constant.

* for non-isolated system, entropy of both system and surrounding are to be taken into account, therefore the condition of spontanity is

$$\Delta s \text{ total} = \Delta s \text{ system} + \Delta s \text{ surrounding} > 0$$

Entropy change for ideal gas:-

Case-1 (Temp. and volume are variable):

The entropy change for an infinitsimally small change is given by

$$ds = \frac{dq_{rev.}}{T}$$

$$dq_{rev.} = TdS \quad \text{--- (1)}$$

According to 1st law of thermodynamics,

$$\Delta E = q + W$$

$$\Delta E = q_{rev.} + W$$

for infinitsimal small change,

$$dE = dq_{rev.} + dW$$

$$dq_{rev.} = dE - dW \quad \text{--- (2)}$$

If work is done due to the expansion of a gas only

$$dW = -PdV$$

$$\& \; dE = C_v dT$$

Putting above values in equation (2), we get

$$dq_{rev.} = C_v dT + PdV \quad \text{--- (3)}$$

Comparing eq. (1) and (3), we get

$$TdS = C_v dT + PdV$$

$$\text{or } TdS = C_v dT + \frac{RT}{V} dV \quad (\because PV = RT \text{ for 1mole})$$

Divide both sides by T

$$dS = C_v \frac{dT}{T} + \frac{RdV}{V} \quad \text{--- (4)}$$

Assuming the heat capacity is independent over the temp. range then the integration of above equation between T_1 & T_2 & corresponding volumes (V_1 & V_2) we get

$$\int dS = C_v \int_{T_1}^{T_2} \frac{dT}{T} + R \int_{V_1}^{V_2} \frac{dV}{V}$$

$$\Rightarrow \Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{V_2}{V_1} \quad \text{--- (5)}$$

for 'n' moles of ideal gas

$$\boxed{\Delta S = nC_v \ln \frac{T_2}{T_1} + nR \ln \frac{V_2}{V_1}} \quad \text{--- (6)}$$

Case - 2 (Temperature and Pressure are variable):

$$P_1V_1 = RT_1 \quad \& \quad P_2V_2 = RT_2$$

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

Putting this value in eq. (6), we get

$$\Delta S = C_v \ln \frac{T_2}{T_1} + R \ln \frac{T_2}{T_1} \cdot \frac{P_1}{P_2}$$

$$= (C_v + R) \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}$$

$$\boxed{\Delta S = C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}} \quad \text{——— (7)}$$

for 'n' moles,

$$\boxed{\Delta S = n C_p \ln \frac{T_2}{T_1} + n R \ln \frac{P_1}{P_2}} \quad \text{——— (8)}$$

for isothermal process,

$$\boxed{\Delta S = R \ln \frac{V_2}{V_1} = R \ln \frac{P_1}{P_2}}$$

for isobaric process,

$$\boxed{\Delta S = C_p \ln \frac{T_2}{T_1} = C_p \ln \frac{V_2}{V_1}} \quad \left(\because \frac{T_2}{T_1} = \frac{V_2}{V_1} \text{ Charles law}\right)$$

for isochoric process,

$$\boxed{\Delta S = C_v \ln \frac{T_2}{T_1} = C_v \ln \frac{P_2}{P_1}} \quad \left(\because \frac{T_2}{T_1} = \frac{P_2}{P_1} \text{ Gay-Lussac law}\right)$$

- Entropy of mixing:

$$\boxed{\Delta S_{mix} = -R \sum n_i \ln X_i}$$

(n_i = number of moles, X_i = mole fraction)

$$\boxed{\Delta S_{mix}/\text{mole} = -R \sum X_i \ln X_i}$$

(Valid when total number of mole is 1)

Dt. 17.9.12

Q) 10 mole of an ideal gas expands reversibly & isothermally from a volume of 10 lt to 20 lt at 300K. Calculate the entropy change.

Q) 64gm of oxygen is expanded from 10 atm to 0.25 atm at 300 K. Calculate the entropy change assuming gas to be ideal.

Q) 1 mole of hydrogen & 9 moles of N_2 are mixed at 298K & 1 atm press. Assuming the ideal behaviour calculate the ΔS of mixing per mole of the mixture form.

1) Given $n = 10$ mole

$V_1 = 10$ lt

$V_2 = 20$ lt

$\Delta S = nR \ln \frac{V_2}{V_1}$

$= 10 \times 8.314 \times \ln 2$

$= 57.62$ J/K

2) Given Mass of $O_2 = 64$ gm

moles of $O_2 = \frac{64}{32} = 2$

$P_1 = 10$ atm

$P_2 = 0.25$ atm

$\therefore \Delta S = nR \ln \frac{P_1}{P_2}$

$= 2 \times 8.314 \times \ln 40$

$= 23.05$ J/K

3) Given moles of $H_2 = 1$

moles of $N_2 = 9$

$X_{H_2} = \frac{1}{10}$ $X_{N_2} = \frac{9}{10}$

$\Delta S = X_{H_2} \ln X_{H_2} + X_{N_2} \ln X_{N_2}$

$= \frac{1}{10} \ln 0.1 + \frac{9}{10} \ln 0.9$

$= -0.23 - 0.095$

$= -0.325 \ J/K$

3) Given moles of $H_2 = 1$

" " $N_2 = 9$

$x_{H_2} = 0.1$ $\quad$ $x_{N_2} = 0.9$

$\Delta S_{mix/mole} = -R\left[x_{H_2} \ln x_{H_2} + x_{N_2} \ln x_{N_2}\right]$

$= -8.314\left[-0.325\right]$

$= 2.704 \ J/K$.

4) 1 mole of an ideal gas $C_v = 12.55 \ JK^{-1}mol^{-1}$ is expanded from 298 K & 2 atm press. to 283 K & 0.4 atm press. Calculate ΔS assuming ideal behaviour.

5) 1 mole of an ideal gas $C_v = 12.471 \ JK^{-1}mol^{-1}$ is heated from 300 K to 600 K. Calculate ΔS

i) when volume is kept const.

ii) when press. is kept const.

4) Given $n = 1 \ mol$

$C_v = 12.55 \ JK^{-1}mol^{-1}$

$T_1 = 298K$ $\quad$ $T_2 = 283 \ K$

$P_1 = 2 \ atm$ $\quad$ $P_2 = 0.4 \ atm$

$C_p = C_v + R$

$= (12.55 + 8.314) \ JK^{-1}mol^{-1}$

$\Delta S = n\left[C_p \ln \frac{T_2}{T_1} + R \ln \frac{P_1}{P_2}\right]$

$= 12.303 \ J/K$

5) Given $n = 1$ mole

$C_v = 12.471\ JK^{-1}mol^{-1}$

$T_1 = 300K$

$T_2 = 600K$

i) Isochoric process:

$$\Delta S = nC_v \ln \frac{T_2}{T_1}$$

$$= 8.644\ J/K$$

ii) Isobaric process:

$$\Delta S = nC_p \ln \frac{T_2}{T_1}$$

$$= 14.407\ J/K$$

6) The entropy of liquid water is $0.47\ JK^{-1}g^{-1}$ at 32.5°C. The vapour press is P at this temp. & heat of vapourisation is $2422\ Jg^{-1}$. Assuming the vapours to behave as ideal gas calculate the Δentropy of the system at 200°C at 20P press. given specific heat of steam is $1.97\ JK^{-1}g^{-1}$

$$\text{Water (v) } 32.5°C \xrightarrow{\Delta S_1} \text{Water (v) } 32.5,\ P \xrightarrow{\Delta S_2} \text{W(vapour) } 200,\ P \xrightarrow{\Delta S_3} \text{Water (v) } 200,\ 20P$$

$$\Delta S_1 = \frac{\Delta H}{T} = \frac{2422}{305.5} = 7.93\ JK^{-1}g^{-1}$$

$$\Delta S_2 = C_p \ln \frac{T_2}{T_1}$$
(isobaric)

$$= 1.97 \ln \frac{473}{305.5} = 0.86\ JK^{-1}g^{-1}$$

$$\Delta S_3 = R \ln \frac{P_1}{P_2} = \frac{8.314}{18} \ln \frac{1}{20} = -1.38\ JK^{-1}g^{-1}$$

$$\Delta S = 0.47 + 7.93 + 0.86 - 1.38$$

$$= 7.88\ JK^{-1}g^{-1}$$

Q) The molar heat capacity at const. press. of O_2 is given by $C_p = 25.723 + 12.98 \times 10^{-3} T - 36.618 \times 10^{-7} T^2$.

If a system containing 2 mole of O_2 is heated from 27°c to 227°c & expanded from 2 lt to 8 lt then calculate the entropy change by assuming gas to be ideal & process is carried out reversibly.

$$\Delta S = \left[C_p \int \frac{dT}{T} + R \int \frac{dV}{V}\right] \times n$$

$$\Rightarrow \Delta S = 2 \times \left[25.723 \int \frac{dT}{T} + 12.98 \times 10^{-3} \int \frac{dT}{T} \times T - \int 36.618 \times 10^{-7} \frac{dT}{T^2} \times T^2 + R \ln \frac{V_2}{V_1}\right]$$

$$\Rightarrow \Delta S = 2 \times \left[25.723 \ln \frac{T_2}{T_1} + 12 \times 10^{-3} (T_2 - T_1) - 36.618 \times 10^{-7} \left(\frac{T_2^2 - T_1^2}{2}\right) + 8.314 \ln \frac{8}{2}\right]$$

$$= 2 \times \left[25.723 \ln \frac{500}{3} + 12 \times 10^{-3} \times 200 - 36.618 \times 10^{-7} \times 800 + 8.314 \ln 4\right]$$

$$= 54.1 \text{ J/K}.$$

2nd
Dt 18.9.12

Concept of free energy:

As the sum total of entropy change of the system & surrounding serve as a condition for spontanity of a process, so in order to predict the spontanity we have to determine the entropy change of the system and surrounding which is not always convient, so we must consider entropy change in terms of other state fun^n which can be determined conviniently. 2 such state fun^ns are

i) Free energy fun^n (G)
ii) Work fun^n. (A).

Defined by eq.

$$G = H - TS \qquad A = E - TS$$

- Since H, E, T & S are all state functions, so both G & A are state function. Like H & E or S the absolute value of G & A can't be determined, however the change in free energy can be determined as

$$\Delta G = G_2 - G_1 = \Delta H - T\Delta S$$
$$\Delta A = A_2 - A_1 = \Delta E - T\Delta S$$

Significance of ΔA:

$$\Delta A = A_2 - A_1 = \Delta E - T\Delta S \quad \text{—— (1)}$$

Let the change is carried out reversibly at a const. temp. T & the amount of heat absorbed is q_{rev}.

$$\Delta S = \frac{q_{rev}}{T}$$

$$\Rightarrow T\Delta S = q_{rev}$$

$$\therefore \Delta A = \Delta E - q_{rev} \quad \text{—— (2)}$$

A/c to 1st law of thermodynamics,

$$\Delta E = q + W = q_{rev} + W_{rev}$$

Since the work is done by the system,

$$\Delta E = q_{rev} - W_{rev}$$

$$\Rightarrow \Delta E - q_{rev} = -W_{rev} \quad \text{—— (3)}$$

Comparing (2) & (3), we get,

$$\Delta A = -W_{rev}$$

$$\Rightarrow \boxed{-\Delta A = W_{rev}}$$

Thus the decrease in work fun or Helmholtz' free energy represents the max^m work that can be done by system during the given change.

Significance of ΔG:

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

But $\Delta H = \Delta E + P\Delta V$

$$\therefore \Delta G = \Delta E + P\Delta V - T\Delta S$$
$$= \Delta E - T\Delta S + P\Delta V$$
$$= \Delta A + P\Delta V$$
$$\Rightarrow \Delta G = -W_{rev} + P\Delta V$$
$$\Rightarrow \boxed{-\Delta G = W_{rev} - P\Delta V}$$

Thus, the decrease in free energy represents the max^m work that can be done by the system other than the work due to change of volume as const. temp. & press.

Relation bet^n free energy change & spontanity:

$\Delta G < 0 \Rightarrow$ Spontaneous Process

$\Delta G > 0 \Rightarrow$ Non-spontaneous / Non-feasible Process

$\Delta G = 0 \Rightarrow$ Equilibrium.

- The standard free energy change at equilibrium is not zero.

Free energy of formation:

- It is the free energy change when 1 mole of the compd is formed from its constituent elements.
- By knowing the values of free energy of form^n of reactants & products the free energy change of the reaction can be calculated as

$$\Delta G = \Sigma G_f(\text{products}) - \Sigma G_f(\text{reactants}).$$

$$\boxed{\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S^\circ}$$ – For standard state

Variation of free energy with T & P:

We know, $G = H - TS$

$= E + PV - TS$

Upon differentiation

$$dG = dE + PdV + VdP - TdS - SdT \quad \text{--- (1)}$$

A/c to 1st law of thermodynamics,

$$dE = dq + dW$$

$$\Rightarrow dq = dE - dW$$

If work is done by the system, then

$$dW = -PdV$$

$$\Rightarrow dq = dE + PdV \quad \text{--- (2)}$$

For a reversible process the increase in entropy is given by

$$dS = \frac{dq}{T}$$

$$\Rightarrow dq = TdS \quad \text{--- (3)}$$

From eq. (2) & (3) $TdS = dE + PdV$ --- (4)

Combining eq. (1) & (4), we get

$$dG = \cancel{TdS} + VdP - \cancel{TdS} - SdT$$

$$\Rightarrow \boxed{dG = VdP - SdT}$$

At const T, $dG = VdP$

$$\boxed{\left(\frac{\partial G}{\partial P}\right)_T = V} \quad \text{--- (6)}$$

At const P, $dG = -SdT$

$$\boxed{\left(\frac{\partial G}{\partial T}\right)_P = -S} \quad \text{--- (7)}$$

Dt 25/9/12

Q) Calculate the free energy change of the reac^n

$$CO + \frac{1}{2}O_2 \longrightarrow CO_2$$

Given $\Delta H^\circ = -282.84$ KJ, ΔS° of CO_2, CO, O_2 are 213.8, 197.9 & 205.01 JK^{-1} mol^{-1} respectively. ($T = 25^\circ C$)

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

$$\Delta H = -282.84 \times 10^3 J$$

$$\Delta S = 213.8 - (197.9 + \frac{1}{2} \times 205.01)$$

$$= -86.605 \ JK^{-1} mol^{-1}$$

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

$$= -282.84 \times 10^3 - 298(-86.605)$$

$$= -257.03 \ KJ$$

The free energy change while the pressure changes from P_1 to P_2 at a constant temperature is given by

$$\Delta G = \int dG = \int_{P_1}^{P_2} VdP = \int_{P_1}^{P_2} \frac{RT}{P} dP$$

$$\Rightarrow \boxed{\begin{aligned} \Delta G &= RT \ln \frac{P_2}{P_1} = RT \ln \frac{V_1}{V_2} \\ \Delta G &= nRT \ln \frac{P_2}{P_1} = nRT \ln \frac{V_1}{V_2} \end{aligned}}$$

Q) The standard ΔG for decomposition of water $H_2O(g) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$ is 118.08 KJ at 2300K and 1 atomospheric pressure calculate the degree of dissociation.

$$H_2O(g) \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$$

1	0	0
$1-\alpha$	α	$\frac{1}{2}\alpha$

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

$$\Rightarrow 118.08 \times 10^3 = -8.314 \times \overset{2360}{\cancel{298}} \times \ln K_p$$

$$\Rightarrow \ln K_p = -6.175$$

$$\Rightarrow K_p = 2.08 \times 10^{-3}$$

Total number of moles

$$= 1-\alpha+\alpha+\frac{\alpha}{2} = 1+\frac{\alpha}{2}$$

$$P_{H_2O} = \left(\frac{1-\alpha}{1+\frac{\alpha}{2}}\right)P$$

$$P_{H_2} = \left(\frac{\alpha}{1+\frac{\alpha}{2}}\right)P$$

$$P_{O_2} = \left(\frac{\alpha/2}{1+\alpha/2}\right)P$$

$$K_p = \frac{\left(\frac{\alpha}{1+\alpha/2}\right)\left(\frac{\alpha/2}{1+\frac{\alpha}{2}}\right)^{1/2}}{\frac{1-\alpha}{1+\alpha/2}} = \frac{\alpha}{1-\alpha}\cdot\frac{\alpha^{1/2}}{\sqrt{2}\left(1+\frac{\alpha}{2}\right)^{1/2}}$$

$$= \frac{\alpha^{3/2}}{(2+\alpha)^{1/2}(1-\alpha)}$$

Since ΔG° is +ve, so the value of equilibrium constant is very low and hence value of α is very small. So it can be negelected as compared to 2 or 1.

$$K_p = \frac{\alpha^{3/2}}{\sqrt{2}} \Rightarrow 2.08 \times 10^{-3} \times \sqrt{2} = \alpha^{3/2}$$

$$\Rightarrow \alpha = \left(2.08 \times 10^{-3} \times \sqrt{2}\right)^{2/3}$$

$$= 0.02$$

$$CH_3COOC_2H_5 + H_2O \rightleftharpoons CH_3COOH + C_2H_5OH$$

$$K_c = \frac{[CH_3COOH][C_2H_5OH]}{[CH_3COOC_2H_5]}$$

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$$

In second case we have no control on H_2O production, so it is taken in K_c but in 1st. case we take H_2O in excess amount, so it is taken as 1.

1) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

2) $2HBr(g) \rightleftharpoons H_2(g) + Br_2(g)$

3) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

4) $2NO + O_2 \rightleftharpoons 2NO_2(g)$

Write K_p in terms of α.

Gibb Helmoltz's free energy:-

Let G_1 represent the free energy of a system at a temperature T at initial state. When temperature changes to T+dT the free energy change becomes $G_1 + dG_1$

Similarly let G_2 is the free energy change of the system at final state at temperature T. When temperature changes to T+dT the free energy changes to $G_2 + dG_2$

According to 1st. law of thermodynamics concept of free energy, we know

$$dG = VdP - SdT$$

At constant pressure $dG = -SdT$

for initial state $dG_1 = -S_1 dT$

for final state $dG_2 = -S_2 dT$

$$dG_2 - dG_1 = -S_2 dT + S_1 dT$$

$$\Rightarrow d(G_2 - G_1) = -(S_2 - S_1) dT$$

$$\Rightarrow d(\Delta G) = -\Delta S dT$$

$$\Rightarrow \left[\frac{\partial(\Delta G)}{\partial T}\right]_P = -\Delta S \quad \text{------} (1)$$

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

$$\Rightarrow -\Delta S = \frac{\Delta G - \Delta H}{T} \quad \text{----} (2)$$

$$\therefore \left[\frac{\partial(\Delta G)}{\partial T}\right]_P = \frac{\Delta G - \Delta H}{T}$$

$$\Rightarrow \Delta G - \Delta H = T\left[\frac{\partial(\Delta G)}{\partial T}\right]_P$$

$$\boxed{\Delta G = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_P} \quad \text{----} (3)$$

$$\Delta G^\circ = \Delta H + T\left[\frac{\partial \Delta G}{\partial T}\right]_P \quad \text{----} (4)$$

Equation (3) and (4) are known as Gibb Helmotz's equation.

Temperature dependance of equilibrium constant :-
(Vant Hoff's equation)

We know $\Delta G^\circ = -RT\ln K_P$

$$\Rightarrow \frac{\Delta G^\circ}{T} = -R\ln K_P$$

Difference with respect to temperature at constant pressure

$$\left[\frac{\partial\left(\frac{\Delta G^\circ}{T}\right)}{\partial T}\right]_P = -R\frac{d\ln K_P}{dT} \quad \text{----} (1)$$

According to Gibb Helmolte's equation

$$\Delta G^\circ = \Delta H^\circ + T\left[\frac{\partial(\Delta G^\circ)}{\partial T}\right]_P$$

$$\Rightarrow -\Delta H^\circ = T\left[\frac{\partial(\Delta G^\circ)}{\partial T}\right]_P - \Delta G^\circ$$

Divide both the sides by T^2

$$-\frac{\Delta H^\circ}{T^2} = \frac{T\left[\frac{\partial \Delta G^\circ}{\partial T}\right]_P - \Delta G^\circ}{T^2} \quad \left[\frac{VdU - UdV}{V^2} = d\left(\frac{U}{V}\right)\right]$$

$$\Rightarrow -\frac{\Delta H^\circ}{T^2} = \left[\frac{\partial(\Delta G^\circ/T)}{\partial T}\right]_P \quad \text{-----} \quad (2)$$

$$\Rightarrow \frac{\Delta H^\circ}{T^2} = -\frac{R\,d\ln K_P}{dT}$$

$$\Rightarrow \boxed{\frac{d\ln K_P}{dT} = \frac{\Delta H^\circ}{RT^2}}$$

Compare eq. (1) with eq. (2)

$$\left[\frac{\partial(\Delta G^\circ)}{\partial T}\right]_P = -\frac{\Delta H^\circ}{T^2} \quad \text{-----} \quad (3)$$

Equation (3) is differential form of Vant Hoff Eq.

$$\therefore \int_{K_{P1}}^{K_{P2}} d\ln K_P = \frac{\Delta H^\circ}{R}\int_{T_1}^{T_2}\frac{dT}{T^2}$$

Where K_{P1} and K_{P2} are equilibrium constants at T_1 and T_2

$$\Rightarrow \ln\frac{K_{P2}}{K_{P1}} = \frac{\Delta H^\circ}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\Rightarrow \boxed{\log\frac{K_{P2}}{K_{P1}} = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]}$$

LectureNotes.in

Dt 1/10/12

Q) The equilibrium constant for the reaction

$H_{2(g)} + S_{(g)} \longrightarrow H_2S_{(g)}$ is $20.2\ atm^{-1}$ at $945°C$ & $9.21\ atm^{-1}$ at $1065°C$. Calculate the standard enthalpy change assuming enthalpy change remain const. over the given interval.

$$\log \frac{9.21}{20.2} = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\Rightarrow 2.303 \times 8.314 \log \frac{9.21}{20.2} = \Delta H^\circ \times 7.36 \times 10^{-5}$$

$$\Rightarrow \Delta H^\circ = \frac{2.303 \times 8.314}{7.36 \times 10^{-5}} \log \frac{9.21}{20.2} = \frac{8.314}{7.36 \times 10^{-5}} \ln \frac{9.21}{20.2}$$

$$= -88719.5\ J = -88.719\ kJ$$

Q) For the reaction $CO_{(g)} + SO_{3(g)} \rightleftharpoons CO_{2(g)} + SO_{2(g)}$

$\Delta G^\circ = -187.1\ kJ$, $\Delta H^\circ = -184.7\ kJ$ at $25°C$.

Calculate ΔG° & k_p at $125°C$.

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

$$\Rightarrow -187.1 \times 10^3 = -8.314 \times 298 \times \ln k_p$$

$$\Rightarrow \ln k_p = \frac{-187.1 \times 10^3}{8.314 \times 298}$$

$$\Rightarrow k_p = 6.26 \times 10^{32}$$

$$\ln \frac{k_{p_2}}{k_{p_1}} = \frac{\Delta H^\circ}{2.303}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\Rightarrow \ln \frac{k_{p_2}}{0.927} = \frac{-184.7}{2.303}\left[\frac{398 - 298}{398 \cdot 298}\right]$$

$$\Rightarrow \ln \frac{k_{p_2}}{0.927} =$$

$$\log \frac{k_{p_2}}{k_{p_1}} = \frac{\Delta H^\circ}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\Rightarrow \log \frac{k_{p_2}}{6.26 \times 10^{32}} = \frac{-184.7 \times 10^3}{2.303 \times 8.314}\left[\frac{100}{398 \cdot 298}\right]$$

$\Rightarrow \ln \frac{k_{p_2}}{6.96\times10^{32}} = -18.73$

$\Rightarrow \frac{k_{p_2}}{6.96\times10^{32}} = 7.39\times10^{-9}$

$\Rightarrow k_{p_2} = 4.59\times10^{24}$

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

$= -8.314\times 398\times \ln(4.59\times10^{24})$

$= -187903.02$

$= -187.9\,kJ$

Prove the eqn $\frac{d\ln k_c}{dT} = \frac{\Delta E^\circ}{RT^2}$.

$k_p = k_c(RT)^{\Delta n}$

$\ln k_p = \ln[k_c(RT)^{\Delta n}]$

$\Rightarrow \ln k_p = \ln k_c + \Delta n \ln RT$

Diff. w.r.to T

$\frac{d\ln k_p}{dT} = \frac{d\ln k_c}{dT} + \Delta n \frac{d\ln RT}{dT}$

$\Rightarrow \frac{\Delta H^\circ}{RT^2} = \frac{d\ln k_c}{dT} + \Delta n\left[\frac{1}{T}\right]$

$\Rightarrow \frac{d\ln k_c}{dT} = \frac{\Delta H^\circ}{RT^2} - \frac{\Delta n}{T} = \frac{\Delta H^\circ - \Delta nRT}{RT^2} = \frac{\Delta E^\circ}{RT^2}$

$\Rightarrow \boxed{\frac{d\ln k_c}{dT} = \frac{\Delta E^\circ}{RT^2}}$ (Proved)

Maxwell's relationship:

If $T = f(P,V)$ for 1 mole of ideal gas, then show that dT is an exact diff.

Ideal gas eq. $PV = nRT$

$\Rightarrow T = \frac{PV}{R}$

$$\left(\frac{\partial T}{\partial P}\right)_V = \frac{V}{R} \qquad \left(\frac{\partial T}{\partial V}\right)_P = \frac{P}{R}$$

$$\frac{\partial^2 T}{\partial P \cdot \partial V} = \frac{1}{R} \quad \text{—} (1) \qquad \frac{\partial T^2}{\partial V \partial P} = \frac{1}{R} \quad \text{—} (2)$$

From (1) & (2)

$$\frac{\partial}{\partial P \partial V} = \frac{\partial^2 T^2}{\partial V \partial P}$$

So T is an exact differential & state fun.

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Q) For 1 mole of ideal gas it

$V = f(P, T)$ then prove that V is a state fun.

Ideal gas eq. $PV = nRT$

$$\Rightarrow V = \frac{RT}{P}$$

$$\left(\frac{\partial V}{\partial P}\right)_T = \frac{-RT}{P^2} \qquad \left(\frac{\partial V}{\partial T}\right)_P = \frac{R}{P}$$

$$\frac{\partial V^2}{\partial P \partial T} = \frac{-R}{P^2} \quad \text{—} (1) \qquad \frac{\partial V^2}{\partial T \partial P} = \frac{-R}{P^2} \quad \text{—} (2)$$

From (1) & (2)

$$\frac{\partial V^2}{\partial P \partial T} = \frac{\partial V^2}{\partial T \partial P}$$

∴ V is an exact differential & a state fun.

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Maxwell's relationship:

From concept of enthalpy, ~~entropy~~, free energy, internal energy & 1st law of thermodynamics,

$$dE = TdS - PdV \quad \text{—} (1)$$
$$dH = TdS + VdP \quad \text{—} (2)$$
$$dG = -SdT + VdP \quad \text{—} (3)$$
$$dA = -SdT - PdV \quad \text{—} (4)$$

① $dE = TdS - PdV$

If "S" is kept const. $dE = -PdV$

$$\left(\frac{\partial E}{\partial V}\right)_S = -P \quad \text{—— (5)}$$

If "V" is const. $dE = TdS$

$$\Rightarrow \left(\frac{\partial E}{\partial S}\right)_V = T \quad \text{—— (6)}$$

Diff. eq. (5) w.r.to S

$$\frac{\partial^2 E}{\partial V \partial S} = -\left(\frac{\partial P}{\partial S}\right)_V \quad \text{—— (7)}$$

Diff. eq. (6) w.r.to V

$$\frac{\partial^2 E}{\partial S \partial V} = \left(\frac{\partial T}{\partial V}\right)_S \quad \text{—— (8)}$$

Since dE is an exact differential

$$\frac{\partial^2 E}{\partial V \partial S} = \frac{\partial^2 E}{\partial S \partial V}$$

So from eq. (7) & (8)

$$\boxed{\left(\frac{\partial T}{\partial V}\right)_S = -\left(\frac{\partial P}{\partial S}\right)_V}$$

1st Maxwell's relation.

Similarly,

$$\boxed{\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S}$$

$$\boxed{\left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P}$$

$$\boxed{\left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V}$$

Prove

② $dH = TdS + VdP$

If "S" is kept const. then $\Delta H = V\Delta P$

$$\Rightarrow \left(\frac{\partial H}{\partial P}\right)_S = V \quad \text{—— (9)}$$

If "P" is kept const. then $\Delta H = T\Delta S$

$$\Rightarrow \left(\frac{\partial H}{\partial S}\right)_P = T \quad \text{—— (10)}$$

Diff. eq. (9) w.r.to S

$$\frac{\partial^2 H}{\partial P \cdot \partial S} = \left(\frac{\partial V}{\partial S}\right)_P \quad \text{--- (11)}$$

Diff. eq. (10) w. r. to P

$$\frac{\partial^2 H}{\partial S \cdot \partial P} = \left(\frac{\partial T}{\partial P}\right)_S \quad \text{--- (12)}$$

As H is a state fun., so

$$\boxed{\left(\frac{\partial V}{\partial S}\right)_P = \left(\frac{\partial T}{\partial P}\right)_S}$$

2nd Maxwell's relation.

(3) $dG = -SdT + VdP$

If "T" is kept const. then $dG = -VdP$

$$\Rightarrow \left(\frac{\partial G}{\partial P}\right)_T = +V \quad \text{--- (13)}$$

If "P" is kept const., then $dG = -SdT$

$$\Rightarrow \left(\frac{\partial G}{\partial T}\right)_P = -S \quad \text{--- (14)}$$

Diff. eq. (13) w. r. to T,

$$\frac{\partial^2 G}{\partial P \cdot \partial T} = +\left(\frac{\partial V}{\partial T}\right)_P \quad \text{--- (15)}$$

Diff. eq. (14) w. r. to P

$$\frac{\partial^2 G}{\partial T \cdot \partial P} = -\left(\frac{\partial S}{\partial P}\right)_T \quad \text{--- (16)}$$

As G is a state fun.,

$$+\left(\frac{\partial V}{\partial T}\right)_P = -\left(\frac{\partial S}{\partial P}\right)_T$$

$$\Rightarrow \boxed{\left(\frac{\partial V}{\partial T}\right)_P = \left(\frac{\partial S}{\partial P}\right)_T}$$

3rd Maxwell's eq.

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(4) $dA = -SdT - PdV$

If "T" is kept const., $dA = -PdV$

$$\Rightarrow \left(\frac{\partial A}{\partial V}\right)_T = -P \quad \text{--- (17)}$$

If "V" is kept const, $dA = -SdT$

$$\Rightarrow \left(\frac{\partial A}{\partial T}\right)_V = -S \quad \text{--- (18)}$$

Diff eq. (17) w.r.to T

$$\frac{\partial^2 A}{\partial V \cdot \partial T} = \left(-\frac{\partial P}{\partial T}\right)_V \quad \text{--- (19)}$$

Diff. eq. (18) w.r.to V

$$\frac{\partial^2 A}{\partial V \cdot \partial T} = \left(-\frac{\partial S}{\partial V}\right)_T \quad \text{--- (20)}$$

As A is a state fun. so

$$-\left(\frac{\partial P}{\partial T}\right)_V = -\left(\frac{\partial S}{\partial V}\right)_T$$

$$\Rightarrow \boxed{\left(\frac{\partial P}{\partial T}\right)_V = \left(\frac{\partial S}{\partial V}\right)_T}$$

4th maxwell's eq.

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Dt. 8/10/12

Application of Maxwell's relationship:

1) Derive $\left(\frac{\partial E}{\partial S}\right)_P = T - P\left(\frac{\partial T}{\partial P}\right)_S$

$dE = TdS - PdV$

$\Rightarrow \left(\frac{\partial E}{\partial S}\right)_P = T - P\left(\frac{\partial V}{\partial S}\right)_P$

$\Rightarrow \left(\frac{\partial E}{\partial S}\right)_P = T - P\left(\frac{\partial T}{\partial P}\right)_S$

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2) By applying 1st law & 2nd law of thermodynamics & appropriate maxwell's relation prove that

i) $\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial V}\right)_V - P$ [First thermodynamic eq. of state]

ii) $\left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$ [Second thermodynamic eq. of state]

i) $dE = TdS - PdV$

$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial S}{\partial V}\right)_T - P$

$\Rightarrow \left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P$ (Proved) $\left[\because \left(\frac{\partial S}{\partial V}\right)_T = \left(\frac{\partial P}{\partial T}\right)_V\right]$

ii) $dH = TdS + VdP$

$\left(\frac{\partial H}{\partial P}\right)_T = T\left(\frac{\partial S}{\partial P}\right)_T + V$

$\Rightarrow \left(\frac{\partial H}{\partial P}\right)_T = V - T\left(\frac{\partial V}{\partial T}\right)_P$ (Proved) $\left[\because \left(\frac{\partial S}{\partial P}\right)_T = -\left(\frac{\partial V}{\partial T}\right)_P\right]$

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