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## Metallurgical Thermodynamics & Kinetics

Thermo-Heat  
dynamics Power ] Heat engines

Tells about -!

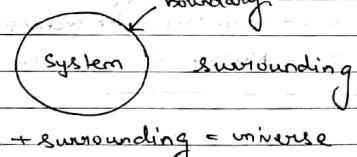
feasibility of process

If yes, then at what rate? (Kinetics)

- Thermodynamic System - Prescribed region of space under thermodynamic study.

- System boundary - A real or hypothetical envelope surrounding the system is called system boundary (or simply 'boundary')

Surrounding - It is a space outside the system boundary.



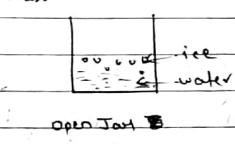
system + surrounding = universe

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### Types of System - (Definition + Example)

#### Open System

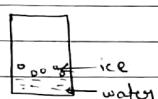


open Jar

I

~~Example~~

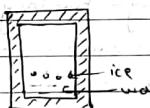
#### Closed System



Jar with Lid

II

#### Isolated System



Thermos flask

III

~~definition~~

O.S. - mass & energy both can be exchanged

C.S. - mass cannot be exchanged but energy can be exchanged

I.S. - Neither heat nor energy can be exchanged.

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### Approach to Thermodynamic Study

#### Microscopic Approach

This approach involves study at the level of molecular or atomic movement.

This involves rapid motion of molecules inside the container, collision between molecules (after each collision, the velocity changes), collision of molecules with the container walls. This involves probability factor. Also, very sophisticated instruments are

needed for the measurement of velocity, velocity, impulse, impact, etc. of the molecules.

This approach leads to the branch of thermodynamics known as Statistical Thermodynamics.

#### Macroscopic Approach

In this app. This approach involves a certain amount of molecules so that average properties like pressure, and temperature can be measured with simple instruments. This branch of thermodynamics is called Classical Thermodynamics.

fcc melting pt. of Cu  $\rightarrow$   $1083^{\circ}\text{C}$   
 fcc melting pt. of Ni  $\rightarrow$   $1453^{\circ}\text{C}$



- (P) Phase - Phase is a small portion of the system which is -  
 • chemically homogeneous  
 • mechanically separable  
 • physically distinct

Eg:- vapour, water, ice.

- (C) Component - Components are the constituents which makes the system.

Note:-  
 [ ] solid state  
 { } liquid state  $\langle \text{CaCO}_3 \rangle = \langle \text{CaO} \rangle + \langle \text{CO}_2 \rangle$   
 ( ) Gaseous state No. of phases = 3 ✓  
 [ ] dissolved state No. of components = 3-1  
 = 2 ✓

If  $C = 1$ , then we call it unary system

If  $C = 2$ , then we call it binary system

If  $C = 3$ , then we call it ternary system

If  $C = 4$ , then we call it tertiay system

- (Q) How to identify the number of phases?

Solid	Liquid	Gas
No. of phases = no. of solid species	For miscible liquids, $P = 1$ <small>(exception: Provided they don't form a solid solution)</small>	$P = 1$ <small>(irrespective of no. of gaseous species)</small>
	For immiscible liquids, $P = \text{no. of liquid species}$	

- (Q) How to identify no. of components?

- ① In case of non-reacting components,  $C = \text{no. of species}$   
 ② In case of reacting components,  $C = N - R$  where

$N = \text{no. of chemical species}$

$R = \text{No. of independent Reactions}$

Thermodynamic Equilibrium: A system is said to be under thermodynamic equilibrium if the system is under Thermal Equilibrium, Mechanical eqn. and Chemical equi. together.

Thermal Eqn.  $\rightarrow$  TE  
 Mechanical Eqn.  $\rightarrow$  ME  
 Chemical Eqn.  $\rightarrow$  CE  
 E.  $\rightarrow$  E.  $\rightarrow$  E.  
 Temp. is constant throughout the system  
 Press. is constant throughout the system  
 chemical Potential is uniform throughout the system.

(T) Thermodynamic Properties - are characteristics of a system. Its types are -

Extensive Properties - These are those TP which depend upon mass. Eg- Enthalpy, entropy, etc.

Intensive Properties - These are those TP which do not depend upon mass. Eg- temp., press., refractive index, etc.

Note - If we divide extensive properties by mass, it becomes intensive properties.

State - State is the condition of a system at a particular instant. A state is specified by assigning atleast two properties (for a closed system).

Thermodynamic Process - Suppose, the system is at state 1. If the state properties are changed, then change of state will take place to state 2. For each state, unique set of thermodynamic properties must be assigned.

The mode of change of state is called a process.

① Isothermal Process - If the change of state is taking place at constant temperature.

② Isobaric Process - If the change of state is taking place at constant pressure.

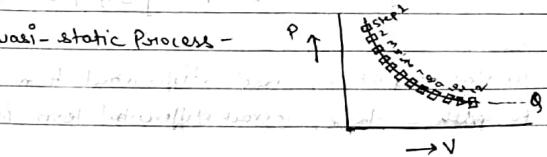
③ Isochoric Process - If the change of state is taking place at constant volume.

④ Irreversible Process - If the process cannot be reverted back to its original state even when the external agency responsible for change of state is removed then, such a process is called Irreversible Process.

All Natural Processes are Irreversible Processes.

⑤ Reversible Process - If the process is reverted back to its original state after removal of external agency responsible for change of state through the same path, then it is called a Reversible Process.

⑥ Quasi-static Process -



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If the process is carried out so slowly that each intermediate step is very close to thermodynamic equilibrium, then such a process is called quasi-static process.

Thermodynamic Path - The Jcii of change of state is called Path.

State function/Point function - Those thermodynamic properties which do not depend upon path are called state properties or state functions.

$$\text{For e.g.: } \int^2 dV = V_2 - V_1, \quad \int^2 dP = P_2 - P_1, \quad \int^2 dT = T_2 - T_1$$

These values in the plot can be plotted as points, hence, these are known as point functions as well.

Path function - The properties which depend upon path are called path function. In the plot, they cannot be indicated as points.

$$\text{For e.g.: } \int^2 \delta W \neq W_2 - W_1, \quad \int^2 \delta Q \neq Q_2 - Q_1$$

For state properties, exact differential term is used.  
for path functions, inexact differential term is used.

Q: How to identify a state function?

Let 'z' be a state function

$$\therefore z = z(x, y)$$

$$dz = \frac{\partial z}{\partial x} dx + \frac{\partial z}{\partial y} dy$$

(i) If second differential of z is independent of the order of differentiation, then z is a state function.

$$\text{i.e. } \frac{\partial^2 z}{\partial x \partial y} = \frac{\partial^2 z}{\partial y \partial x}$$

(ii) If cyclic integral of z is 0 then z is a state function i.e.  $\oint dP=0$ ,  $\oint dV=0$ ,  $\oint dT=0$

Indicator Diagram -

An Indicator Diagram

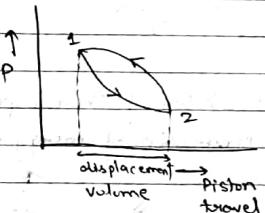
is the record of

trace of pressure

gauge readings attach

to the cylinder of the

engine.



If the trace of indicator diagram is clockwise, then work is done by the system and if it is anticlockwise, then work is done on the system.

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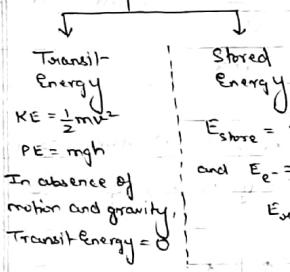
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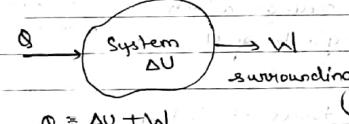
Work and Heat are 2 different forms of the same entity.

There is change of form i.e. heat can be converted into work or work can be converted into heat.

### Stored Energy -

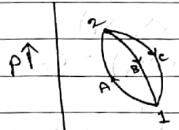


FLT states that First Law of Thermodynamics is based upon conservation of energy.  
 It simply converts from one form to another form of energy.



In differential form,  $dU = \delta Q - \delta W$

### # Proof that internal energy is a state function



The process can be completed through path ABA or through path A → A → ACA.

#### I For path ABA:

$$\Delta U_A = Q_A - W_A$$

$$\Delta U_B = Q_B - W_B$$

for a cyclic process,  $\sum \text{work} = \sum \text{heat}$

$$\therefore Q_A + Q_B = W_A + W_B$$

$$\Rightarrow Q_A - W_A = W_B - Q_B$$

$$\Rightarrow Q_A - W_A = -(Q_B - W_B)$$

$$\therefore \Delta U_A = -\Delta U_B \quad (1)$$

Similarly,

#### II For path A → CA:

$$\Delta U_A = -\Delta U_C \quad (2)$$

From eqs (1) & (2), we can say that Internal Energy is a state function.

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pressure

- For constant pressure process,

$$\Delta U = Q - W$$

$$\Rightarrow U_2 - U_1 = Q_p - P(V_2 - V_1)$$

$$\Rightarrow (U_2 + PV_2) - (U_1 + PV_1) = Q_p$$

$$\therefore H_2 - H_1 = \Delta H = Q_p$$

where  $H$  is the enthalpy and  $H = U + PV$

$\therefore$  change in enthalpy  $\Delta H = \text{amount of heat absorbed or released at constant pressure process}$

$\because$  by definition,  $H = U + PV$

where  $U, P, V$  are state functions

∴  $H$  is also a state function

- For constant volume process,

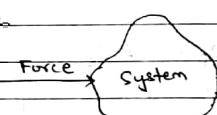
$$\Delta U = Q - W$$

$$W = PdV = 0$$

$$\Delta U = Q_V$$

change in differential form,  $dU = Q_V dV$

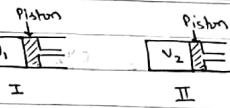
Work Transfer



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- Displacement Work:



$$W_{1-2} = \int_{v_1}^{v_2} PdV = \int_{v_1}^{v_2} PdA \cdot L$$

$$= \int_{v_1}^{v_2} PdV$$

$$= P(v_2 - v_1)$$

- In case of Isochoric Process, volume is constant so, workdone is zero.

- In case of Isothermal Process,

$$W = \int_{v_1}^{v_2} PdV$$

We know that for ideal gas law,  $PV = \text{constant} = C$

$$\therefore W = \int_{v_1}^{v_2} PdV = \int_{v_1}^{v_2} \frac{C}{V} dV = C \int_{v_1}^{v_2} \frac{dV}{V}$$

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

- In case of Polytropic Process,  $PV^n = \text{constant} = C$

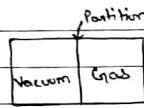
$$W = \int_{v_1}^{v_2} PdV = C \int_{v_1}^{v_2} \frac{dV}{V^n} = P_1 V_1^n \left[ \frac{V^{-n+1}}{-n+1} \right]_1^2$$

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$$= \frac{cv_2^{n+1} - cv_1^{n+1}}{-n+1}$$

$$W = \frac{P_2 V_2^n \cdot V_2^{-n+1} - P_1 V_1^n \cdot V_1^{-n+1}}{-n+1}$$

$$= \frac{P_2 V_2 - P_1 V_1}{-n+1} = \frac{P_1 V_1 - P_2 V_2}{n-1}$$

Zero Work Transfer or Free Expansion:

Since, the gas is not facing any resistance  $\Rightarrow$  it is

once the partition is removed, the gas rushes to fill the vacuum, therefore the gas does not encounter any resistance during its movement  $\Rightarrow$  this is the case of free expansion or zero work.

Heat Transfer - If heat  $\cancel{\text{is}}$ 

Heat absorbed is +ve

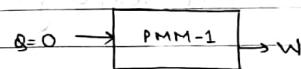
Heat released is -ve

If the process does not allow exchange of heat, it is called Adiabatic Process.

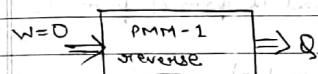
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If the system boundary allows heat transfer, then it is called Diathermic Wall and if it does not allow, then it is called Adiabatic Wall.

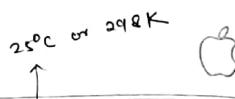
Perpetual Motion machine of first kind or PMM-1

PMM-1 is a hypothetical machine which keeps on doing work without absorbing any heat. Such a machine is not possible as it is against FLT which is based upon conservation of energy.



Reverse of PMM-1 is a hypothetical machine which keeps on producing heat without any workdone on the system. Such a machine is not possible because it is against FLT which is based upon conservation of energy.

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**Standard State -** The standard state of an element is its most stable state at room temp. and atmospheric press. is taken as the standard state.

**Heat of Reaction -** Amount of heat evolved or absorbed when the reactants react completely to produce products.

**Heat of Formation -** The heat of formation per mole of a compound is the heat evolved or absorbed when 1 mole of the compound is formed from its constituent elements.

The heat of formation of a compound from its elements in their standard states is called Standard Heat of formation and it is denoted by  $\Delta H_f^\circ$ . In the case of an element (say M), the standard heat of formation is conventionally taken as zero i.e.  $\Delta H_f^\circ = 0$ .

**Heat of Solution -** When 1 mole of substance dissolves in another, there will be change in enthalpy. This is called Heat of Solution.

**ZnO + H<sub>2</sub>O → Zn(OH)<sub>2</sub>**  
**Law of Thermodynamics -** If system 'A' is in thermal equilibrium with system 'B' and system 'B' is in thermal equilibrium with system 'C', then system 'A' will be in thermal equilibrium with system 'C'.

#### Hess's Law

The Law states that 'Change of heat content for a chemical reaction is same whether the reaction takes place in one or several stages, provided temperature and either ~~or~~ volume or pressure remains constant'.

#### Le Chatelier Principle

When a system which is in thermodynamic equilibrium, is acted upon by an external agency such that the equilibrium is disturbed; then the tendency of the system is to act against the external agency i.e. to resist the change.

**Heat Capacity -**  $C = \frac{q}{\Delta T}$  q is the amount of heat required to raise the

For small changes,  $C = \frac{\delta q}{\delta T}$  temp. of a body by  $1^\circ C$ .

To define a state, atleast 2 thermodynamic properties are needed. Here temp. is the only state property i.e., a 2<sup>nd</sup> state property is needed which can be either pressure or volume which can be kept constant.

$$C_p = \frac{\partial q}{\partial T} \quad \text{specific Heat}$$

$$\frac{C_v}{n} = \frac{\partial q}{\partial T}$$

# For 1 mole of an ideal gas, prove that  $c_p - c_v = R$

$$c_p = \left( \frac{\partial H}{\partial T} \right)_p = \left( \frac{\partial U}{\partial T} \right)_p \quad dH = c_p dT$$

$$c_v = \left( \frac{\partial u}{\partial T} \right)_V = \left( \frac{\partial u}{\partial T} \right)_V \quad dU = c_v dT$$

$$\text{Ansatz: } \nu_p - \nu_v = \left( \frac{\partial H}{\partial T} \right)_p - \left( \frac{\partial u}{\partial T} \right)_v \\ = \left( \frac{\partial u}{\partial T} \right)_p + p \left( \frac{\partial v}{\partial T} \right)_p - \left( \frac{\partial v}{\partial T} \right)_v - (6)$$

$U$  can be expressed as a function of volume and temp.  
 i.e.  $U = U(V, T)$

$$dU = \left(\frac{\partial U}{\partial V}\right)_T dV + \left(\frac{\partial U}{\partial T}\right)_V dT$$

$$\left(\frac{\partial U}{\partial T}\right)_P = \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + \left(\frac{\partial U}{\partial T}\right)_V$$

Putting this value in eq (1), we get

$$x_P - x_V = \left( \frac{\partial v}{\partial P} \right)_T \cdot \left( \frac{\partial T}{\partial P} \right)_V + \left( \frac{\partial v}{\partial T} \right)_P \neq P \left( \frac{\partial v}{\partial T} \right)_P - \left( \frac{\partial v}{\partial P} \right)_T$$

$$\Rightarrow v_p - v_v = \left( \frac{\partial v}{\partial p} \right)_T \left( \frac{\partial T}{\partial v} \right)_p + p \left( \frac{\partial v}{\partial T} \right)_p$$

$P \left( \frac{\partial V}{\partial T} \right)_P$  is the work done against the external pressure P per degree rise in temp.

represents the work done against the cohesive forces present in the system per degree rise in temp. Since we have considered 1 mole of ideal gas, the cohesive forces are absent - hence the work done = 0

$$\therefore \left(\frac{\partial U}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P = 0$$

$$\text{do, } v_p - v_r = \frac{P \left( \frac{\partial V}{\partial T} \right)_P}{V}$$

For one mole of an ideal gas,  $PV = RT$

$$\omega_v \left( \frac{\partial V}{\partial T} \right)_P = \frac{R}{P}$$

$$\text{thus, } x_p - s_y = \frac{P_x R}{y_p}$$

$$\text{i.e. } \boxed{v_p - v_v = R}$$

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### Reversible Isothermal Process -

$$dU = \delta Q - \delta W$$

$$\therefore dU = C_V dT = 0$$

$$\delta Q = \int_1^2 \delta W = P dV$$

$$W = \int P dV = RT \int_1^2 \frac{dV}{V} = RT \ln \frac{V_2}{V_1} = RT \ln \frac{P_1}{P_2}$$

### Reversible Adiabatic Process -

$$dU = \delta Q - \delta W$$

$$\therefore dU = C_V dT \quad \text{and} \quad \delta Q = 0$$

$$\therefore C_V dT = -P dV = -\frac{RT}{V} dV$$

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

$$C_V \frac{dT}{T} = -R \frac{dV}{V}$$

Assuming  $C_V$  to remain constant in the temperature

change  $T_1$  to  $T_2$

$$\therefore C_V \int \frac{dT}{T} = -R \int \frac{dV}{V}$$

$$C_V \ln \frac{T_2}{T_1} = -R \ln \frac{V_2}{V_1} = R \ln \frac{V_1}{V_2}$$

$$\Rightarrow \ln \left( \frac{T_2}{T_1} \right)^{C_V} = \ln \left( \frac{V_1}{V_2} \right)^R$$

$$\Rightarrow \left( \frac{T_2}{T_1} \right)^{C_V} = \left( \frac{V_1}{V_2} \right)^R$$

$$\text{or } \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{R/C_V}$$

$$\therefore C_P - C_V = R \quad \text{specific Heat Ratio}$$

$$\text{dividing by } C_V, \frac{C_P}{C_V} - 1 = \frac{R}{C_V} \quad \text{or} \quad \gamma - 1 = \frac{R}{C_V}$$

$$\therefore \frac{T_2}{T_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

$$\text{From Ideal Gas Law, } \frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2}$$

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

Now, we can write

$$\frac{P_2 V_2}{P_1 V_1} = \left( \frac{V_1}{V_2} \right)^{\gamma-1}$$

$$\Rightarrow \frac{P_1 V_1^{\gamma-1}}{P_2 V_2^{\gamma-1}} = P_1 V_1^{\gamma-1}$$

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

$$\Rightarrow P V^{\gamma} = \text{constant}$$

### Variation of enthalpy change with temperature -

$$\frac{dH}{dT} = C_P$$

$$\Rightarrow dH = C_P dT$$

$$d(\Delta H^\circ) = \Delta C_P dT \quad \text{where } \Delta C_P = C_{P,\text{product}} - C_{P,\text{reactant}}$$

$$\text{where } \Delta C_P = C_{P,\text{product}} - C_{P,\text{reactant}}$$

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$$\int_{T_1}^{T_2} d(\Delta H^\circ) = \int_{T_1}^{T_2} \Delta C_p dT$$

$$\frac{\Delta H^\circ}{T_2} - \frac{\Delta H^\circ}{T_1} = \int_{T_1}^{T_2} \Delta C_p dT \quad \text{or} \quad \left[ \frac{\Delta H^\circ}{T_2} = \frac{\Delta H^\circ}{T_1} + \int_{T_1}^{T_2} \Delta C_p dT \right]$$

Kirchhoff's Law

Note:  
 $C_p = \frac{\delta Q}{\delta T}$  cannot be used

because during phase transformation, temp. remains constant

### (3) Metallurgical Thermochimistry - O. Kubaschek

Prob-1) Calculate standard heat of formation of solid  $WO_3$  from solid 'W' and  $O_2$  gas at  $25^\circ C$  and 1 atm. pressure from following data:

$$\langle W \rangle + \langle O_2 \rangle = \langle WO_2 \rangle, \Delta H_{298}^\circ = -560.6 \text{ kJ}$$

$$3 \langle WO_2 \rangle + \langle O_2 \rangle = \langle W_3O_8 \rangle, \Delta H_{298}^\circ = -550.20 \text{ kJ}$$

$$\langle W_3O_8 \rangle + \frac{1}{2}\langle O_2 \rangle = 3\langle WO_3 \rangle, \Delta H_{298}^\circ = -278.24 \text{ kJ}$$

$$19.73 = \Delta \text{ enthalpy}$$

(sol-1)

$$\langle W \rangle + \langle O_2 \rangle = \langle WO_2 \rangle, \Delta H_{298}^\circ = -560.6 \text{ kJ}$$

$$\langle WO_2 \rangle + \frac{1}{3}\langle O_2 \rangle = \frac{1}{3}\langle W_3O_8 \rangle, \Delta H_{298}^\circ = -183.4 \text{ kJ}$$

$$\langle W \rangle + \langle O_2 \rangle + \frac{1}{3}\langle O_2 \rangle = \langle WO_2 \rangle + \frac{1}{3}\langle W_3O_8 \rangle, \Delta H_{298}^\circ = -744 \text{ kJ}$$

$$\langle W \rangle + \frac{4}{3}\langle O_2 \rangle = \frac{1}{3}\langle W_3O_8 \rangle, \Delta H_{298}^\circ = -744 \text{ kJ}$$

$$\frac{1}{3}\langle W_3O_8 \rangle + \frac{1}{6}\langle O_2 \rangle = \langle WO_3 \rangle, \Delta H_{298}^\circ = -92.75 \text{ kJ}$$

$$\langle W \rangle + \frac{4}{3}\langle O_2 \rangle + \frac{1}{3}\langle W_3O_8 \rangle + \frac{1}{6}\langle O_2 \rangle = \frac{1}{3}\langle W_3O_8 \rangle + \langle WO_3 \rangle$$

$$\Delta H_{298}^\circ = -836.75 \text{ kJ}$$

$$\langle W \rangle + \frac{3}{2}\langle O_2 \rangle = \langle WO_3 \rangle, \Delta H_{298}^\circ = -836.75 \text{ kJ}$$

+ 839 kJ

Prob-2) Calculate standard heat of formation of  $PbO$  at  $227^\circ C$  from 'Pb' and ' $O_2$ ' from the following data-

$$\Delta H_{298, 2 Phos}^\circ = -219.24 \text{ kJ/mole}$$

$$C_p \langle Pb \rangle = 44.35 + 16.74 \times 10^{-3} T \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_p \langle O_2 \rangle = 23.56 + 9.75 \times 10^{-3} T \text{ J K}^{-1} \text{ mol}^{-1}$$

$$C_p \langle O_2 \rangle = 29.96 + 4.184 \times 10^{-3} T - 1.67 \times 10^{-5} T^{-2} \text{ J K}^{-1} \text{ mol}^{-1}$$

Note:- because of very high Temp. (i.e.  $227^\circ C$ ), this problem will be solved

by Kirchhoff's Law.

$$\text{Sol-2) } \Delta H_{500}^{\circ} = \Delta H_{298}^{\circ} + \int_{298}^{500} (C_p_{\text{product}} - C_p_{\text{reactant}}) dT \quad (1)$$

$$\langle P \rangle + \frac{1}{2} \langle O_2 \rangle = \langle P \rangle$$

$$C_p_{\text{product}} = 44.35 + 16.74 \times 10^{-3} T \quad \text{JK}^{-1} \text{mol}^{-1}$$

$$C_p_{\text{reactant}} = (23.56 + 9.75 \times 10^{-3} T) + \frac{29.96 + 4.184 \times 10^{-3} T - 1.67 \times 10^{-5} T^{-2}}{2}$$

Now, from eq (1)

$$\Delta H_{500}^{\circ} = -219.24 \times 10^3 + \int_{298}^{500} [44.35 + 16.74 \times 10^{-3} T - (23.56 + 9.75 \times 10^{-3} T - \frac{29.96 + 4.184 \times 10^{-3} T}{2} + \frac{1.67 \times 10^{-5} T^{-2}}{2})] dT$$

$$\Delta H_{500}^{\circ} = -219.24 \times 10^3 + \left[ \frac{44.35 T + 16.74 \times 10^{-3} T^2}{2} - \frac{23.56 T - 9.75 \times 10^{-3} T^2}{2} - \frac{29.96 T - 4.184 \times 10^{-3} T^2}{2} + \frac{1.67 \times 10^{-5} T^{-1}}{2} \right]_{298}^{500}$$

$$\Delta H_{500}^{\circ} = -219.24 \times 10^3 + \left[ 44.35 T + 8.37 \times 10^{-3} T^2 - 23.56 T - 4.075 \times 10^{-3} T^2 - 14.98 T - 1.046 \times 10^{-3} T^2 + 0.835 \times 10^{-5} T^{-1} \right]_{298}^{500}$$

$$\Delta H_{500}^{\circ} = -219.24 \times 10^3 + [3360.25 - 1668.86]$$

$$\Delta H_{500}^{\circ} = -217558.61 \text{ J/mol} = -217.56 \text{ kJ/mol}$$

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$$\Delta H_{\text{gas}}^{\circ} = 0$$



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Ques-3) In the dead roasting of zinc sulphide, the reaction occurs as  $2<\text{ZnS}> + 3(\text{O}_2) = 2<\text{ZnO}> + 2(\text{SO}_2)$ . With the help of following data, find the heat of reaction at  $25^{\circ}\text{C}$  &  $827^{\circ}\text{C}$ .

$$\text{For ZnS: } \Delta H_{298}^{\circ} = -201.67 \text{ kJ/mol}$$

$$C_p = 50.88 + 5.19 \times 10^{-3} T - 5.69 \times 10^5 T^{-2} \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{For O}_2: C_p = 29.96 + 4.184 \times 10^{-3} T - 1.67 \times 10^5 T^{-2} \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{For ZnO: } \Delta H_{298}^{\circ} = -348.11 \text{ kJ/mol}$$

$$C_p = 48.99 + 5.10 \times 10^{-3} T - 9.12 \times 10^5 T^{-2} \text{ J K}^{-1} \text{ mol}^{-1}$$

$$\text{For SO}_2: \Delta H_{298}^{\circ} = -296.85 \text{ kJ/mol}$$

$$C_p = 43.43 + 10.63 \times 10^{-3} T - 5.94 \times 10^5 T^{-2} \text{ J K}^{-1} \text{ mol}^{-1}$$

Sol-3) At  $25^{\circ}\text{C}$ ,

$$\begin{aligned} \text{Heat of Reaction} &= 2(-348.11) + 2(-296.85) \\ &\quad - 2(-201.67) \cancel{-} \\ &= -886.58 \text{ kJ/mol} \end{aligned}$$

At  $827^{\circ}\text{C}$ ,

$$\Delta H_{1100}^{\circ} = \Delta H_{298}^{\circ} + \int_{298}^{1100} \Delta C_p dT$$

$$\begin{aligned} \Delta C_p_{\text{product}} &= 2(48.99 + 5.10 \times 10^{-3} T - 9.12 \times 10^5 T^{-2}) \\ &\quad + 2(43.43 + 10.63 \times 10^{-3} T - 5.94 \times 10^5 T^{-2}) \end{aligned}$$

$$\begin{aligned} \Delta C_p_{\text{reactant}} &= 2(50.88 + 5.19 \times 10^{-3} T - 5.69 \times 10^5 T^{-2}) \\ &\quad + 3(29.96 + 4.184 \times 10^{-3} T - 1.67 \times 10^5 T^{-2}) \end{aligned}$$

$$\begin{aligned} \Delta C_p &= 97.98 + 10.2 \times 10^{-3} T - 18.24 \times 10^5 T^{-2} + 86.86 \\ &\quad + 21.26 \times 10^{-3} T - 11.88 \times 10^5 T^{-2} - 101.76 - 10.38 \times 10^{-3} T \\ &\quad + 11.38 \times 10^5 T^{-2} - 89.88 - 12.552 \times 10^{-3} T \\ &\quad + 5.01 \times 10^5 T^{-2} \end{aligned}$$

$$\Delta C_p = -6.8 + 8.528 \times 10^{-3} T - 13.73 \times 10^5 T^{-2}$$

$$\Delta H_{1100}^{\circ} = -886.58 \times 10^3 + \int_{298}^{1100} (-6.8 + 8.528 \times 10^{-3} T - 13.73 \times 10^5 T^{-2}) dT$$

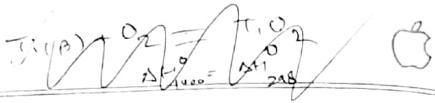
$$= -886580 + \left[ -6.8T + \frac{8.528 \times 10^{-3} T^2}{2} - \frac{13.73 \times 10^5 T^{-1}}{-1} \right]_{298}^{1100}$$

$$< -886580 + \left[ -6.8T + 4.264 \times 10^{-3} T^2 + \frac{13.73 \times 10^5}{T} \right]_{298}^{1100}$$

$$= -886580 + \left[ -1072.38 - 2959.64 \right]$$

$$= -890612 \text{ J/mole}$$

$$= -890 \text{ kJ/mol}$$



Prob 4)  $Ti(\alpha)$  transforms to  $Ti(\beta)$  at  $882^\circ C$  with a heat of transformation equal to  $3473 \text{ J/mol}$ . Calculate the heat of reaction when  $Ti(\beta)$  is oxidized by pure oxygen gas to form  $TiO_2$  at  $1400^\circ C$ .

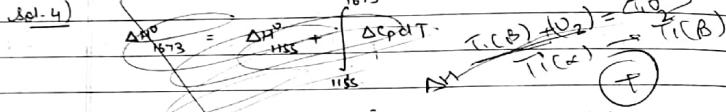
$$\text{Given: } \langle Ti(\alpha) \rangle + (O_2) = \langle TiO_2 \rangle, \Delta H^\circ = -943.49 \text{ J/K/mol}$$

$$C_p \langle Ti(\alpha) \rangle = 22.09 + 10.04 \times 10^3 T \text{ J/K/mol}$$

$$C_p \langle Ti(\beta) \rangle = 28.91 \text{ J/K/mol}$$

$$C_p \langle TiO_2 \rangle = 75.31 + 1.17 \times 10^3 T - 18.2 \times 10^5 T^{-2} \text{ J/K/mol}$$

$$C_p (O_2) = 29.96 + 4.184 \times 10^3 T - 1.67 \times 10^5 T^{-2} \text{ J/K/mol}$$



$$\Delta H^\circ_{1673} = \Delta H^\circ_{298} + \int_{298}^{1155} \Delta C_p dT + 3473 + \int_{1155}^{1673} \Delta C_p dT$$

$$Ti(\beta) \rightarrow Ti(\alpha)$$

for temp range  $298\text{K}$  to  $1155\text{K}$ :

$$\Delta C_p = \Sigma C_p \text{ product} - \Sigma C_p \text{ reactant}$$

$$= (75.31 + 1.17 \times 10^3 T - 18.2 \times 10^5 T^{-2}) - (28.91 + 29.96 + 4.184 \times 10^3 T - 1.67 \times 10^5 T^{-2})$$

$$\Delta C_p = 46.4 \quad 16.44 - 3.014 \times 10^3 T - 16.53 \times 10^5 T^{-2}$$

for temp range from  $1155\text{K}$  to  $1673\text{K}$ :

$$\Delta C_p = \Sigma C_p \text{ product} - \Sigma C_p \text{ reactant}$$

$$= (75.31 + 1.17 \times 10^3 T - 18.2 \times 10^5 T^{-2}) - (22.09 + 10.04 \times 10^3 T - 29.96 + 4.184 \times 10^3 T - 1.67 \times 10^5 T^{-2})$$

$$\Delta C_p = 23.26 - 13.054 \times 10^3 T - 16.53 \times 10^5 T^{-2}$$

$$\Delta H^\circ_{1673} = -943.49 \times 10^3 + \int_{298}^{1155} (16.44 - 3.014 \times 10^3 T - 16.53 \times 10^5 T^{-2}) dT$$

$$+ 3473 + \int_{1155}^{1673} (23.26 - 13.054 \times 10^3 T - 16.53 \times 10^5 T^{-2}) dT$$

$$\Delta H^\circ_{1673} = -940017 + \frac{16.44 T - 3.014 \times 10^3 T^2}{2} - \frac{16.53 \times 10^5 T^{-1}}{-1}$$

$$Ti(\beta) + O_2 \rightarrow TiO_2$$

$$\Delta H^\circ_{1673} = -940017 + \left[ \frac{16.44 T - 1.507 \times 10^3 T^2 + 16.53 \times 10^5}{T} \right]_{298}^{1155}$$

$$\Delta H^\circ_{1673} = -940017 + \left[ \frac{23.26 T - 6.527 \times 10^3 T^2 + 16.53 \times 10^5}{T} \right]_{1155}^{1673}$$

$$\Delta H^\circ_{1673} = -940017 + [18408.99 - 10312.27] + [21633.4 - 19589.29]$$

$$= -936 \text{ kJ/mol}$$

$$\langle T_i(\alpha) \rangle = \langle T_i(\beta) \rangle$$

$$\langle T_i(\alpha) \rangle + (O_2) = \langle T_i(O_2) \rangle$$

Correction

$$\begin{aligned} \Delta H_{1673}^{\circ} &= \Delta H_{298}^{\circ} + \int_{298}^{1155} \Delta C_p dT + 3473 + \int_{1155}^{1673} \Delta C_p dT \\ \Delta H_{1673}^{\circ} &\equiv \Delta H_{298}^{\circ} + \int_{298}^{1155} (28.91 - 22.09 - 10.04 \times 10^{-3} T) dT + 3473 \\ &\quad + \left[ 75.31 + 1.17 \times 10^{-3} T - 1.8 \times 10^{-5} T^2 - 28.91 - 29.96 \right. \\ &\quad \left. - 4.184 \times 10^{-3} T + 1.67 \times 10^{-5} T^2 \right] dT \\ \Rightarrow \Delta H_{1673}^{\circ} &= -943.49 \times 10^3 + \int_{298}^{1155} (6.82 - 10.04 \times 10^{-3} T) dT + 3473 \\ &\quad + \int_{1155}^{1673} (16.44 - 3.014 \times 10^{-3} T - 1.653 \times 10^{-5} T^2) dT \\ \Rightarrow \Delta H_{1673}^{\circ} &= -943.49 \times 10^3 + \left[ \frac{6.82T}{2} - \frac{10.04 \times 10^{-3} T^2}{2} \right]_{298}^{1155} + 3473 \\ &\quad + \left[ \frac{16.44T}{2} - \frac{3.014 \times 10^{-3} T^2}{2} - \frac{1.653 \times 10^{-5} T^3}{-1} \right]_{1155}^{1673} \\ \Rightarrow \Delta H_{1673}^{\circ} &= -943.49 \times 10^3 + \left[ \frac{6.82T}{2} - \frac{5.02 \times 10^{-3} T^2}{2} \right]_{298}^{1155} + 3473 \\ &\quad + \left[ \frac{16.44T}{2} - \frac{1.507 \times 10^{-3} T^2}{2} + \frac{1.653 \times 10^{-5} T^3}{T} \right]_{1155}^{1673} \\ \Rightarrow \Delta H_{1673}^{\circ} &= -943.49 \times 10^3 + \left[ 1180.29 - 1586.56 \right] + 3473 \\ &\quad + [24274.18 - 18408.99] \\ \Delta H_{1673}^{\circ} &= -935 \text{ kJ/mol (Ans)} \end{aligned}$$

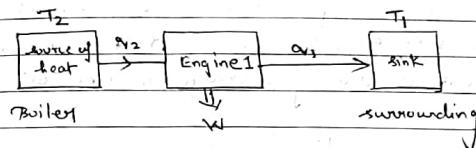


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Second law of Thermodynamics →

Limitation of First Law →

- 1) It does not tell how much of heat is converted into work and vice-versa.
- 2) It does not tell about the feasibility of a process.
- 3) It does not tell about the direction of flow of heat.



$$\text{Efficiency } \eta = \frac{W}{Q_2} = \frac{Q_2 - Q_1}{Q_2}$$

Let us consider another engine which (Engine 2) which is more efficient than Engine 1. So, this can happen in 2 ways :-

Case 1: Suppose, the Engine 2 does more work  $W'$  by absorbing the same amt. of heat  $Q_2$  but rejecting less heat  $Q_1'$  to the surrounding.

$$\text{Thus, } W' > W \text{ and } Q_1' > Q_1$$

Case 2: Suppose, Engine 2 does same work  $W$  but absorbs less heat  $Q_2'$  and also rejects less heat  $Q_1'$  to the surrounding.

$$\text{Thus, } Q_2' < Q_2 \text{ and } Q_1' < Q_1$$

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Let us now assume that forward stroke is carried out by Engine 2 and return stroke by Engine 1.

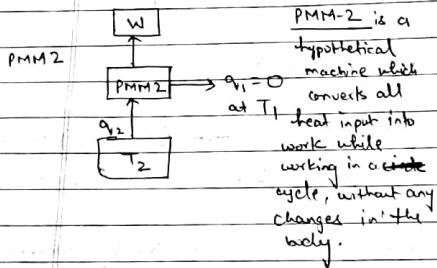
$$\text{Case 1: } W' = q_2 - q_1'$$

$$-W = q_1 - q_2$$

$$W' - W = q_1 - q_1'$$

without any change occurring

But this is contrary to human experiments. Such a process corresponds to PMM-2 i.e. heat is converted into work without leaving a change in any other body.

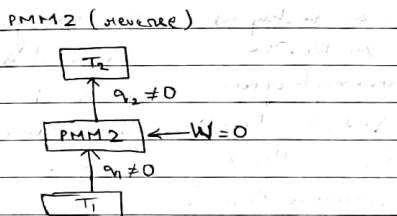


This leads to Kelvin Planck Statement of 2nd Law -  
 "It is impossible by means of a cyclic process to take heat from a reservoir & convert it into work without transferring heat to a cold reservoir."

Case 2: In the forward stroke,  $w_1 = q_2' - q_1'$   
 In the return stroke,  $-w_1 = q_1 - q_2$

$$q_2 - q_2' = q_1 - q_1' = \gamma$$

An amt. of heat  $\gamma$  at one temp.  $T_1$  has been converted to heat at a higher temp.  $T_2$  without any other change occurring. This corresponds to spontaneous flow of heat up a temp. gradient. ~~which is true~~, it is even more contrary to human experiments. (Reverse of PMM-2)



The above leads to Clausius Statement of 2nd Law.  
 "It is impossible to transfer heat from a cold to hot reservoir without converting a certain amt. of work into heat".

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### Spontaneous Process

System

System

System

I In equilibrium

II Not in equilibrium

III In equilibrium

If the system  
is in eq., it  
will like to  
remain in  
eq.

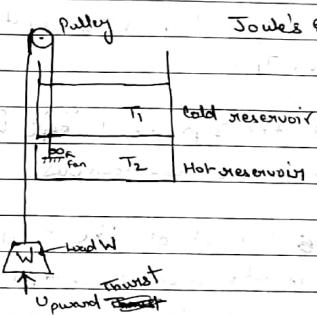
Since the system is  
not in equilibrium,  
the tendency of the  
system will be  
to attain eq.  
as quickly as  
possible. The  
movement of non-  
eq. system towards  
eq. is called a

"Spontaneous Process".

Degradation of Energy - Suppose, a process involves conversion of heat into work. As the system approaches equilibrium, its capacity for doing work is reduced or degraded. As the system approaches equilibrium, some of the work is converted into heat which is lost & hence is not available for useful work. This is known as 'Degradation of Energy'.

since the lost energy cannot be recovered, this is also known as 'degree of irreversibility'.

Quantification of Degradation of Energy or degree of irreversibility  
Since, degradation of energy varies from process to process, it can be quantified.



As ~~soon~~ as the upward thrust is removed, the load W starts falling. Due to fall of weight, the fan starts rotating which does mechanical work. This mechanical work is converted into an amount of heat q. Once, the upward thrust is applied again the process stops. The entire process can be summarised into 3 steps -

Physical Interpretation



Step 1: An amount of heat  $q_1$  is generated in the thermal reservoir  $T_2$  as a result of mechanical work.

Step 2: An amount of heat  $q_2$  is transferred from reservoir  $T_2$  to reservoir  $T_1$  as they are in thermal contact.

Step 3: An amount of heat  $q_3$  is generated in thermal reservoir  $T_1$ .

Since, all the 3 processes <sup>are</sup> happening, all the 3 processes are spontaneous.

A close look at all the 3 steps reveals that Step 3 is the sum of Step 1 and Step 2 which means ~~more~~ degree of irreversibility / degradation of energy is maximum in rate of Step 3 compared to Step 1 or Step 2. The variables involved in this process are  $q_3, T_2$  and  $T_1$ . So,

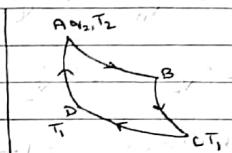
$$\frac{q_3}{T_1} > \frac{q_2}{T_2} \text{ because } T_2 > T_1$$

This means degree of irreversibility is more in case of Step 3 compared to Step 1. This degree of

irreversibility is related to the term entropy.  
 $\therefore \Delta S = \frac{q}{T}$

In differential form,  $dS = \frac{dq_{\text{rev}}}{T}$

Physical Interpretation through Carnot cycle -



Path AB - Reversible Isothermal Expansion

Path BC - Reversible Adiabatic Expansion

$$W_{AB} = RT_2 \ln \frac{V_B}{V_A}$$

Path BC - Reversible Adiabatic expansion

$$W_{BC} = - \int_{T_2}^{T_1} C_v dT = \int_{T_2}^{T_1} C_p dT$$

Path CD - Reversible Isothermal contraction

$$W_{CD} = RT_1 \ln \frac{V_D}{V_C}$$

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Path DA - Reversible Adiabatic Contraction

$$W_{DA} = - \int_{T_1}^{T_2} C_v dT$$

Total work done during the cycle

$$= RT_2 \ln \frac{V_B}{V_A} + \int_{T_1}^{T_2} cvdT + RT_1 \ln \frac{V_D}{V_C} - \int_{T_1}^{T_2} cvdT$$

$$W_{\text{Total}} = RT_2 \ln \frac{V_B}{V_A} + RT_1 \ln \frac{V_B}{V_C}$$

$$W_{\text{Total}} = R T_2 \ln \frac{V_B}{V_A} - R T_1 \ln \frac{V_C}{V_D} \quad \text{--- (1)}$$

Now, Using the substitution  $\frac{T_2}{T_1} = \left(\frac{V_1}{V_2}\right)^{\gamma-1}$

$$\text{for Path B C, } \frac{T_1}{T_2} = \left( \frac{V_B}{V_C} \right)^{\gamma - 1}$$

$$\text{for path DA, } \frac{T_2}{T_1} = \left( \frac{V_D}{V_A} \right)^{1-1} \quad \text{or} \quad \frac{T_1}{T_2} = \left( \frac{V_A}{V_D} \right)^{1-1}$$

$$S_2, \quad \left( \frac{V_B}{V_C} \right)^{n-1} = \left( \frac{V_A}{V_D} \right)^{n-1}$$

$$\Rightarrow \frac{v_B}{v_c} = \frac{v_f}{v_d}$$

$$\Rightarrow \frac{V_B}{V_1} = \frac{V_C}{V_2}$$

$\sqrt{A}$        $\sqrt{B}$

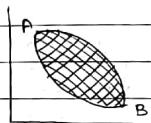
from eq (1),

$$W_{\text{total}} = RT_2 \ln \frac{V_B}{VA} - RT_1 \ln \frac{V_B}{VA}$$

$$W_{\text{Total}} = R \ln \frac{V_B}{V_A} (T_2 - T_1)$$

$$\therefore \eta = \frac{w}{q_2} = \frac{R \ln \frac{V_B}{V_A} (T_2 - T_1)}{R T_2 \ln \frac{V_B}{V_A}} = \frac{T_2 - T_1}{T_2}$$

$$\eta = \frac{T_2 - T_1}{T_2}$$



$$\eta = \frac{\eta_2 - \eta_1}{\eta_2}$$

$$= 1 - \frac{q_1}{q_2} = 1 - \frac{T_1}{T_2}$$

$$\text{or} \quad \frac{q_1}{q_2} = \frac{T_1}{T_2}$$

$$\text{or } \frac{\sigma_1}{T_1} = \frac{\sigma_2}{T_2}$$

$$6Y \frac{q_2}{T_2} - \frac{q_1}{T_1} = 0$$

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Let us divide the Carnot Cycle ABA' into very small Carnot cycles such that the entire path ABA' is covered. fully with Carnot cycles.

$$\oint \frac{\delta q}{T} = 0$$

$$dS = \frac{\delta q_{\text{rev}}}{T}$$

$$\text{i.e. } \Delta S = \frac{q}{T}$$

If  $\Delta S = 0$ , system is in equilibrium

If  $\Delta S > 0$ , (spontaneous)

If  $\Delta S < 0$ , (spontaneous in reverse direction)

Q: Why spontaneity criteria for entropy failed?

A: Determination of  $(\Delta S)_{\text{surroundings}}$  is not error free bcoz surroundings cannot be assumed to be at constant temp.

Combined statement of 1<sup>st</sup> and 2<sup>nd</sup> Law -

$$(1) dU = \delta q - \delta W$$

$$dU = TdS - PdV$$

$$(2) H = U + PV$$

$$dH = dU + PdV + VdP$$

$$dH = TdS - PdV + PdV + VdP$$

$$dH = TdS + VdP$$

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Available Energy = Total Energy - Unavailable Energy

(3) Helmholtz free energy, 'A' = U - TS

$$dA = dU - TdS - SdT$$

$$dA = TdS - PdV - TdS - SdT$$

$$dA = -PdV - SdT$$

(4) Gibbs free energy, G = H - TS

$$dG = dH - TdS - SdT$$

$$dG = TdS + VdP - TdS - SdT$$

$$dG = VdP - SdT$$

∴ There are 4 combined statements of 1<sup>st</sup> and 2<sup>nd</sup> Law

viz. (1)  $dU = TdS - PdV$  (S,V) }  
 (2)  $dH = TdS + VdP$  (S,P) } Variables  
 (3)  $dA = -PdV - SdT$  (V,T) }  
 (4)  $dG = VdP - SdT$  (P,T) }

(Press. & Temp. are controllable)

Maxwell Relations  $\rightarrow$

Let  $z = z(x,y)$  be a state function

$$\text{Then, } dz = \left(\frac{\partial z}{\partial x}\right)_y dx + \left(\frac{\partial z}{\partial y}\right)_x dy$$

$$\text{Let } \left(\frac{\partial z}{\partial x}\right)_y = M, \left(\frac{\partial z}{\partial y}\right)_x = N$$

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Then the equation becomes

$$dz = Mdx + Ndy$$

Now,

$$\frac{\partial}{\partial y} \left( \frac{\partial z}{\partial x} \right)_y = \frac{\partial}{\partial x} \left( \frac{\partial z}{\partial y} \right)_x$$

$$\Rightarrow \frac{\partial^2 z}{\partial y \partial x} = \frac{\partial^2 z}{\partial x \partial y} \quad (\text{since } 'z' \text{ is a state function})$$

$$\text{Therefore, } \left( \frac{\partial M}{\partial y} \right)_x = \left( \frac{\partial N}{\partial x} \right)_y \quad (\text{This is known as Maxwell Relation})$$

Application of Maxwell: One set of variables can be replaced by another set of variables, as per the need.

$$(1) \text{ Now, WKT } dU = TdS - PdV$$

$$dz = Mdx + Ndy$$

$$S_i \left( \frac{\partial T}{\partial V} \right)_S = - \left( \frac{\partial P}{\partial S} \right)_V \quad (1^{\text{st}} \text{ Maxwell Relation})$$

$$(2) dH = TdS + VdP$$

$$\left( \frac{\partial T}{\partial P} \right)_S = \left( \frac{\partial V}{\partial S} \right)_P \quad (2^{\text{nd}} \text{ Maxwell Relation})$$

$$(3) dA = - PdV - SdT$$

$$\left( \frac{\partial P}{\partial T} \right)_V = \left( \frac{\partial S}{\partial V} \right)_T \quad (3^{\text{rd}} \text{ Maxwell Relation})$$

$$(4) dG = VdP - SdT$$

$$\left( \frac{\partial V}{\partial T} \right)_P = - \left( \frac{\partial S}{\partial P} \right)_T \quad (4^{\text{th}} \text{ Maxwell Relation})$$

Ques-5) Small droplets of gold have been observed to supercool by a maximum amount of approx.  $230^{\circ}\text{C}$ . What is the entropy change associated with isothermal solidification of 1 gm-atom of such supercooled liquid? What is the entropy change of the surroundings if they are assumed to remain at the same temperature as the supercooled gold? Also calculate the total entropy change.

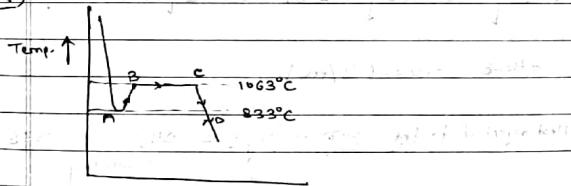
$$\text{Given: } C_p \text{ of Au} = 20.92 \text{ J/K/mol}$$

$$C_p \text{ of Au} = 29.29 \text{ J/K/mol}$$

$$\text{m.p. of Gold} = 1063^{\circ}\text{C}$$

$$\text{Heat of freezing of Gold } \Delta H_f = 12761 \text{ J/mol}$$

Ans)



Time →

(Pure Metal)

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$$(\Delta S)_{\text{system}} = \int_{1106}^{1336} C_p \frac{dT}{T} - \frac{12761}{1336} + \int_{1336}^{1106} C_p \frac{dT}{T}$$

$$= 29.29 \int_{1106}^{1336} \frac{dT}{T} - \frac{12761}{1336} - \int_{1336}^{1106} C_p \frac{dT}{T}$$

$$= 29.29 \ln \frac{1336}{1106} - \frac{12761}{1336} - 20.92 \int_{1106}^{1336} \frac{dT}{T}$$

$$= -4.0179 - 3.9524$$

$$= -7.97 \text{ J/K/mol (Ans)}$$

$$(\Delta H)_{\text{system}} = \int_{1106}^{1336} C_p dT - 12761 + \int_{1336}^{1106} C_p dT$$

$$= 29.29 \int_{1106}^{1336} dT - 12761 - 29.29 \int_{1336}^{1106} dT$$

$$= 29.29 [1336 - 1106] - 12761 - 20.92 [1336 - 1106]$$

$$= -10836 \text{ J/mol}$$

$$\therefore \text{Heat rejected to the surroundings} = (\Delta H)_{\text{surrounding}} = 10836 \text{ J/mol}$$

$$\therefore (\Delta S)_{\text{surrounding}} = \frac{(\Delta H)_{\text{surrounding}}}{T} = \frac{10836}{1106} = 9.79 \text{ J/K/mol (Ans)}$$

$$\therefore \text{Total Entropy change } (\Delta S)_{\text{Total}} = (\Delta S)_{\text{system}} + (\Delta S)_{\text{surrounding}}$$

$$= -7.97 + 9.79$$

$$= 1.82 \text{ J/K/mol (Ans)}$$

**Activity** - Activity is the probability of fraction of atoms (concentration) actually taking part in a reaction. It is denoted by ' $a$ '. For pure solid,  $a = 1$ .

$$a_i = \frac{p_i}{p_i^0} \quad \text{where } p_i = \text{partial pressure of } i\text{th species}$$

$$p_i^0 = \text{partial pressure of } i\text{th species when 'i' is in standard state}$$

$$\text{Under Standard state, } p_i^0 = 1$$

**Fugacity** - For non-ideal gases, the activity term is substituted by the term 'fugacity' which is denoted by 'f'.

In the case of non-ideal gases & substances, activity is defined as the ratio:  ~~$\frac{f_i}{f_i^0}$~~   $f_i$  i.e. activity =  $\frac{f_i}{f_i^0}$  where  $f_i$  is known as fugacity.

$f_i$  = fugacity of  $i$ th species

$f_i^0$  = fugacity of  $i$ th species when 'i' is in standard state.

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When pressure is high & temp. is low, there is large deviation from ideal behavior but at high temp. & low pressure, the deviation is certain minimum.

In pyrometallurgical applications, the temperature is very high & the pressure is lower / very low.

Therefore, the deviation from ideal behaviour is certain minimum. If  $T$  is very high &  $P \rightarrow 0$ .

Then  $f_i \rightarrow p_i$

Thus, we find that  $f_i$  is a substitute for  $P_i$  in case of non-block games.

$$\therefore \delta G = VdP - SdT$$

at constant temp.,

$$dG = vdp = RT \frac{dp}{p} = RT d \ln p = RT d \ln P_i$$

$$\int dG_i = \int_{P_0}^{P_i} RT d\ln P_i$$

$$\Delta G_i = RT \ln \frac{P_i}{P_i^0} = RT \ln a_i$$

RTE \_\_\_\_\_

$Z'$  = total resist property



Thermodynamics of Solution - In case of a closed system, a state can be defined by ~~two~~ a minimum of 2 properties but in case of open system, a third property (composition) must be defined.

$$z' = z' (P, T, \text{composition})$$

where  $Z$  is an extensive thermodynamic function which can be replaced later on by  $\mathcal{Q}, S, H, V$ .

$$\text{Also, } dz' = \left( \frac{\partial z'}{\partial P} \right)_{T, \text{comp}} dP + \left( \frac{\partial z'}{\partial T} \right)_{P, \text{comp}} dT + \left( \frac{\partial z'}{\partial n_i} \right)_{P, T, r} dn_i$$

$$+ \left( \frac{\partial z^1}{\partial n_2} \right) d n_2 + \left( \frac{\partial z^1}{\partial n_3} \right) d n_3 + \dots$$

P, T, n<sub>1</sub>, n<sub>2</sub>, n<sub>3</sub>, ...      P, T, n<sub>1</sub>, n<sub>2</sub>, n<sub>3</sub>, ...  
 except n<sub>2</sub>                                    except n<sub>3</sub>

$n_1, n_2, n_3$  are no of moles of the component

Now, let us replace  $z'$  by  $g'$

$$\text{Hence, } dG' = \left(\frac{\partial G'}{\partial P}\right)_{T, \text{comp}} dP + \left(\frac{\partial G'}{\partial T}\right)_{P, \text{comp}} dT + \left(\frac{\partial G'}{\partial n_i}\right)_{P, T, n_j} dn_i, \text{ except}$$

$$+ \left( \frac{\partial G}{\partial n_2} \right) d n_2 + \left( \frac{\partial G}{\partial n_3} \right) d n_3 + \dots$$

$P, T, n_1, n_2, n_3, \dots$

$\text{except } n_2$

$P, T, n_1, n_2, n_3, \dots$

$\text{except } n_3$

$$\therefore dG = VdP - SdT$$

$$dV, \left(\frac{\partial G'}{\partial P}\right)_{T, \text{comp.}} = V_{\text{ext}}$$

$$\text{and } \left(\frac{\partial G'}{\partial T}\right)_{P, \text{comp.}} = -S$$

$$\therefore dG' = VdP - SdT + \left(\frac{\partial G'}{\partial n_1}\right) dn_1 + \left(\frac{\partial G'}{\partial n_2}\right) dn_2 + \left(\frac{\partial G'}{\partial n_3}\right) dn_3$$

At constant Pressure & Temp:

$$dG' = \left(\frac{\partial G'}{\partial n_1}\right) dn_1 + \left(\frac{\partial G'}{\partial n_2}\right) dn_2 + \left(\frac{\partial G'}{\partial n_3}\right) dn_3 + \dots$$

Lets on!!

$$\text{Generally } \left(\frac{\partial G'}{\partial n_i}\right) = \overline{G}_i = \mu_i$$

chemical Potential  
of 'i'

Partial Molar  
free energy  
of ith species

when infinitesimal  
amount of 'i' goes

into the  
solution

In other words, free  
energy of the solution

will increase by  $\overline{G}_i$  when infinitesimal amount of 'i' goes into  
the solution

$$\Delta G = RT \ln a_i$$

$$\overline{G}_i - G_i^\circ = RT \ln a_i$$

$\downarrow$   
 $\downarrow$   
free energy of  
the species  
when it  
has entered  
the soln.

$$\mu_i - \mu_i^\circ = RT \ln a_i$$

$$\mu_i = \mu_i^\circ + RT \ln a_i$$

Gibbs free Energy criteria for spontaneity -

$$(\Delta S)_{\text{Total}} = (\Delta S)_{\text{system}} + (\Delta S)_{\text{surroundings}}$$

At equilibrium,

$$(\Delta S)_{\text{Total}} = 0$$

$$\therefore 0 = (\Delta S)_{\text{system}} + (\Delta S)_{\text{surroundings}}$$

$$\text{i.e., } (\Delta S)_{\text{surroundings}} = -(\Delta S)_{\text{system}} = -(\Delta H)_{\text{system}}$$

From eq (1) & (2), we can write

$$(\Delta S)_{\text{system}} - (\Delta H)_{\text{system}} = 0 \quad (\text{At equilibrium})$$

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$$\text{or } T(\Delta S)_{\text{system}} - (\Delta H)_{\text{system}} = 0$$

T

$$\text{or } T(\Delta S)_{\text{system}} - (\Delta H)_{\text{system}} = 0 \quad (\text{At equilibrium})$$

For spontaneity criteria based on entropy change,  
 $T(\Delta S)_{\text{system}} - (\Delta H)_{\text{system}} > 0$

$$\text{or } (\Delta H)_{\text{system}} - T(\Delta S)_{\text{system}} < 0$$

Note  
does not involve surroundings  
so calculation is easier

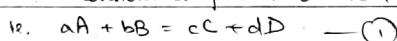
If  $\Delta G$  of the system is negative, process is spontaneous

If  $\Delta G$  is equal to zero, i.e. equilibrium

If  $\Delta G$  is positive, process is spontaneous  
but in reverse direction.

### Gibbs free energy change for a Chemical Reaction

Now, let us consider a general chemical reaction



where A, B are reactants

C, D are products

a, b are the no. of moles of A and B resp. for the overall R<sup>x</sup>

c, d are the no. of moles of C and D resp. for the overall R<sup>x</sup>.

$\mu_A$  = Chemical Potential of A

$\mu_B$  = " " of B

$\mu_C$  = " " of C

$\mu_D$  = " " of D

Let  $\frac{n_A}{n}$  = no. of moles of A at a particular instant

$n_A = -$

$n_B = -$

$n_C = -$

ii. Initial value of free energy

$$G_i = n_A \mu_A + n_B \mu_B + n_C \mu_C + n_D \mu_D \quad (2)$$

Now, let us assume that -

$\delta n_A$  moles of A and  $\delta n_B$  moles of B are consumed to produce  $\delta n_C$  moles of C and  $\delta n_D$  moles of D such that this relationship holds i.e.

$$\frac{\delta n_A}{a} = \frac{\delta n_B}{b} = \frac{\delta n_C}{c} = \frac{\delta n_D}{d} \quad (3)$$

After some certain time t,

$$G_t = (n_A - \delta n_A) \mu_A + (n_B - \delta n_B) \mu_B + (n_C + \delta n_C) \mu_C + (n_D + \delta n_D) \mu_D$$

Now,

Gibbs free energy change

$$\Delta G = G_t - G_i$$

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$$\Delta G = (n_A \mu_A + n_B \mu_B + n_C \mu_C + n_D \mu_D) + (\delta n_C \mu_C + \delta n_D \mu_D - \delta n_A \mu_A - \delta n_B \mu_B) - (n_A \mu_A + n_B \mu_B + n_C \mu_C + n_D \mu_D)$$

$$\Delta G = \delta n_C \mu_C + \delta n_D \mu_D - \delta n_A \mu_A - \delta n_B \mu_B \quad (4)$$

Now from eq(3),  $\delta n_C = \frac{c}{a} \delta n_A$

$$\delta n_D = \frac{d}{a} \delta n_A$$

$$\delta n_B = \frac{b}{a} \delta n_A$$

Now from eq(4),

$$\Delta G = \frac{c}{a} \delta n_A \mu_C + \frac{d}{a} \delta n_A \mu_D - \delta n_A \mu_A - \frac{b}{a} \delta n_A \mu_B$$

$$\Delta G = \frac{\delta n_A}{a} [c \mu_C + d \mu_D - a \mu_A - b \mu_B]$$

At equilibrium

$$\Delta G = 0$$

$$\text{Hence, } c \mu_C + d \mu_D - a \mu_A - b \mu_B = 0 \quad (5)$$

At eq., if the reactants & products are in their standard states then at eq., we can write

$$\Delta G^\circ = c \mu_C^\circ + d \mu_D^\circ - a \mu_A^\circ - b \mu_B^\circ$$

We know that -  $\mu_i = \mu_i^\circ + RT \ln a_i$

So, from eq(5),

$$c(\mu_C^\circ + RT \ln a_C) + d(\mu_D^\circ + RT \ln a_D) - a(\mu_A^\circ + RT \ln a_A) - b(\mu_B^\circ + RT \ln a_B) = 0$$

$$\Rightarrow (c\mu_C^\circ + d\mu_D^\circ - a\mu_A^\circ - b\mu_B^\circ) + [cRT \ln a_C + dRT \ln a_D - aRT \ln a_A - bRT \ln a_B] = 0$$

$$\Rightarrow \Delta G^\circ + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} = 0$$

where  $\frac{a_C^c a_D^d}{a_A^a a_B^b}$  is called  $K_e$  = equilibrium constant

$$\text{Hence, } \Delta G^\circ + RT \ln K_e = 0$$

$$\text{Or, } \boxed{\Delta G^\circ = -RT \ln K_e}$$

$$\Delta G = 0 = \Delta G^\circ + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b}$$

When the system is not at equilibrium, then

$\Delta G \neq 0$ , so the general expression for gibbs free energy change is given as

$$\left( \Delta G = \Delta G^\circ + RT \ln \frac{a_C^c a_D^d}{a_A^a a_B^b} \right)$$

where  $\frac{a_C^c a_D^d}{a_A^a a_B^b}$  is called  $K_a$  = activity quotient.

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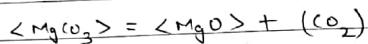


Estimation of  $\Delta G_f^\circ$  at higher temperature -

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S^\circ$$

$$= \left[ \frac{\Delta H^\circ}{298} + \int_{298}^T C_p dT \right] - T \left[ \frac{\Delta S^\circ}{298} + \int_{298}^T \frac{C_p}{T} dT \right]$$

Prob 6) For the Reaction



$$\Delta G^\circ = 117880 - 170.3T$$

Calculate the equilibrium dissociation temp. of  $\text{Mg}(\text{O}_2)$ .

Ans 6)  $\Delta G^\circ = -RT \ln K_e$

$$\Rightarrow 117880 - 170.3T = -8.314 \times T \times \ln \frac{P_{\text{CO}_2} \alpha_{\text{MgO}}}{\alpha_{\text{Mg}(\text{O}_2)}}$$

Assuming  $\text{MgO}$  &  $\text{Mg}(\text{O}_2)$  to be pure initial,

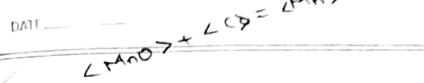
we can take their activity as 1

so,

$$117880 - 170.3T = -8.314 T \ln 1 \quad (\text{At equilibrium} \\ P_{\text{CO}_2} = 1 \text{ atm})$$

$$117880 - 170.3T = 0$$

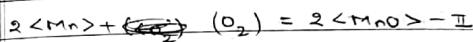
$$T = 692.19 \text{ K (Ans)}$$



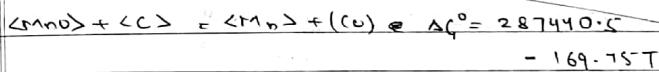
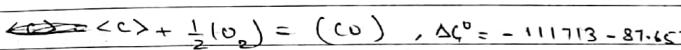
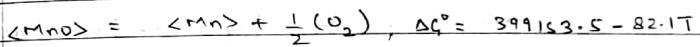
Prob 7) Determine the temp. above or below which reduction of  $\text{MnO}$  by carbon becomes thermodynamically feasible at 1 atm.

Given -

$$2 \langle \text{C} \rangle + \langle \text{O}_2 \rangle = 2 \langle \text{O} \rangle - I \quad \Delta G_I^\circ = -223426 - 175.3 \text{ J}$$



$$\Delta G_{II}^\circ = -798307 + 164.27 \text{ J}$$



$$-RT \ln K_e = 287440.5 - 169.75 \text{ T}$$

$$0 = 287440.5 - 169.75 \text{ T}$$

$$\boxed{T = 1693.32 \text{ K}}$$

Prob-8) Chromium and Carbon present in stainless steel form chromium carbide at  $600^{\circ}\text{C}$ . Show by thermodynamic calculations, which of the metals among Si, Ti & V should be alloyed to stainless steel, so as to prevent the formation of chromium carbide.

Given:

$$3\langle \text{Cr} \rangle + 2\langle \text{C} \rangle = \langle \text{Cr}_3\text{C}_2 \rangle - \text{I}$$

$$\Delta G_1^{\circ} = -87027 - 16.74T$$

$$\langle \text{Si} \rangle + \langle \text{C} \rangle = \langle \text{SiC} \rangle - \text{II}$$

$$\Delta G_2^{\circ} = -53430 + 6.95T$$

$$\langle \text{V} \rangle + \langle \text{C} \rangle = \langle \text{VC} \rangle - \text{III}$$

$$\Delta G_3^{\circ} = -83680 + 6.69T$$

$$\langle \text{Ti} \rangle + \langle \text{C} \rangle = \langle \text{TiC} \rangle - \text{IV}$$

$$\Delta G_4^{\circ} = -188280 + 11.71T$$

$$\Delta G_1^{\circ} = -87027 - 16.74(873) = -101641.02$$

$$\begin{aligned} \Delta G_2^{\circ} &= -53430 + 6.95T = -53430 + (6.95 \times 873) \\ &= -47362.65 \end{aligned}$$

$$\Delta G_3^{\circ} = -83680 + 6.69T = -83680 + (6.69 \times 873)$$

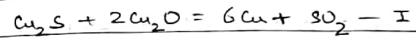
$$= -77839.63$$

$$\Delta G_4^{\circ} = -188280 + 11.71T = -188280 + (11.71 \times 873)$$

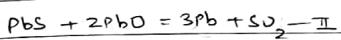
$$= -178057.17$$

So, Ti should be alloyed to stainless steel.

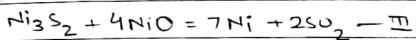
Prob-9) Determine which of the following metals can be produced by the reduction of metal sulphide with metal oxide at  $1000^{\circ}\text{C}$  and 1 atm pressure.



$$\Delta G_{\text{I}}^{\circ} = 119370 + 58.83 \log T - 294.68T$$



$$\begin{aligned} \Delta G_{\text{II}}^{\circ} &= 411873 + 67.36T \log T \\ &\quad - 506.85T \end{aligned}$$



$$\Delta G_{\text{III}}^{\circ} = 584923 - 412.5T$$

$$\Delta G_{\text{I}}^{\circ} = 119370 + 58.83 \log T - 294.68T$$

$$= 119370 + 58.83 \log 1273 - (294.68 \times 1273)$$

$$= -255574.98$$

$$\Delta G_{\text{II}}^{\circ} = 411873 + 67.36T \log T - 506.85T$$

$$= 411873 + (67.36 \times 1273 \log 1273) - (506.85 \times 1273)$$

$$= 32889.75$$

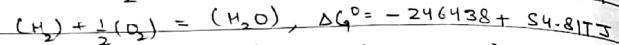
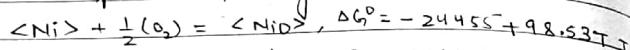
$$\Delta G_{\text{III}}^{\circ} = 584923 - (412.5 \times 1273)$$

$$= 59810.5$$

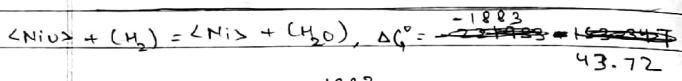
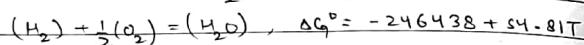
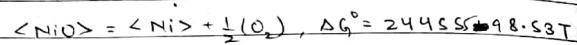
So, copper metal will be produced.

Prob 10) Calculate the equilibrium constant for the reaction  
 $\langle \text{NiO} \rangle + (\text{H}_2) = \langle \text{Ni} \rangle + (\text{H}_2\text{O})$

at  $750^\circ\text{C}$  from the following data



Can pure 'Ni' sheet be annealed at  $750^\circ\text{C}$  in an atmosphere containing 95%  $\text{H}_2\text{O}$  & 5%  $\text{H}_2$  by volume without oxidation?



$$-RT \ln K_e = -\frac{1883}{43.72} T$$

$$-8.314 \times 1023 \ln K_e = -\frac{1883}{43.72} (1023)$$

$$-8505.222 \ln K_e = -65116.18$$

$$\ln K_e = 7.656$$

$$+ 8505.222 \ln K_e = -46608.56$$

$$\ln K_p = 31.358$$

$$- 8505.222 \ln K_e = -46608.56$$

$$K_e = 239.8 \approx 240$$

$$K = \frac{P_{\text{H}_2\text{O}} \cdot a_{\text{Ni}}}{P_{\text{H}_2} \cdot a_{\text{NiO}}}^2$$

$$K = \frac{P_{\text{H}_2\text{O}}}{P_{\text{H}_2}} = \frac{95}{5} = 19$$

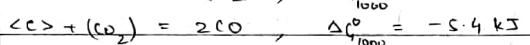
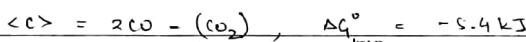
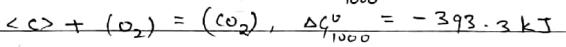
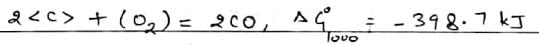
If  $K < K_e \rightarrow$  forward direction

If  $K > K_e \rightarrow$  Reverse direction

Hence  $K < K_e$ , so,  $R^f$  will be in forward direction  
 So, Yes pure 'Ni' sheet can be annealed at  $750^\circ\text{C}$ .

Prob 11) Calculate the  $P_{\text{CO}} / P_{\text{CO}_2}$  ratio in equilibrium with 'C' at  $727^\circ\text{C}$  assuming total pressure to be 2 atm.

Given -



$$K = \frac{(P_{\text{CO}})^2}{a_{\text{C}} P_{\text{CO}_2}}$$

$$\text{For pure solid, } a_{\text{C}} = 1, \text{ so, } K = \frac{P_{\text{CO}}^2}{P_{\text{CO}_2}}$$

$$\Delta f^\circ = -RT \ln K_e$$

$$5.4 \times 1000 = -8.314 \times 1000 \times \ln K_e$$

$$5.4 = 8.314 \ln K_e$$

$$\ln K_e = 0.6495$$

$$K_e = 1.915$$

$$\Rightarrow \frac{p_{CO}^2}{p_{CO_2}} = 1.915$$

$$p_{CO} + p_{CO_2} = 2$$

$$\Rightarrow \frac{p_{CO}^2}{2-p_{CO}} = 1.915$$

$$p_{CO_2} = 2 - p_{CO}$$

$$\Rightarrow p_{CO}^2 = 3.83 - 1.915 p_{CO}$$

$$\Rightarrow p_{CO}^2 + 1.915 p_{CO} - 3.83 = 0$$

$$p_{CO} = -1.915 \pm \sqrt{(1.915)^2 - 4(1)(-3.83)}$$

2(1)

$$p_{CO} = \frac{-1.915 \pm 4.357}{2}$$

$$p_{CO} = 1.221 \quad (\text{Neglecting negative})$$

Now,

$$\frac{p_{CO}}{p_{CO_2}} = \frac{p_{CO}}{2-p_{CO}} = \frac{1.221}{2-1.221} = \frac{1.221}{0.779}$$

$$= 1.56 \quad (1-2)$$

Prob 17)

Will a BF Gas analysing 28% CO, 13% CO<sub>2</sub> and 59% N<sub>2</sub> reduce wustite at 727°C?

Given-

$$\langle FeO \rangle + \frac{1}{2}(O_2) = \langle Fe \rangle, \Delta f^\circ = -259617 + 62.55T J$$

$$\langle CO \rangle + \frac{1}{2}(O_2) = \langle CO_2 \rangle, \Delta f^\circ = -282420 + 86.82T J$$

$$\langle FeO \rangle = \langle Fe \rangle + \frac{1}{2}(O_2), \Delta f^\circ = 259617 - 62.55T J$$

$$\langle CO \rangle + \frac{1}{2}(O_2) = \langle CO_2 \rangle, \Delta f^\circ = -282420 + 86.82T J$$

$$\langle FeO \rangle + \langle CO \rangle = \langle Fe \rangle + \langle CO_2 \rangle, \Delta f^\circ = -22803 + 24.27T J$$

$$-RT \ln K_e = -22803 + 24.27T$$

$$-8.314 \times 1000 \ln K_e = -22803 + 24.27(1000)$$

$$\ln K_e = -0.176$$

$$K_e = 0.838$$

$$\text{Now, } K = \frac{p_{CO_2}}{p_{CO}} = \frac{13}{28} = 0.46$$

$$\therefore K < K_e$$

Hence, the rx will be in forward direction.

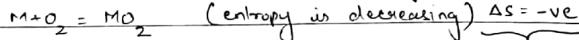
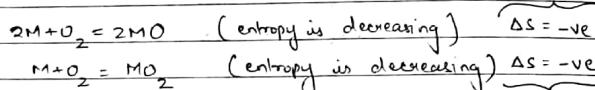
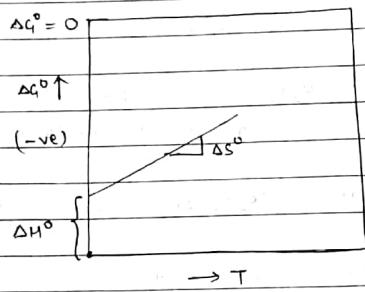
∴ The BF top gas can reduce wustite at 727°C.

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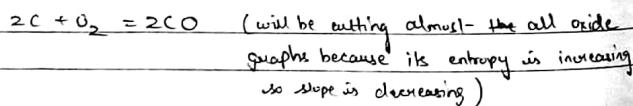
Ellingham Diagrams →

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

$$y = c + xm$$



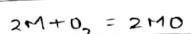
→ Gentle change of slope indicates change of phase  
→ Abrupt change of slope indicates sublimation or condensation.



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1710°C (Silica)  
2050°C (Alumina)

Sustaining Temperature  
(Refractory)



$$\Delta G^\circ = -RT \ln \frac{a_{MO}}{a_M^2 \cdot P_{O_2}}$$

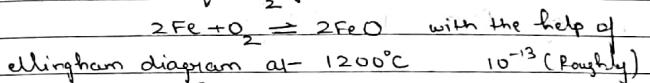
[For pure solid,

$$a_{MO} = 1$$

$$a_M = 1$$

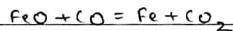
$$\Delta G^\circ = RT \ln P_{O_2}, \text{ if } P_{O_2} = 1 \text{ then } \Delta G^\circ = 0$$

Find the value of  $P_{O_2}$  for the Reaction:



Q. Calculate  $P_{CO}$  using Ellingham Diagram:

$$2CO + O_2 = 2CO_2 \quad K = \frac{P_{CO_2}^2}{P_{CO}^2 P_{O_2}}$$



$$\Delta G^\circ = -19506 + 23.45T$$

Find  $P_{CO}$  at  $1000^\circ C$

$$\text{Method 1: } \Delta G^\circ = -19506 + 23.45T$$

$$\text{Analytically: } -RT \ln K_p = -19506 + 23.45T$$

$$-8.314 \times 1273 \ln K_p = -19506 + 23.45(1273)$$

b.p. of sulphuric  $\rightarrow 444^\circ\text{C}$

$$\Rightarrow K_p = 0.376$$

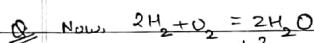
$$\Rightarrow \frac{\alpha_{\text{Fe}} \beta_{\text{CO}_2}}{\alpha_{\text{FeO}} \beta_{\text{CO}}} = 0.376$$

$$\frac{\beta_{\text{CO}_2}}{\beta_{\text{CO}}} = 0.376$$

$$\text{so, } \frac{\beta_{\text{CO}}}{\beta_{\text{CO}_2}} = 2.65$$

Method 2:

Graphically Around  $2/1$  is coming.

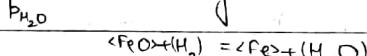


$$K = \frac{\beta_{\text{H}_2\text{O}}^2}{\beta_{\text{H}_2}^2} \quad \text{H}_2 \text{ is not a good reducing agent}$$

because it is unstable & it lies above in the Ellingham

Diagram as compared to CO.

Q Find  $\beta_{\text{H}_2}$  for the following reaction at  $1000^\circ\text{C}$ .



$$\Delta G^\circ = 13180 - 7.74T \text{ J}$$

$$13180 - 7.74T = -RT \ln K_p$$

$$13180 - 7.74(1273) = -8.314 \times 1273 \ln K_p$$

$$K_p = 0.73$$

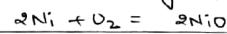
$$\frac{\beta_{\text{H}_2\text{O}} \alpha_{\text{Fe}}}{\beta_{\text{H}_2} \alpha_{\text{FeO}}} = 0.73$$

Considering Fe and FeO to be pure solids, their activity is 1.

$$\text{so, } \frac{\beta_{\text{H}_2\text{O}}}{\beta_{\text{H}_2}} = 0.73$$

$$\text{or } \frac{\beta_{\text{H}_2}}{\beta_{\text{H}_2\text{O}}} = 1.36$$

Find  $\beta_{\text{O}_2}$  for the following reaction at  $1000^\circ\text{C}$



$$\Delta G^\circ = -471200 + 172T \text{ J}$$

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

$$-471200 + 172(1273) = -8.314 \times 1273 \ln K_p$$

$$K_p = 2.24 \times 10^{10}$$

$$\frac{\alpha_{\text{NiO}}^2}{\alpha_{\text{Ni}}^2 \beta_{\text{O}_2}} = 2.24 \times 10^{10}$$

∴ Ni and NiO are pure solids, so their activity is 1.

$$\text{i.e. } \frac{1}{\beta_{\text{O}_2}} = 2.24 \times 10^{10}$$

$$\text{or } \beta_{\text{O}_2} = 4.4 \times 10^{-11} \text{ atm}$$

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### Ellingham Diagram for Sulphides -

1) Carbon cannot reduce sulphide ores because CS analogous to CO line in the case of sulphide diagram barely intersects sulphide lines.

Since, CS line lies at top of the diagram, it means it is not stable.

2) H<sub>2</sub> also cannot reduce sulphides because this line ( $2H_2 + S_2 \rightarrow 2H_2S$ ) lies at the top of sulphide diagram which means H<sub>2</sub>S is not stable hence, sulphide ores can't be reduced by hydrogen.

It is very difficult to dissolve sulphide ores into aqueous media. Hence, hydrometallurgy won't also not feasible. Thus the only way left is to change the chemical composition of the ore by roasting / partial roasting.

④ Calculate  $b_{S_2}$  starting with point S

⑤ Calculate  $b_{H_2}/b_{H_2S}$  starting with point H.

### (Effective Desulphuriser)

Mg is an effective desulphuriser because the compound formed is very stable and it should be economical as well.)

Limitations of ED: ① It assumes all substances are assumed to be in standard state. ② It assumes all the metals are in crystalline state. ③ Activity of a substance in pure state will be different compared to activity of a substance in solution. ④ It does not tell anything about the rate of rx.

⑥ Matte it a miscible sulphide (copper sulphide and iron sulphide) Cu<sub>2</sub>S / FeS because standard free energy formation of both of them is similar.

⑦ Since PbS and FeS are quite far in the sulphide diagram they don't form a matte hence matte-smelting can't be done.

⑧ Cu<sub>2</sub>S and FeS is converted to their respective oxides, but copper oxide and iron oxide lines are closed to each other in oxide diagram if Cu is used as a reducing agent both the oxides will be reduced together, therefore instead of pure copper, an alloy of Fe & Cu will be formed.

⑨ But - PbS and FeS/ZnS can be smelted to PbO and FeO. Both lines are quite apart in the oxide diagram and hence can be reduced separately.

### Third law of Thermodynamics -

$$dS = \int \frac{\delta q_{rev}}{T} = \int \frac{dH}{T} = \int \frac{C_p dT}{T}$$

$$\int \frac{dS}{T} = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

$$S_{T_2} - S_{T_1} = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

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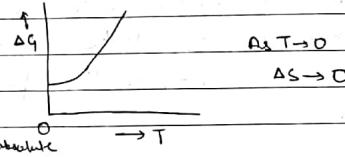
If the Temp. is absolute zero, then

$$S_f - S_0 = \int_0^T \frac{C_p}{T} dT$$

Determination of  $S_0$  (entropy at absolute zero) lead to the development of Third law of Thermodynamics.

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

$$y = c + xm$$

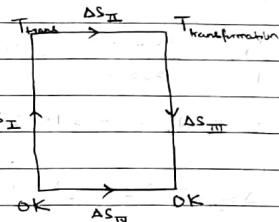


This lead to a statement of a theorem known as Neurath Heat Theorem.

"for all reactions involving substances in condensed state,  $\Delta S$  is zero at 0 Kelvin".

Neurath Heat Theorem was modified by Plank and the statement is-  
third law of Thermodynamics "The entropy of any homogeneous substance which is in complete internal equilibrium, may be taken as zero at 0 Kelvin".

Experimental proof of Third law of Thermodynamics -



$\alpha \rightarrow \beta$

$\alpha, \beta$  = allotropes of a solid

Since, entropy is a state property, so for a cyclic process  $\Delta S$  should be equal to zero.

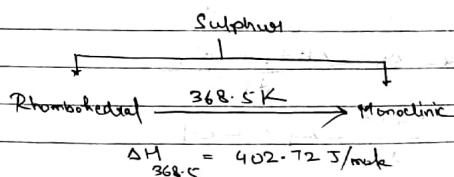
So, this means  $\Delta S_I + \Delta S_{II} + \Delta S_{III} = \Delta S_{IV}$

For third law to be obeyed,  $\Delta S_{IV}$  must be equal to zero.

Then,  $\Delta S_{II} = -(\Delta S_I + \Delta S_{III})$  where  $\Delta S_{II}$  is equal to experimental entropy change and  $-(\Delta S_I + \Delta S_{III})$  is called Third law entropy change.

Acknowledgment

Sulphur exists in 2 allotropic forms: rhombohedral and monoclinic. The transformation temp. is 368.5 K



$$\Delta H_{368.5} = 402.72 \text{ J/mole}$$

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$$\Delta S_I = \int_{368.5}^{\infty} \frac{C_p(Rn)}{T} dT = 36.95 \text{ J/K}$$

$$\Delta S_{II} = \frac{\Delta H_T}{T} = \frac{402.72}{368.5} = 1.09 \text{ J/K}$$

$$\Delta S_{III} = \int_{368.5}^{\infty} \frac{C_p(mn)}{T} dT = -37.92 \text{ J/K}$$

$$\Delta S_I + \Delta S_{III} = (\Delta S_I + \Delta S_{III}) = 0.97 = \Delta S_{II}$$

Thus within experimental range of errors, Third Law of Thermodynamics is verified.

#### Gibbs-Helmholtz Equation

From 4th combined statement of 1st & 2nd Law,

$$dG = Vdp - SdT$$

$$\text{At constant pressure, } \frac{dG}{dT} = -S$$

$$\text{or } \frac{dG}{dT} = -\Delta S$$

We know that,

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

$$\text{or } \Delta G = \Delta H + T\frac{d\Delta S}{dT}$$

~~$$\text{or } \Delta G = \frac{\Delta H dT + T d\Delta S}{dT}$$~~

$$\text{or } \frac{T d\Delta S}{dT} - \Delta S = -\Delta H$$

$$\text{or } \frac{T d\Delta G - \Delta G dT}{dT} = -\Delta H$$

Dividing by  $T^2$  both sides, we get,

$$\frac{T d\Delta G - \Delta G dT}{T^2 dT} = -\frac{\Delta H}{T^2} \quad \left| \begin{array}{l} \frac{d(\frac{x}{y})}{dx} \\ = \frac{y dx - x dy}{y^2} \end{array} \right.$$

$$\text{or } \frac{d(\Delta G/T)}{dT} = -\frac{\Delta H}{T^2}$$

If the substances are in their standard state then,

$$\frac{d(\Delta G^\circ/T)}{dT} = -\frac{\Delta H^\circ}{T^2} \quad (1)$$

This is Gibbs-Helmholtz Equation.

#### Application

The Gibbs-Helmholtz Equation permits the calculation of  $\Delta G^\circ$  for a  $R^x$  at any temp. from its value at another temperature.

We know that,

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

$$\text{from eq(1), } \frac{d(-RT \ln K_p/T)}{dT} = -\frac{\Delta H^\circ}{T^2}$$

$$\left[ \frac{d(\ln K_p)}{dT} = \frac{\Delta H^\circ}{RT^2} \right]$$

Nernst-Hoff Equation

### Application

This indicates that the effect of temp. on equilibrium constant  $K_p$  is determined by the sign and magnitude of  $\Delta H^\circ$  for a rx.

(i) If  $\Delta H^\circ$  is positive, (endothermic) then  $K_p$  will increase with increase in temp.

(ii) If  $\Delta H^\circ$  is negative (exothermic) then  $K_p$  will decrease with increase in temp.

### Claussius-Clapeyron Equation

It is possible to maintain equilibrium b/w solid and liquid phases by simultaneous variation of pressure and temp. in such a manner that  $\Delta G$  remains zero.

$$G_{(l)} = G_{(s)}$$

for infinitesimal changes in P and T,

$$dG_{(l)} = dG_{(s)}$$

Since,

$$dG = VdP - SdT \text{ from 4th combined statement of 1st 2nd law}$$

$$\therefore dG_{(s)} = V_{(s)}dP - S_{(s)}dT$$

$$\text{and } dG_{(l)} = V_{(l)}dP - S_{(l)}dT$$

$$dG_{(l)} = dG_{(s)}$$

$$\Rightarrow V_{(l)}dP - S_{(l)}dT = V_{(s)}dP - S_{(s)}dT$$

$$\text{or } S_{(s)}dT - S_{(l)}dT = V_{(s)}dP - V_{(l)}dP$$

$$\Rightarrow [S_{(s)} - S_{(l)}]dT = [V_{(s)} - V_{(l)}]dP$$

$$\text{or } \frac{dP}{dT} = \frac{[S_{(s)} - S_{(l)}]}{[V_{(s)} - V_{(l)}]}$$

$$\Rightarrow \frac{dP}{dT} = \frac{\Delta S_{l \rightarrow s}}{\Delta V_{l \rightarrow s}}$$

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

$$\text{At equilibrium, } \Delta G = 0$$

$$\therefore \Delta S = \frac{\Delta H}{T}$$

$$\text{or } \left( \frac{dP}{dT} \right)_{eq.} = \frac{\Delta H}{T\Delta V}$$

This is Clausius-Clapeyron Equation.

### Richard's Rule

$$\frac{\Delta H_m}{T_m} = \Delta S_m \approx 2 \text{ cal/deg.}$$

For most of the metals, entropy of melting is approx. equal to 2 cal/deg.

### Taitoun's Rule

$$\frac{\Delta H_v}{T_v} = \Delta S_v \approx 21 \text{ cal/deg.}$$

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For most metallic liquids, entropy of vapourisation is approx. equal to 21 cal/deg.

Continuing from Thermodynamics of solution

Separate!

$$dG' = \bar{G}_1 dn_1 + \bar{G}_2 dn_2 + \bar{G}_3 dn_3 + \dots \quad (1)$$

$$G' = n_1 \bar{G}_1 + n_2 \bar{G}_2 + n_3 \bar{G}_3 + \dots \quad (2)$$

Total Molar energy  $\downarrow$   
Molar Energy for 1 Molar Energy for 2

On differentiation,

$$dG' = n_1 d\bar{G}_1 + n_2 d\bar{G}_2 + n_3 d\bar{G}_3 + \dots + \bar{G}_1 dn_1 + \bar{G}_2 dn_2 + \bar{G}_3 dn_3 + \dots \quad (3)$$

Subtracting eq(1) from eq(3), we get-

$$n_1 d\bar{G}_1 + n_2 d\bar{G}_2 + n_3 d\bar{G}_3 + \dots = 0$$

Dividing by total no. of moles, we get-

$$x_1 d\bar{G}_1 + x_2 d\bar{G}_2 + x_3 d\bar{G}_3 + \dots = 0$$

For a binary solution of 'A' and 'B'

$$x_A d\bar{G}_A + x_B d\bar{G}_B = 0 \quad \text{This is known as Gibbs-Duhem equation.}$$

Application

If the activity of a component at a given composition is known, then activity of the 2nd component at a given composition can be calculated with the help of Gibbs-Duhem equation.

Calculation of  $a_B$  at a given composition ( $x_A = x_A$ ) when  $a_A$  is known:

$$x_A d\bar{G}_A + x_B d\bar{G}_B = 0 \quad \bar{G}_i = RT \ln a_i$$

$$d\bar{G}_i = RT d\ln a_i$$

$$\Rightarrow x_A \cdot RT d\ln a_A + x_B \cdot RT d\ln a_B = 0$$

$$\Rightarrow x_A d\ln a_A + x_B d\ln a_B = 0 \quad (1)$$

$$\Rightarrow d\ln a_A = - \frac{x_B}{x_A} d\ln a_B$$

$$\text{Now, } \int_{x_A=1}^{x_A=x_A} d\ln a_A = - \int_{x_A=1}^{x_A=x_A} \frac{x_B}{x_A} d\ln a_B$$

The upper limit will be obviously  $x_A = x_A$  because we are calculating  $a_A$  at  $x_A = x_A$ .

The lower limit should be such that atleast the value of  $a_A$  is known. So, we keep the lower limit as  $x_A = 1$ .

$$\text{Now, LHS} = \left. \ln a_A \right|_{x_A=1} - \left. \ln a_A \right|_{x_A=1} \quad \text{at } x_A = 1 \\ \ln a_A = 0$$

$$\left. \ln a_A \right|_{x_A=1} = \ln a_A$$

$$\left. \ln a_A \right|_{x_A=1} = \ln a$$

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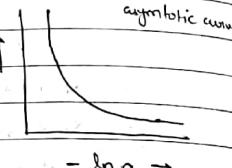


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$$\text{d}x_B \left. \ln \gamma_A \right|_{x_A=x_A} = - \int_{x_A}^{x_B} \frac{x_B}{x_A} d \ln \gamma_B$$

Since the nature of the curve is asymptotic, the calculation of area under the curve will be full of errors. Hence, activity calculation will also be full of errors.



$$\frac{x_B}{x_A} = \frac{1-x_A}{x_A}$$

If  $x_A \rightarrow 1$ ,  $\frac{x_B}{x_A} \rightarrow 0$  } That's why curve is going parallel to y-axis.  
If  $x_A \rightarrow 0$ ,  $\frac{x_B}{x_A} \rightarrow \infty$

Again,

If  $x_A \rightarrow 1$   
then  $x_B \rightarrow 0$  } That's why curve is going parallel to x-axis.  
then  $a_B \rightarrow 0$   
 $\ln(0) = -\infty$

We know that,

$$x_A + x_B = 1$$

on differentiation,  $d x_A + d x_B = 0$ 

Now, multiplying and dividing by  $x_A$  the first term by  $x_A$ . Also, multiplying and dividing the second term by  $x_B$ , we get-

$$x_A \frac{d x_A}{x_A} + x_B \frac{d x_B}{x_B} = 0$$

$$\Rightarrow x_A d \ln \gamma_A + x_B d \ln \gamma_B = 0 \quad (2)$$

Now, subtracting eq(2) from eq(1), we get

$$x_A d \ln \gamma_A + x_B d \ln \gamma_B = 0 \quad \text{where } \gamma_i = \frac{a_i}{x_i}$$

$$\Rightarrow d \ln \gamma_A = - \frac{x_B}{x_A} d \ln \gamma_B$$

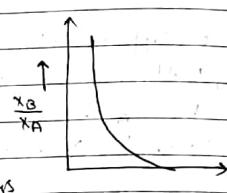
$$\text{Now, } \int d \ln \gamma_A = - \int \frac{x_B}{x_A} d \ln \gamma_B$$

$$\text{LHS} = \ln \gamma_A \Big|_{x_A=x_A} - \ln \gamma_A \Big|_{x_A=1} \quad \begin{array}{l} x_A=x_A \\ x_A=1 \end{array} \quad \therefore \gamma_A = 1$$

$$= \ln \gamma_A \Big|_{x_A=x_A} \quad \text{So, } \ln \gamma_A = 0$$

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$$\text{So, } \ln \gamma_A = - \int_{x_n=1}^{x_n=x_A} \frac{x_B}{x_A} d \ln \gamma_B$$



For X-axis: Since, activity coefficient  $\gamma$  has always a finite value,  $-\ln \gamma_B$  has also will always have a finite value. This means the curve will intersect at some point on the X-axis.

$$\text{For Y-axis: } \frac{x_B}{x_A} \quad \text{If } x_A \rightarrow 1 \text{, then } \frac{x_B}{x_A} \rightarrow 0$$

$$\text{If } x_A = 0 \text{, then } \frac{x_B}{x_A} \rightarrow \infty$$

Since the curve is still asymptotic, the calculation of area under curve is still error prone.

$\therefore$  calculation of activity is not error free

Now,

$$x_A d \ln \gamma_A + x_B d \ln \gamma_B = 0$$

dividing by  $d x_B$  both sides, we get-

$$x_A \frac{d \ln \gamma_A}{d x_B} + x_B \frac{d \ln \gamma_B}{d x_B} = 0$$

$$\Rightarrow d \ln \gamma_A = - \frac{x_B}{x_A} \frac{d \ln \gamma_B}{d x_B} \cdot d x_B$$

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$$\text{So, } \int d \ln \gamma_A = - \int_{x_n=1}^{x_n=x_A} \frac{x_B}{x_A} \frac{d \ln \gamma_B}{d x_B} \cdot d x_B$$

$$\text{Again, } \ln \gamma_A = - \int_{x_n=x_A}^{x_n=x_A} \frac{x_B}{x_A} \frac{d \ln \gamma_B}{d x_B} \cdot d x_B$$

$$\text{Note:- } \frac{d}{dx} [f(x) g(x)] = g(x) f'(x) + f(x) g'(x)$$

$$f(x) g(x) = \frac{d}{dx} [f(x) g(x)] - f'(x) g(x)$$

on integration,

$$\int f(x) g(x) = \int \frac{d}{dx} [f(x) g(x)] - \int f'(x) g(x)$$

$$\int f(x) g'(x) dx = f(x) g(x) - \int g(x) f'(x) dx$$

$$\text{or } \int u v' dx = u v - \int u' v dx$$

$$\int v \frac{du}{dx} dx = u v - \int u \frac{dv}{dx} dx$$

$$\text{Let } U = \ln \gamma_B$$

$$\text{and } V = \frac{x_B}{x_A}$$

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Ques,

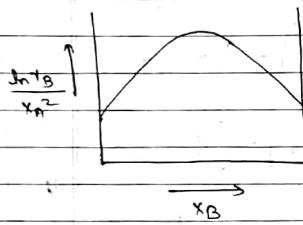
$$\ln \gamma_B = - \int_{x_A}^{x_B} \frac{dx_B}{x_A} \frac{d \ln \gamma_B}{dx_B} = - \left[ \frac{x_B \ln \gamma_B}{x_A} \right] + \int_{x_A=1}^{x_A=x_A} \frac{d \ln \gamma_B}{dx_B} \cdot dx_B$$

$$= - \left[ \frac{x_B \ln \gamma_B}{x_A} \right] + \int_{x_A=1}^{x_A=x_A} \frac{d \ln \gamma_B}{x_A^2} dx_B$$

$$d(\frac{\gamma_B}{y}) = \frac{y dy - x_B dx_B}{y^2}$$

$$d(\frac{x_B}{x_A}) = x_A dx_B - x_B dx_A$$

$$dx_B = \frac{x_A^2 dy_B}{x_A^2 dx_B}$$



$$\begin{aligned} \frac{x_B \ln \gamma_B}{x_A^2} &= x_B dx_B + x_B dy_B \\ \frac{x_B \ln \gamma_B}{x_A^2 dx_B} &= 0 \\ \frac{x_B \ln \gamma_B}{x_A^2 dx_B} &= -\frac{dy_B}{dx_B} \\ \frac{1}{x_A^2 dx_B} &= (x_A + x_B) dx_B = \frac{1}{x_A^2} \end{aligned}$$

Prob-1 The activities of copper in Al-Cu alloys at 1100°C are given below -

$x_{Al}$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8
$a_{Cu}$	0.86	0.61	0.34	0.18	0.08	0.045	0.02	0.01

Calculate activity of 'Al' containing 5 atom% 'Al' at 1100°C.

$$\ln \gamma_A = - \left[ \frac{x_B \ln \gamma_B}{x_A} \right] + \int_{x_A=1}^{x_A=x_A} \frac{d \ln \gamma_B}{x_A^2} dx_B$$

$$\text{or } \ln \gamma_{Al} = - \left[ \frac{x_{Cu} \ln \gamma_{Cu}}{x_{Al}} \right] + \int_{x_{Al}=0.05}^{x_{Al}=0.05} \frac{d \ln \gamma_{Cu}}{x_{Al}^2} dx_{Cu}$$

$$\text{or } \ln \gamma_{Al} = - \left[ \frac{x_{Cu} \ln \gamma_{Cu}}{x_{Al}} \right] + \int_{x_{Al}=0.05}^{x_{Al}=0.95} \frac{d \ln \gamma_{Cu}}{x_{Al}^2} dx_{Cu}$$

$x_{Al}$	$x_{Cu}$	$a_{Cu}$	$\gamma_{Cu} = \frac{a_{Cu}}{x_{Cu}}$	$\ln \gamma_{Cu}$	$\ln \gamma_{Cu}$
0.05	0.95	0.05	0.0005	-4.679	-4.679
0.1	0.9	0.86	0.005	-0.05	-0.05
0.2	0.8	0.61	0.012	-0.21	-0.21
0.3	0.7	0.34	0.024	-0.723	-0.723
0.4	0.6	0.18	0.03	-1.203	-1.203
0.5	0.5	0.08	0.016	-1.832	-1.832
0.6	0.4	0.045	0.01125	-2.185	-2.185
0.7	0.3	0.02	0.0066	-2.718	-2.718
0.8	0.2	0.01	0.005	-4.679	-4.679

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$$\begin{aligned}
 & R.W. \ln \gamma_{Cu} = ? \quad x_{Cu} = 0.95 \\
 & \frac{\ln \gamma_{Cu}}{x_{Cu}} = -4.5 \\
 & \ln \gamma_{Cu} = -4.5 \times (1 - 0.95)^2 \\
 & = -0.01125
 \end{aligned}$$

$x_i$	$y_i$	
$x_0$ 0.00	- 3.80	$y_0$
$x_1$ 0.05	- 4.05	$y_1$
$x_2$ 0.10	- 4.25	$y_2$
$x_3$ 0.15	- 4.45	$y_3$
$x_4$ 0.20	- 4.70	$y_4$
$x_5$ 0.25	- 5.10	$y_5$
$x_6$ 0.30	- 5.50	$y_6$
$x_7$ 0.35	- 5.80	$y_7$
$x_8$ 0.40	- 6.10	$y_8$
$x_9$ 0.45	- 6.90	$y_9$
$x_{10}$ 0.50	- 7.30	$y_{10}$
$x_{11}$ 0.55	- 7.40	$y_{11}$
$x_{12}$ 0.60	- 7.50	$y_{12}$
$x_{13}$ 0.65	- 7.75	$y_{13}$
$x_{14}$ 0.70	- 8.00	$y_{14}$
$x_{15}$ 0.75	- 7.60	$y_{15}$
$x_{16}$ 0.80	- 6.70	$y_{16}$
$x_{17}$ 0.85	- 6.00	$y_{17}$
$x_{18}$ 0.90	- 5.00	$y_{18}$
$x_{19}$ 0.95	- 4.50	$y_{19}$

$$\text{Now, } \ln \gamma_{Al} = - \left[ \frac{x_{Cu} \ln \gamma_{Cu}}{x_{Al}} \right] + \left[ \frac{\ln \gamma_{Cu} d x_{Cu}}{x_{Cu}^2} \right] \quad x_{Cu} = 0.95$$

$$= - \left[ \frac{0.95}{0.05} (-0.01125) \right] + (-5.94)$$

$$= 0.21375 - 5.94$$

$$= -5.73 \quad \text{So, } \gamma_{Al} = \frac{3.25 \times 10^{-3}}{3.25 \times 10^{-3}} x^{0.05} = 1.625 \times 10^{-9}$$

Prob-2 Calculate the activity of Tin in an Al-Sn alloy (Ans) containing 40 atom % Tin at 727°C from the following data -

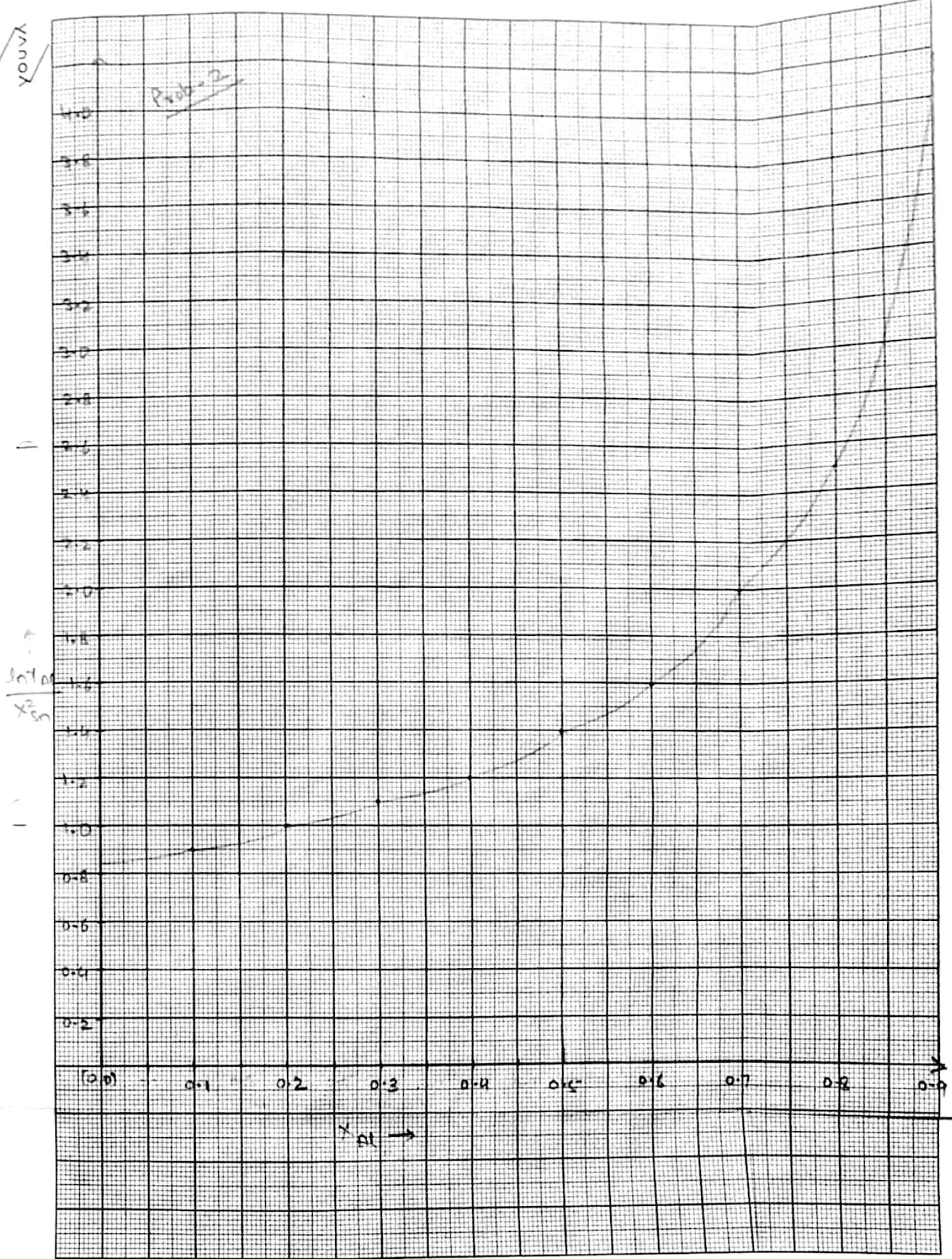
$x_{Al}$	0.9	0.8	0.7	0.6	0.5	0.4	0.3	0.2	0.1
$\gamma_{Al}$	1.041	1.106	1.199	1.292	1.415	1.557	1.722	1.933	2.148

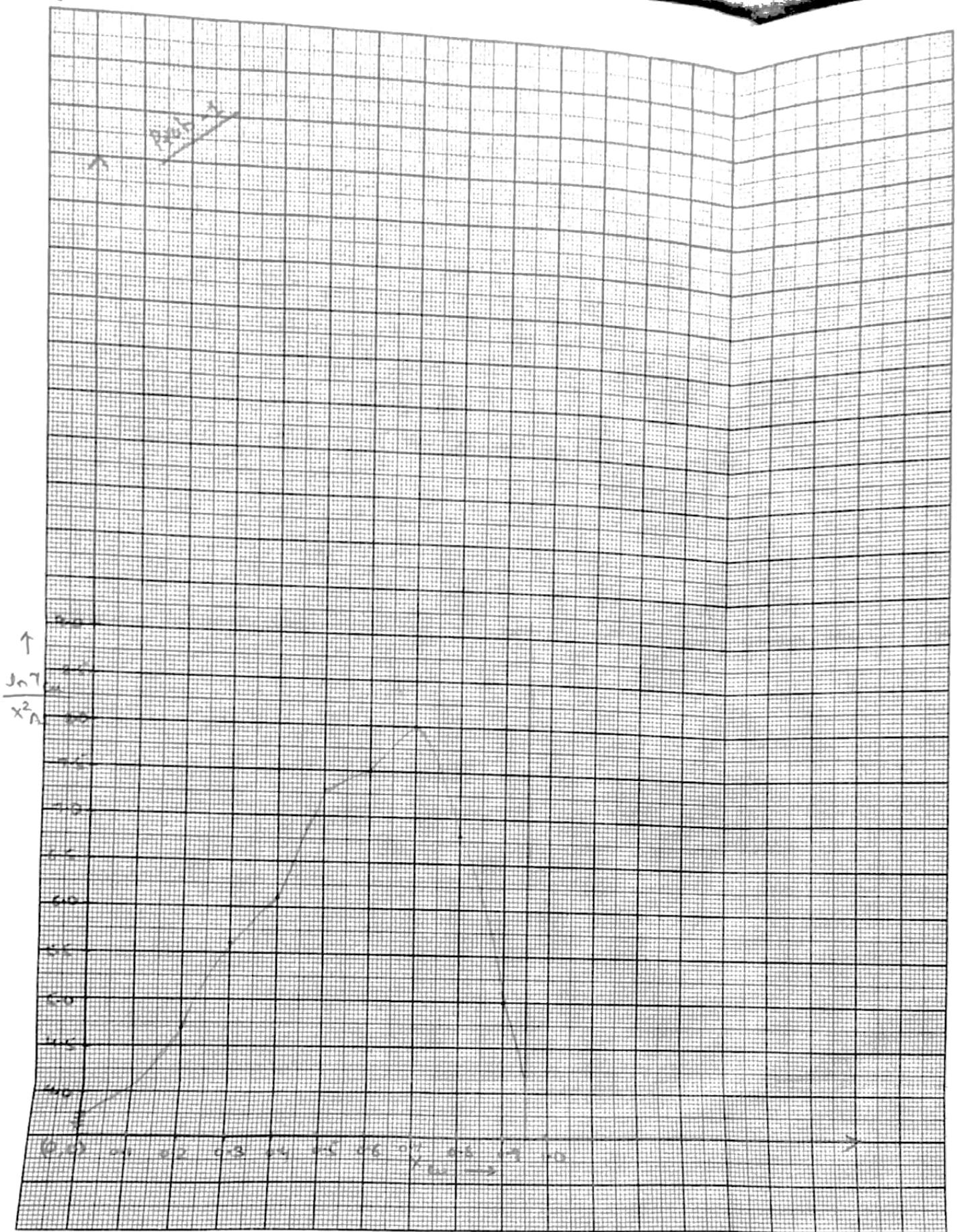
$$\text{Sol-2 } \ln \gamma_A = - \left[ \frac{x_B \ln \gamma_B}{x_A} \right] + \left[ \frac{\ln \gamma_B d x_B}{x_A^2} \right] \quad x_A = x_A$$

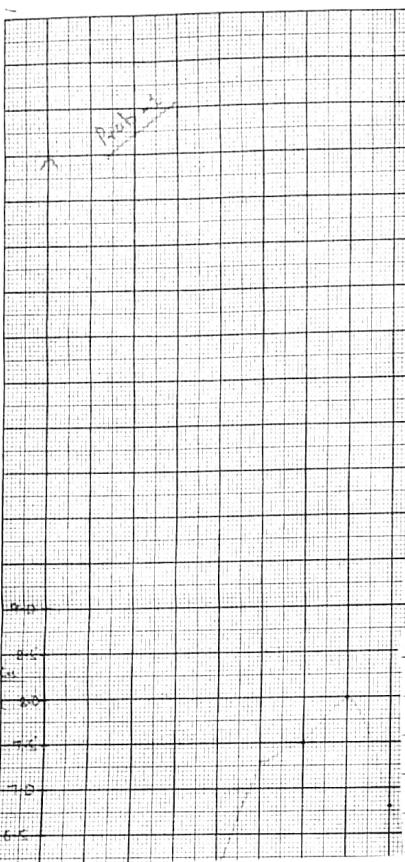
Here, A = Sn and B = Al

$$\text{Now, } \ln \gamma_{Sn} = - \left[ \frac{x_{Al} \ln \gamma_{Al}}{x_{Sn}} \right] + \left[ \frac{\ln \gamma_{Al} d x_{Al}}{x_{Sn}^2} \right] \quad x_{Sn} = 0.4$$

$$= - \left[ \frac{x_{Al} \ln \gamma_{Al}}{x_{Sn}} \right] + \left[ \frac{\ln \gamma_{Al} d x_{Al}}{x_{Sn}^2} \right] \quad x_{Al} = 0.6$$







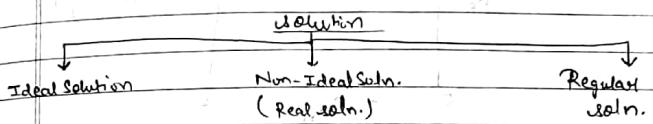
Teacher's Signature

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### Solution-

A soln. is a homogeneous mixture (single phase) in which suitable addition of solutes can be made without precipitation of a second phase.



### Raoult's Law of Relative Lowering of Vapour Pressure:

The relative lowering of vapour pressure of a solvent is equal to the mole fraction of the solute added.

Let us consider a binary soln. of 'A' and 'B' where 'A' is the solvent and 'B' is the solute.

$P_A - P_A^0 = \frac{P_A}{P_A^0}$  Vapour pressure of pure A

$P_A =$  Vapour pressure of A when solute B is added.

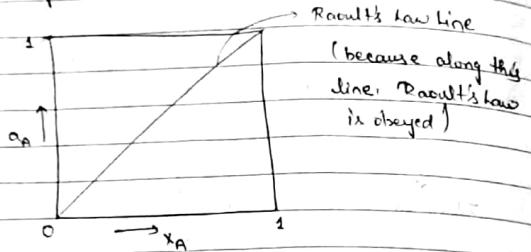
$$\frac{P_A^0 - P_A}{P_A^0} = x_B$$

$$\Rightarrow 1 - \frac{P_A}{P_A^0} = x_B$$

$$\Rightarrow \frac{P_A}{P_A^0} = 1 - x_B = x_A$$

$$\text{i.e. } \alpha_A = x_A$$

In the case of Ideal soln.,  $a_A = x_A$



Raoult's law line  
(because along this line, Raoult's law is obeyed)

In the case of Real soln.,  $a_i \neq x_i$

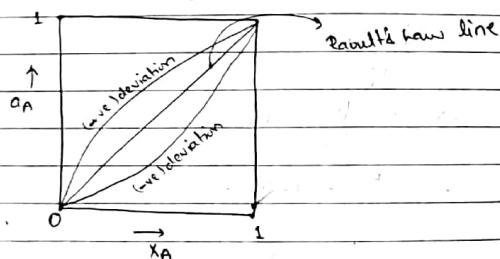
ie.,  $a_i = \gamma_i x_i$  where

$\gamma_i$  is known as activity coefficient of component i

Now,  $\gamma_i$  can be less than 1 or more than 1.

If  $\gamma_i < 1$ , there will be -ve deviation

If  $\gamma_i > 1$ , there will be +ve deviation



Henry's Law: Henry's law is for dilute solution and states that partial pressure of a solute in a solution is proportional to the mole fraction of the solute in the solution.

$$\text{ie. } p_B \propto x_B$$

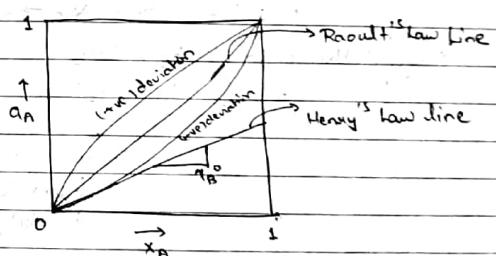
$$\text{or, } p_B = K_B x_B$$

$$\text{Now, } \frac{p_B}{p_B^0} = \frac{K_B x_B}{p_B^0}$$

$$\text{or } a_B = \gamma_B^0 x_B$$

↓  
Henry's Law Constant-

(also called as Raoultian activity coefficient in case of dilute soln.)



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### Alternate Standard State -

Henry's law provides 2 choices for standard state other than conventional standard state. Conventional standard state is applied in case of Raoult's law.

(1) Atom-% standard state, infinitely dilute solution

$$h_B = x_B \text{ when } x_B \rightarrow 0$$

where  $h_B$  is known as Henrian activity of B.

Beyond Henry's law,  $h_B \neq x_B$

$$\text{Now, now } h_B = f_B x_B$$

↓  
Henrian activity coefficient of  
B.

(2) Weight-% standard state, infinitely dilute solution.

$$h_B = w_B \text{ when } w_B \rightarrow 0$$

Beyond Henry's law,  $h_B \neq w_B$

$$\text{Now, now } h_B = f_B w_B$$

↓  
Henrian activity coefficient of  
B (weight-% standard state,  
infinitely dilute solution).

(3) 1 weight-% standard state, infinitely dilute solution -

- It is assumed (hypothetically) that Henry's law is valid upto 1 weight % (i.e.  $w_B = 1$ )

$$h_B = 1 \text{ at } w_B = 1$$

The value of  $\Delta G^\circ$  available in the literature is for conventional standard state. In case of alternate standard state, therefore this  $\Delta G^\circ$  value must be converted into  $\Delta G$  value of the alternate standard state.

# Prove that in case of a Binary solution; if the solute obeys Henry's law, the solvent will obey Raoult's law since, the solute follows Henry's law we have,  $a_B = f_B^\circ x_B$

Taking logarithm both sides, we get

$$\ln a_B = \ln f_B^\circ + \ln x_B$$

On differentiation,

$$d \ln a_B = d \ln x_B \quad \dots \dots \dots (1)$$

Inserting this into Gibbs-Duhem equation

$$\text{WKT, } x_A d\bar{G}_A + x_B d\bar{G}_B = 0$$

$$\text{where, } d\bar{G}_A = RT d \ln a_A$$

$$\text{and } d\bar{G}_B = RT d \ln a_B$$

So now,

$$x_A RT d \ln a_A + x_B RT d \ln a_B = 0$$

$$\Rightarrow x_A d \ln a_A + x_B d \ln x_B = 0$$

$$\Rightarrow d\ln \alpha_A = -\frac{x_B}{x_A} dx_B$$

$$= -\frac{x_B}{x_A} \frac{1}{x_B} dx_B$$

$$= -\frac{dx_B}{x_A} = \frac{dx_A}{x_A} = d\ln x_A$$

On Integration, we get-

$$\ln \alpha_A = \ln x_A + \ln K$$

Integration constant

$$\ln \alpha_A = \text{constant. } \ln x_A$$

~~Int.~~

By definition,  $\alpha_i = 1$  when  $x_i = 1$

$$\text{thus, } \therefore K = 1$$

$$\text{thus, } \ln \alpha_A = \ln x_A$$

$$\text{or } \alpha_A = x_A$$

For a binary (A-B) solution,

$$\text{wt.\% B} = \frac{\text{atom\% B} \times M_B}{(\text{atom\% A} \times M_A + \text{atom\% B} \times M_B)} \times 100$$

$$\text{atom\% B} = \frac{\frac{\text{wt.\% B}}{M_B}}{\left[ \frac{\text{wt.\% A}}{M_A} + \frac{\text{wt.\% B}}{M_B} \right]} \times 100$$

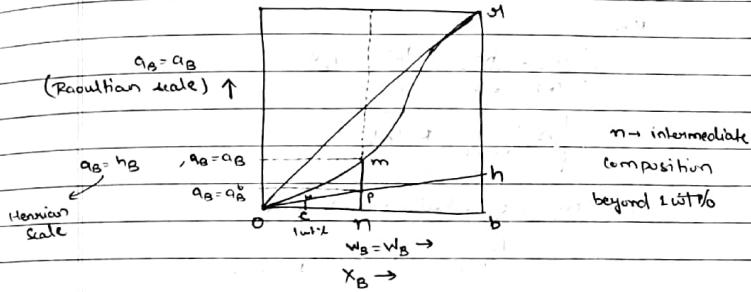
In case of infinitely dilute soln,  $\frac{\text{wt.\% B}}{M_B}$  can be neglected,

$$\text{so, atom\% B} = \frac{\text{wt.\% B} \times M_A}{M_B \times 100}$$

$$\text{If wt.\% B} = 1 \text{ wt.\%}$$

$$\text{Then, atom\% B} = \frac{M_A}{100 M_B}$$

~~if wt.\% B  $\neq$  1 wt.~~ Thus, there will be no need of converting of % WB into atom\%.

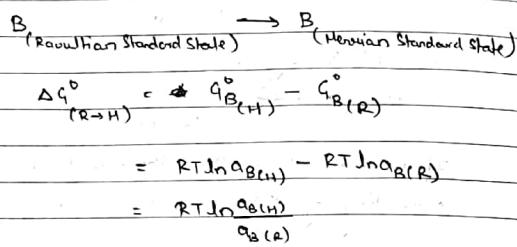


Let us consider similar  $\Delta S_{OCW}$  and  $\Delta S_{OB}$

$$\frac{w_C}{h_B} = \frac{\Delta S_{OC}}{\Delta S_{OB}} = \frac{x_B}{1} = \frac{1 \text{ wt.\% B} \times M_A}{100 M_B} = \frac{M_A}{100 M_B}$$

Thus, the value of  $K$  for any  $R^*$  depends upon the choice of standard states for the  $R^*$  components. Similarly,  $\Delta G^\circ$  for the  $R^*$  depends upon the choice of standard states.

hence, in order to convert from the use of standard state to another, it is necessary that free energy difference is b/w various standard states  $\gamma_B^\circ$

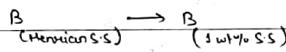


Now,

$$\frac{\alpha_{B(H)}}{\alpha_{B(R)}} = \frac{nb}{nb} = \frac{\gamma_B^\circ}{1} = \gamma_B^\circ$$

$$\therefore \Delta G^\circ_{(R \rightarrow H)} = RT \ln \gamma_B^\circ$$

If the change of standard state is from



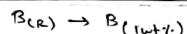
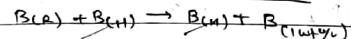
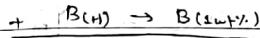
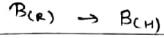
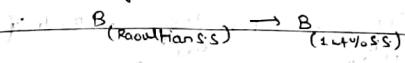
$$\begin{aligned} \Delta G^\circ_{(H \rightarrow 1wt\%)} &= \gamma_B^\circ_{(1wt\% S.S.)} - \gamma_B^\circ_{(Henrian\ S.S.)} \\ &= RT \ln \frac{\gamma_B^\circ_{(1wt\% S.S.)}}{\gamma_B^\circ_{(Henrian\ S.S.)}} \end{aligned}$$

Now,

$$\frac{\gamma_B^\circ_{(1wt\%)}}{\gamma_B^\circ_{(Henrian)}} = \frac{nb}{nb} = \frac{nb}{nb} = \frac{MA}{100MB}$$

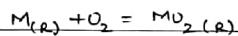
$$\therefore \Delta G^\circ_{(H \rightarrow 1wt\%)} = RT \ln \frac{MA}{100MB}$$

If the change of standard state is from



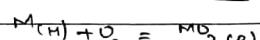
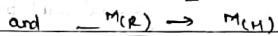
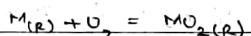
$$\therefore \Delta G^\circ_{(R \rightarrow 1wt\%)} = RT \ln \frac{\gamma_B^\circ MA}{100 MB}$$

Let us consider the oxidation of metal M to oxide  $MO_2$  at temperature T



$$\Delta G^\circ_{(R)} = -RT \ln \frac{AMO_2(R)}{A_{M(R)} P_{O_2}}$$

If 'M' occurs in dilute usm, it may be more convenient to use Henrian S.S. for M



$$\text{Hence, } \Delta G^\circ_H = \Delta G^\circ_{(R)} - \Delta G^\circ_{(R \rightarrow H)}$$

$$\Rightarrow -RT \ln K_b = -RT \ln K_e - RT \ln \gamma_m^\circ$$

$$\Rightarrow RT \ln \frac{a_{M\text{O}_2}}{h_M P_{O_2}} = RT \ln \frac{a_{M\text{O}_2}}{a_M P_{O_2}} + RT \ln \gamma_m^\circ$$

$$\Rightarrow \ln \frac{a_{M\text{O}_2}}{h_M P_{O_2}} = \ln \frac{a_{M\text{O}_2}}{a_M P_{O_2}} + \ln \gamma_m^\circ$$

$$\Rightarrow \frac{a_{M\text{O}_2}}{h_M P_{O_2}} = \frac{a_{M\text{O}_2} \cdot \gamma_m^\circ}{a_M \cdot P_{O_2}}$$

or  $a_M = h_M \gamma_m^\circ / M$

Relation b/w Raoultian activity and Henry's activity.

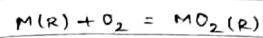
$$m_n = h_B$$

$$b_n = w_B$$

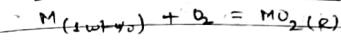
$$\text{Hence, } \frac{m_n}{b_n} = \frac{h_B}{w_B} = \frac{a_B}{a_B^\circ}$$

$$\Rightarrow \frac{a_B}{h_B} = \frac{a_B^\circ}{w_B} = \frac{\gamma_B^\circ w_B}{w_B}$$

$$\Rightarrow a_B = \gamma_B^\circ \cdot h_B \quad (\text{ie. If } w_B \text{ is beyond } 1\%, \text{ result will be the same})$$



$$M(R) = M(1 \text{ wt\%})$$



$$\Delta G^\circ(1 \text{ wt\%}) = \Delta G^\circ_{(R)} - \Delta G^\circ_{(R \rightarrow 1 \text{ wt\%})}$$

$$-RT \ln K(1 \text{ wt\%}) = -RT \ln K_{(R)} - RT \ln \gamma_M^\circ M_A$$

100MM

$$\ln \frac{a_{M\text{O}_2}}{f_M(1 \text{ wt\%}) P_{O_2}} = \ln \frac{a_{M\text{O}_2}}{a_M P_{O_2}} - \frac{\gamma_M^\circ M_A}{100MM}$$

$$\frac{a_{M\text{O}_2}}{f_M(1 \text{ wt\%}) P_{O_2}} = \frac{a_{M\text{O}_2} \cdot \gamma_M^\circ M_A}{a_M P_{O_2} / M_A \cdot 100MM}$$

$$\text{or } a_M = f_M(1 \text{ wt\%}) \frac{\gamma_M^\circ M_A}{100MM}$$

Prob:- A heat of steel contains 0.002 wt% oxygen. 'V' is to be added in the ladle at  $1557^\circ C$  to make a product containing 1 wt% V. To what extent must the oxygen content of the heat be lowered to prevent loss of 'V'.

Given:-

$$2[V]_{\text{Fe, wt\%}} + 3[O]_{\text{Fe, wt\%}} = < V_2O_3 >$$

$$\Delta G^\circ = -780400 + 267 \cdot 8 T \text{ J}$$



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### Mixing Function:

$$A + B = AB$$

Let us consider two components A and B which combine to form AB solution. When a solution is formed, it results in a change of thermodynamic property.

Let the thermodynamic property is G.

Then, change in free energy is known as free-energy of mixing, denoted by  $\Delta G^M$  (M=mixing)

$$\Delta G^M = G_{\text{final}} - G_{\text{initial}}$$

$$= \left( \frac{\partial G}{\partial n_A} \right)_B$$

$$= (x_A \bar{G}_A + x_B \bar{G}_B) - (x_A G_A^\circ + x_B G_B^\circ)$$

$$= x_A (\bar{G}_A - G_A^\circ) + x_B (\bar{G}_B - G_B^\circ)$$

$$\Delta G^M = x_A \Delta \bar{G}_A^M + x_B \Delta \bar{G}_B^M$$

where,

$\Delta \bar{G}_A^M$  and  $\Delta \bar{G}_B^M$  are known as partial molar free

energy of mixing.

Similarly,

$$\Delta H^M = x_A \Delta \bar{H}_A^M + x_B \Delta \bar{H}_B^M$$

$$\Delta S^M = x_A \Delta \bar{S}_A^M + x_B \Delta \bar{S}_B^M$$

$$\Delta V^M = x_A \Delta \bar{V}_A^M + x_B \Delta \bar{V}_B^M$$

and other properties.

$$\int dG = \int RTdn_A$$

$$\Rightarrow \bar{G}_i - G_i^\circ = RTdn_A$$

$$\Rightarrow \Delta \bar{G}_i^M = RTdn_A$$

$$\Delta G^M = x_A RTdn_A + x_B RTdn_B$$

$$\Delta G_{\text{real}}^M = RT(x_A dn_A + x_B dn_B) \quad (i)$$

↓

free energy of mixing of real solution.

and,

$$\Delta G_{\text{id}}^M = RT(x_A \ln x_A + x_B \ln x_B)$$

↓

free energy of mixing of ideal solution

differentiate (i) wrt T,

$$\left( \frac{\partial \Delta G}{\partial T} \right)^M = R(x_A dn_A + x_B dn_B) + RT \left[ x_A \left( \frac{\partial \ln x_A}{\partial T} \right)_{P, \text{comp.}} + x_B \left( \frac{\partial \ln x_B}{\partial T} \right)_{P, x_B} \right]$$

$$+ x_B \left( \frac{\partial \ln x_B}{\partial T} \right)_{P, x_B}$$

$$\Delta S_{\text{real}}^M = -R(x_A dn_A + x_B dn_B) - RT \left[ x_A \left( \frac{\partial \ln x_A}{\partial T} \right)_{P, x_A} + x_B \left( \frac{\partial \ln x_B}{\partial T} \right)_{P, x_B} \right]$$

↑ entropy of mixing of real solution

$$\Delta S_{id}^M = -R(x_A \ln x_A + x_B \ln x_B)$$

In case of ideal solution, the activity is not a function of temperature.

∴ the second term is zero

$$\Delta q^M = \Delta H^M - T\Delta S^M$$

$$\Delta H^M = \Delta q^M + T\Delta S^M$$

$$= RT(x_A \ln x_A + x_B \ln x_B) - RT(x_A \ln x_A + x_B \ln x_B)$$

$$-RT^2 \left[ x_A \left( \frac{\partial \ln x_A}{\partial T} \right)_{P, x_A} + x_B \left( \frac{\partial \ln x_B}{\partial T} \right)_{P, x_B} \right]$$

$$\text{∴ } \Delta H_{real}^M = -RT^2 \left[ x_A \left( \frac{\partial \ln x_A}{\partial T} \right)_{P, x_A} + x_B \left( \frac{\partial \ln x_B}{\partial T} \right)_{P, x_B} \right]$$

$$\boxed{\Delta H_{id}^M = 0}$$

Enthalpy of ideal solution is zero because not a function of

T.

$$\Delta V^M = x_A \bar{\Delta V}_A^M + x_B \bar{\Delta V}_B^M$$

$$dG_i = \bar{V}_i dP - S dT$$

At constant temperature and composition,

$$\left( \frac{\partial \bar{C}_{ii}}{\partial P} \right)_{T, \text{comp}} = \bar{V}_i$$

$$\left( \frac{\partial C_i^0}{\partial P} \right)_{T, \text{comp}} = \bar{V}_i^0$$

$$\left[ \frac{\partial (\bar{C}_i - \bar{C}_i^0)}{\partial P} \right]_{T, \text{comp}} = \bar{V}_i - \bar{V}_i^0 \\ = \bar{\Delta V}_i^M$$

$$\therefore \Delta \bar{q}_i^M = RT \ln \bar{x}_i$$

$$\Delta \bar{q}_{id}^M = RT \ln x_i$$

Since,  $x_i$  is not a function of pressure, therefore  $\bar{\Delta V}_i^M = 0$

$$\Delta V_{id}^M = x_A \bar{\Delta V}_A^M + x_B \bar{\Delta V}_B^M$$

$$\boxed{\Delta V_{id}^M = 0}$$

For ideal solution of mixing -

$$\Delta q_{id}^M = RT(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta S_{id}^M = -R(x_A \ln x_A + x_B \ln x_B)$$

$$\Delta H_{id}^M = 0$$

$$\boxed{\Delta V_{id}^M = 0}$$

$$\Delta q_{id}^M = RT \ln x_i$$

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Excess function

$$\underline{Z}^{xs} = \Delta Z^M_{\text{real}} - \Delta Z^M_{\text{ideal}}$$

It helps in the derivation of eq. for regularity tests

~~Z~~ is a thermodynamic fn. which can be  
G, H, S, V, etc.

& this excess fn ~~Z~~ is denoted by superscript- over the  
thermodynamic fn ~~Z~~  $\underline{Z}^{xs}$ .

Let us take  $Z$  as  $G$ . Then,

$$G^{xs} = \Delta G^M_{\text{real}} - \Delta G^M_{\text{ideal}}$$

$$= RT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

$$- RT(x_A \ln x_A + x_B \ln x_B)$$

$$G^{xs} = RT(x_A \ln \gamma_A + x_B \ln \gamma_B) \quad \text{--- (1)}$$

eq for excess free energy.

$$S^{xs} = -R(x_A \ln \gamma_A + x_B \ln \gamma_B) - RT \left[ x_A \left( \frac{\partial \ln \gamma_A}{\partial T} \right)_{P, x_A} + x_B \left( \frac{\partial \ln \gamma_B}{\partial T} \right)_{P, x_B} \right]$$

$$H^{xs} = -RT^2 \left[ x_A \left( \frac{\partial \ln \gamma_A}{\partial T} \right)_{P, x_A} + x_B \left( \frac{\partial \ln \gamma_B}{\partial T} \right)_{P, x_B} \right]$$

For a binary soln. of (A-B),

$$G^{xs} = x_A \bar{G}_A^{xs} + x_B \bar{G}_B^{xs} \quad \text{--- (2)}$$

Comparing eq (1) &amp; (2),

$$\text{Then, } \bar{G}_A^{xs} = RT \ln \gamma_A$$

$$\bar{G}_B^{xs} = RT \ln \gamma_B$$

Regular solution

$$\frac{\Delta G^M}{\text{reg}} = \frac{\Delta G^M_{\text{real}}}{\text{reg}} = RT(x_A \ln x_A + x_B \ln x_B)$$

$$\frac{\Delta H^M}{\text{reg}} = \frac{\Delta H^M_{\text{real}}}{\text{reg}} = -RT^2 \left[ x_A \left( \frac{\partial \ln x_A}{\partial T} \right)_{P, x_A} + x_B \left( \frac{\partial \ln x_B}{\partial T} \right)_{P, x_B} \right]$$

$$\text{but } \frac{\Delta S^M}{\text{reg}} = \frac{\Delta S^M_{\text{real}}}{\text{reg}} = -R(x_A \ln x_A + x_B \ln x_B)$$

$$\frac{\Delta G^M}{\text{reg}} = \frac{\Delta H^M}{\text{reg}} - T \frac{\Delta S^M}{\text{reg}}$$

$$\Rightarrow \frac{\Delta H^M}{\text{reg}} = \frac{\Delta G^M}{\text{reg}} + T \frac{\Delta S^M}{\text{reg}}$$

$$= RT(x_A \ln x_A + x_B \ln x_B) - RT(x_A \ln x_A + x_B \ln x_B)$$

$$= RT(x_A \ln \gamma_A + x_B \ln \gamma_B)$$

$$= G^{xs}$$

d-function

$$\alpha_i = \frac{\ln \gamma_i}{(1-x_i)^2}$$

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For a binary solution,

$$\alpha_B = \frac{\ln \gamma_B}{(1-x_B)^2} = \frac{\ln \gamma_B}{x_B^2}$$

$\alpha$  is a constant, independent of composition and has the same value for all the components of the system  
 $\therefore \alpha_A = \alpha_B = \alpha$

Test of Regularity -

$$(1) RT \ln \gamma_A = \alpha' x_B^2$$

$$\ln \gamma_A = \frac{\alpha'}{RT} x_B^2$$

$$(2) RT \ln \gamma_B = \alpha' x_A^2$$

$$\ln \gamma_B = \frac{\alpha'}{RT} x_A^2$$

(The model is known as Quasi-chemical Model of Regular Solution)

Interaction parameters (multicomponent dilute solutions)

Carl Wagner developed an eq. for  $\ln f_i$  based upon

Taylors series expansion

Let A is solvent- and ~~i, j~~ 1, 2, 3, ..., i, j are no. of solutes.

$$\ln f_i = \ln f_i^\circ + \left[ x_1 \left( \frac{\partial \ln f_i}{\partial x_1} \right) + x_2 \left( \frac{\partial \ln f_i}{\partial x_2} \right) + \dots \right]$$

$$+ \frac{1}{2} x_1^2 \left( \frac{\partial^2 \ln f_i}{\partial x_1^2} \right) + \frac{1}{2} x_2^2 \left( \frac{\partial^2 \ln f_i}{\partial x_2^2} \right) + \dots + \frac{1}{2} x_j^2 \left( \frac{\partial^2 \ln f_i}{\partial x_j^2} \right) + \dots$$

In case of dilute soln., the values of  $x_1, x_2, \dots, x_j$  are very small  
 $\therefore$  higher order terms can be ignored

$$\therefore \ln f_i = \ln f_i^\circ + \left[ x_1 \left( \frac{\partial \ln f_i}{\partial x_1} \right) + x_2 \left( \frac{\partial \ln f_i}{\partial x_2} \right) + \dots + x_j \left( \frac{\partial \ln f_i}{\partial x_j} \right) \right]$$

The eq. can be re-written as

$$\ln f_i = \ln f_i^\circ + \left[ x_1 \left( \frac{\partial \ln f_i}{\partial x_1} \right)_{x_1=0} + x_2 \left( \frac{\partial \ln f_i}{\partial x_2} \right)_{x_2=0} + \dots + x_j \left( \frac{\partial \ln f_i}{\partial x_j} \right)_{x_j=0} \right]$$

Within Henry's law,  $f_i^\circ = 1$  (by definition)

$$\therefore \ln f_i = x_1 \left( \frac{\partial \ln f_i}{\partial x_1} \right)_{x_1=0} + x_2 \left( \frac{\partial \ln f_i}{\partial x_2} \right)_{x_2=0} + \dots + x_j \left( \frac{\partial \ln f_i}{\partial x_j} \right)_{x_j=0}$$

$$\ln f_i = x_1 \epsilon_1^1 + x_2 \epsilon_2^2 + x_3 \epsilon_3^3 + \dots + x_j \epsilon_j^j$$

$$= \sum_{i=1}^{i=j} x_i \epsilon_i^i \quad \text{where } \epsilon_i^i = \left( \frac{\partial \ln f_i}{\partial x_i} \right)_{x_i=0}$$

Interaction coefficient -  
 (which indicates interaction of  $I_{i,j}, i$ )

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Now the derivation is based upon 1 wt % standard state  
 $\log f_i = \log f_i^0 + w_1 e_i^1 + w_2 e_i^2 + w_3 e_i^3 + \dots + w_J e_i^J$

Within Henry's law,  $f_i^0 = 1$  (by definition)

$$\log f_i = w_1 e_i^1 + w_2 e_i^2 + w_3 e_i^3 + \dots + w_J e_i^J$$

$$\log f_i = \sum_{j=1}^{J-1} w_j e_i^j \quad \text{This is Raoult's eqn. in case of 1 wt% S.S.}$$

Relationship between  $e_i^j$  &  $e_j^i$

We know that,

$$\bar{e}_i = \left( \frac{\delta G'}{S_n i} \right)_{T, P, n_1, n_2, \dots, \text{except } n_i}$$

$$\bar{e}_j = \left( \frac{\delta G'}{S_n j} \right)_{T, P, n_1, n_2, \dots, \text{except } n_j}$$

Again for mixing

$$\bar{e}_{ii}^M = \left[ \frac{\delta (G' - G'^0)}{S_n i} \right]_{n_1, n_2, \dots, \text{except } n_i}$$

$$\bar{e}_{ij}^M = \left[ \frac{\delta (G' - G'^0)}{S_n j} \right]_{n_1, n_2, \dots, \text{except } n_j}$$

where,  $G'^0 = G'$  when  $1, 2, 3, \dots, J$  were present in pure form

$$\frac{S\bar{e}_i^M}{S_n i} = \frac{\delta^2 (G' - G'^0)}{S_n i S_n j}$$

$$\text{and } \frac{S\bar{e}_j^M}{S_n j} = \frac{\delta^2 (G' - G'^0)}{S_n j S_n i}$$

$$\therefore \frac{S\bar{e}_i^M}{S_n j} = \frac{S\bar{e}_j^M}{S_n i}$$

Having substitutions: ①  $\bar{e}_i^M = RT \ln a_i$

$$\text{② } x_j = \frac{n_j}{n_T}$$

$$n_j = x_j n_T \Rightarrow S_n j = \delta x_j n_T$$

$$\text{③ } a_i = x_i X_i$$

$$\left[ \frac{\partial \bar{e}_i^M}{\partial n_j} \right]_{x_j \rightarrow 0} = RT \left[ \frac{\delta (\ln a_i)}{\delta n_j} \right]_{x_j \rightarrow 0} = \frac{RT}{n_T} \left[ \frac{\delta \ln x_i + \delta \ln X_i}{\delta x_j} \right]_{x_j \rightarrow 0}$$

$$= \frac{RT}{n_T} \left[ \frac{\delta (\ln X_i)}{\delta x_j} \right]_{x_j \rightarrow 0}$$

$$= \frac{RT}{n_T} e_i^j$$

$$\frac{\delta \ln x_i}{\delta x_j} = 0 \text{ since } X_i \text{ is not a function of } x_j$$

Since Gibbs free energy is a state fn., the RHS will be independent of the order of differentiation  
 $\Rightarrow$  RHS will be equal  
 $\text{and LHS will also be equal}$

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In the same manner,

$$\left[ \frac{8G_i^M}{S_{i,j}} \right] = \frac{RT}{n_T} e_j^j$$

$x_i \rightarrow 0$

$$\therefore e_i^j = e_j^j$$

Relationship between  $e_i^j$  &  $e_i^i$ 

atm.v.  $\ln f_i = x_1 e_1^i + x_2 e_2^i + \dots + x_j e_j^j$

Standard state

1 wt% S.S.  $\log f_i = w_1 e_1^i + w_2 e_2^i + \dots + w_j e_j^j$

Let us compare these 2 equations term by term, we get -

$$\begin{aligned} w_j e_j^j &= 2.303 \times x_j e_j^j \\ w_j e_j^j &= 2.303 \frac{w_j M_A}{100 M_j} e_j^j \\ e_j^j &= \frac{2.303 M_A}{100 M_j} e_j^j \quad \text{--- (1)} \end{aligned}$$

$$\begin{aligned} x_B &= \frac{w_B M_A}{100 M_B} \\ x_j &= \frac{w_j M_A}{100 M_j} \end{aligned}$$

Similarly,

$$e_j^i = \frac{2.303}{100} \frac{M_A}{M_j} e_j^j \quad \text{--- (2)}$$

from eq (1),

$$e_i^j = \frac{100}{2.303} \frac{M_A}{M_i} e_i^i$$

from (2),  $e_j^i = \frac{100}{2.303} \frac{M_A}{M_i} e_j^j$

$\therefore \frac{100}{2.303} \frac{M_A}{M_i} e_j^j = \frac{100}{2.303} \frac{M_A}{M_i} e_j^i$

$$e_i^j = \frac{M_A}{M_i} e_i^i$$

A  $H_2$ - $H_2S$  Gas mixture with  $P_{H_2}/P_{H_2S}$  ratio of 10 is equilibrated with pure liquid iron at 1850K. On analysis of quenched sample, the iron is found to contain 0.8% sulphur. Calculate the free energy change of the following reaction at 1850K -



1 wt% S.S in Liquid 'Fe' at 1850K

Given -  $\log f_S = -0.028 w_S$

Sol -

$$\{H_2\} + \frac{1}{2}\{S_2\} = \{H_2S\} - I \Delta G_I^\circ = 690 \text{ J/mole}$$

$$\{H_2\} + [S] = \{H_2S\} - II \Delta G_{II}^\circ =$$

$$\frac{1}{2}\{S_2\} = [S] - III \Delta G_{III}^\circ = 690 - \Delta G_{II}^\circ$$

$\{ \} \rightarrow ( )$   
due to gas

$$\log f_S = -0.028(0.8)$$

$$f_S = 0.95$$

Now,

$$\Delta G_f^\circ = -RT \ln \frac{P_{H_2} S}{P_{H_2} \cdot h_{CS}} = -8.314 \times 1973 \ln \frac{1}{10 \cdot f_S \cdot W_S}$$

$$\Delta G_f^\circ = -8.314 \times 1973 \ln \frac{1}{10 \times 0.95 \times 0.8}$$

$$\Delta G_f^\circ = 31194.75 \text{ J/mole}$$

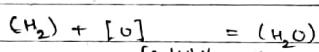
$$\Delta G_f^\circ = 31194.75 \text{ kJ/mole}$$

~~$$\therefore \Delta G_f^\circ = 690 - 31194.75 = 6382.8 \text{ kJ/mole}$$~~

$$\Delta G_f^\circ = 690 - 31194.75 = -30504.75 \text{ J/mole}$$

$$\Delta G_f^\circ = -30.5 \text{ kJ/mole}$$

Prob. An Fe-Cu alloy is brought to equilibrium with  $H_2-H_2O$  mixture in which  $\frac{P_{H_2O}}{P_{H_2}} = 0.00353$ , in a pure alumina crucible at 1973K. The equilibrium is represented by



The alloy at equilibrium contains  $C = 1.90 \text{ wt\%}$ ,  $Al = 0.03 \text{ wt\%}$ ,  $O = 0.0032 \text{ wt\%}$ . The various interaction parameters are

~~$e_0^0 = 0.00, e_0^1 = -0.058, e_0^{Al} = -3.15$~~   
calculate the free energy change of the above reaction at 1973K.

$$\Delta G_f^\circ = -RT \ln K$$

$$\Rightarrow \Delta G_f^\circ = -RT \ln \frac{P_{H_2O}}{P_{H_2} \cdot h_{CO} \cdot h_{CO}}$$

$$\Rightarrow \Delta G_f^\circ = -RT \ln \frac{P_{H_2O}}{P_{H_2} \cdot f_{CO} \cdot W_{CO}}$$

$$\log \frac{P_{H_2O}}{P_{H_2}} = \sum_{i=1}^3 w_i e_i$$

$$\log \frac{P_{H_2O}}{P_{H_2}} = -0.092 (0.0032 \times 0.00) - (0.03 \times 3.15) - (1.90 \times 0.058)$$

$$\log \frac{P_{H_2O}}{P_{H_2}} = -0.2047$$

$$\Rightarrow f_{CO} = 0.81 \quad f_O = 0.624$$

$$\therefore \Delta G_f^\circ = -8.314 \times 1973 \ln \frac{0.00353}{0.624 \times 0.0032}$$

$$\Delta G_f^\circ = -9345.9 \text{ J/mole}$$

$$\Delta G_f^\circ = -9.346 \text{ kJ/mole}$$

Prob. During welding, carbon and oxygen form  $CO_2$  which enters into solution with 'Fe at 1873K according to  $(CO_2) = [C]_{Fe, 1wt\%} + 2[O]_{Fe, 1wt\%}$

$$\Delta G_f^\circ = 1834.89 - 47170 T \text{ J}$$

$$0.059 \text{ wt\% C}$$

$$\text{The final } [\text{O}] \text{ content of the weld is represented by } \log [\text{O}_\text{O}] = -\frac{6320}{T} + 2.734$$

Calculate the equilibrium carbon content of the weld if  $P_{CO} = 1 \text{ atm}$ .

Assume following interacting parameters -

$$\begin{aligned} e_0^c &= -0.13, \quad e_c^o = -0.1, \quad e_o^o = -0.2, \quad e_c^c = 0.22 \\ (e_0^o) &= [c]_{Fe, wt\%} + 2[O]_{Fe, wt\%} \\ \Delta Q^o &= 183489 - 47.70 T J \\ &= 183489 - 47.70(1873) \\ &= 94146.9 T \end{aligned}$$

Guid

$$\log [Y_0] = - \frac{6320}{T} + 2.734$$

$$\log [Y_0] = - \frac{6320}{1873} + 2.734$$

$$\text{Ans. } [\%] = 0.22894$$

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

$$94146.9 = -8.314 \times 1873 J_n K$$

$$K = 2.367 \times 10^{-3}$$

$$\frac{h^2}{[O] \cdot h[C]} = 2.367 \times 10^{-3}$$

$P_{CO_2}$

$$\Rightarrow f(w_1)w_{(0)} \cdot f(w_2)w_{(0)} = 2.367 \times 10^{-3} \quad (1)$$

$$\Rightarrow f_{[0]}^2 w_{[0]}^2 \cdot f_{[0]} w_{[0]} = 2.367 \times 10^{-3}$$

$$\begin{aligned} J_{qfo} &= w_c e_0^c + w_0 e_0^o \\ &= w_c (-0.13) + (0.22894)(-0.2) \\ &= -0.045728 - 0.13w_c \end{aligned}$$

Similarly

$$\begin{aligned} \log f_c &= w_c e_c^0 + w_c e_c^c \\ &= 0.22894(-0.1) + w_c(0.22) \\ &= 0.22w_c - 0.022894 \end{aligned}$$

Now, Taking logarithm on both sides of eq(1), we get-

$$\begin{aligned} & \log f_{107} + \log w_{107} + \log f_{107} + \log w_{107} = \log (2.367 \times 10^{-3}) \\ \Rightarrow & (-0.045788 - 0.13w_c) + \log (0.22894) + (0.22w_c - 0.022894) \end{aligned}$$

$$\Rightarrow 0.04 w_c - \log w_{c0} = 1.2325$$

$\therefore w_c$  is less than  $1w_f - 1$ .

$\therefore 0.04w_c$  will comparatively be very small and hence can be neglected.

$$\therefore \text{Now } -\log w_{(c)} = 1.2325$$

$$\log \omega_{[C]} = -1.2325$$

$$\omega(c) = 0.059$$

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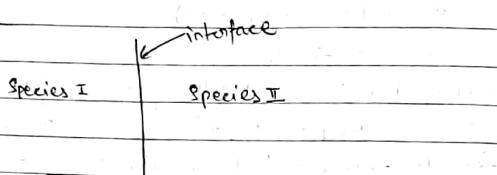


### Kinetics

A chemical Rx can be divided into 2 parts -

(1) Homogeneous Rx - A Rx taking place within the same phase.

(2) Heterogeneous Rx - When 2 or more than 2 ~~class~~ phases are involved in a chemical Rx.



### Kinetics steps involved:

- (a) Diffusion of species I towards the interface
- (b) Diffusion of species II towards the interface
- (c) The chemical Rx b/w species I and species II.
- (d) Diffusion of product I away from the interface
- (e) Diffusion of product II away from the interface,

Steps (a), (b), (d), (e) are diffusion controlled hence the overall chemical Rx will depend on rate of diffusion of chemical species I and II and products I and II.

Step (c) is the rate of chemical Rx.

Rate controlling step - The slowest step among these 5 steps is called the Rate controlling step.

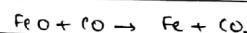
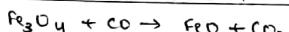
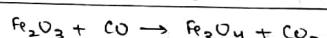
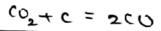
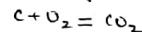
If Rate of diffusion is the rate controlling step, the techniques for increasing rate of diffusion -

- (1) By raising the temperature.
- (2) Inert gas bubbling through the bath.
- (3) Electro-magnetic stirring

### How to increase rate of a chemical Rx?

- (1) By raising the temperature.
- (2) By increasing the concentration of reactants.
- (3) By increasing the surface area of reactants (interface) by reducing the particle size of the reactants.
- (4) Removal of Quick removal of product-species from reaction site.
- (5) By use of catalyst.

### Molten Pig Iron (Blast Furnace)



$SiO_2$   
 $Al_2O_3$

Impurities called  
at gangue.

flux + gangue  $\Rightarrow$  slag

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Indian Blast Furnace -

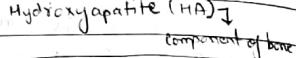
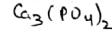
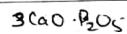
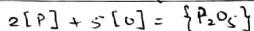
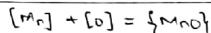
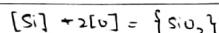
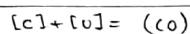
$$\text{C} \approx 4.0\%$$

$$\text{Si} \approx 0.5 - 2.5\%$$

$$\text{Mn} \approx 1.0 - 3.0\%$$

$$\text{P} \approx 0.35 - 0.45\%$$

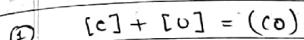
$$\text{S} \approx 0.05\%$$

Mohr's scale of Hardness for naturally occurring minerals -

- 1) Chalc
- 2) Calcite Gypsum
- 3) Fluorite Calcite
- 4) Apatite Fluorite
- 5) Apatite
- 6) Orthoclase or Feldspar
- 7) Quartz ( $\text{SiO}_2$ )
- 8) Topaz
- 9) Corundum ( $\text{Al}_2\text{O}_3$ )
- 10) Diamond  $\longrightarrow$  Hardest

If Cu is present in corundum, its colour is blue  $\rightarrow$  called as sapphires.  
If Cr is present in corundum, its colour is red  $\rightarrow$  called as Ruby (Gem stone).

It was found that there is a naturally occurring mineral whose hardness lies b/w Corundum and Diamond called as Carbocorundum (which is nothing but silicon carbide  $\text{SiC}$ ).



Increase the activity of reactants. Once the composition is fixed, activity of the reactants cannot be altered.

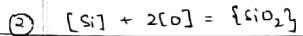
Now, increase the activity of oxygen.  $a_{\text{O}_2} = 1$  in case of pure  $\text{O}_2$ . In case of air,  $a_{\text{O}_2} = 0.21$ .

If slag is used for refining, then  $a_{\text{O}_2}$  (FeO present in slag) =  $10^{-6}$  but once the process is decided,  $a_{\text{O}_2}$  is fixed.

So, the last option left is to reduce the activity of product. Activity of CO can be reduced by reducing the partial pressure of CO.

$\rightarrow$  By inert gas bubbling

$\rightarrow$  By vacuum treatment



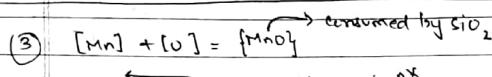
$\textcircled{1}$   $\text{SiO}_2$  is a strong acid oxide

$\textcircled{3}$  From a weak basic oxide

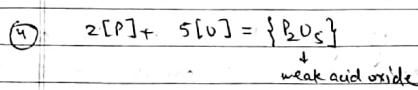
is able to stabilize it

$\textcircled{4}$  A basic oxide is needed to stabilize silica in slag phase

(iv)  $\text{MnO}_2$  weak basic oxide



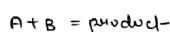
Particularly when external flux is added (say)  $\text{CaO}$  then  $\text{SiO}_2$  will prefer to combine with  $\text{CaO}$  which is a strong basic oxide thereby  $\text{MnO}_2$  will not be consumed and there is every possible chance of Mn-inversion reaction.



∴ to stabilize it, a strong basic oxide is needed hence, external flux in the form of a calcine ( $\text{CaO}$ ) is added which is a strong basic oxide

Note - If the basicity of the slag is very high, Mn-inversion  $\text{Rx}^*$  will take place.

Rate of Reaction :- Let us consider a general reaction



$$\text{Rate of } \text{Rx}^* = -\frac{d[\text{A}]}{dt} = -\frac{d[\text{B}]}{dt} = +\frac{d[\text{P}]}{dt}$$

Order of a  $\text{Rx}^*$  :-  $a[\text{A}] + b[\text{B}] + c[\text{C}] + d[\text{D}] = \text{product}$

$a, b, c, d \rightarrow$  no. of moles for overall  $\text{Rx}^*$

$\text{A}, \text{B}, \text{C}, \text{D} \rightarrow$  Reactants

$$\text{Rate of } \text{Rx}^* = -\frac{dc}{dt} \propto C_A^a C_B^b C_C^c C_D^d$$

Order of  $\text{Rx}^*$  (n) = sum of exponents over the concentration terms

$$[n = a+b+c+d]$$

Rate of  $\text{Rx}^*$  is a strong function of concentration and temperature.

① Effect of concentration on rate of reaction -

Let us consider a  $\text{Rx}^*$   $\text{A} + \text{B} = \text{C} + \text{D}$

$$\text{Rate of forward reaction} \leftarrow V_f = k_f [A][B]$$

$$V_b = k_b [C][D]$$

where  $[A], [B], [C], [D]$  are the molar concentration terms

At equilibrium,

$$V_f = V_b$$

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

② Effect of temperature on rate of reaction -

From Van't Hoff equation,

$$\frac{d \ln K_e}{dT} = \frac{\Delta H}{RT^2}$$

$$\frac{d \ln k_f}{dT} = \frac{d \ln k_b}{dT} = \frac{\Delta H}{RT^2} \quad \left( \because K_e = \frac{k_f}{k_b} \right)$$

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$$\Rightarrow \frac{d \ln K_f}{dT} = \frac{E_a - E_a'}{RT^2}$$

$$\text{and } \frac{d \ln K_b}{dT} = \frac{E_a' - E_a}{RT^2}$$

(where,  $E_a - E_a' = \Delta H$ )

Assuming  $I=0$  and  $E_a$  is independent of temperature, integrating the above equation, we get-

$$\ln K_f = -\frac{E_a}{RT} + \text{constant}$$

$$\ln K_b = -\frac{E_a'}{RT} + \text{constant}$$

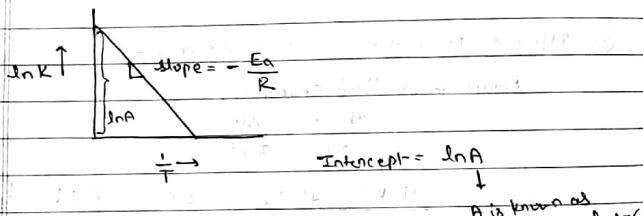
In general,

$$K = Ae^{-\frac{E_a}{RT}} \quad \leftarrow \text{Arrhenius Rate equation}$$

Taking logarithm both sides, we get-

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

$$(y = c + mx)$$



### Theories of Reaction Rate -

- ① Collision Theory
- ② Absolute Reaction Rate Theory

#### Collision Theory -

(for bimolecular rx occurring in gaseous state)

Postulates of Collision Theory:

- ① All molecules travel through space in straight lines.
- ② All molecules are hard, solid spheres.
- ③ The reaction of interest is b/w only 2 molecules.
- ④ Collisions are either hit or miss only.
- ⑤ They occur only when the distance b/w the centre of molecules less than equal to sum of their atomic radii.
- ⑥ Chemical reactions can occur only upon collision b/w reactant molecules.
- ⑦ All collisions do not lead to the formation of products otherwise the reaction will be over in a fraction of second.
- ⑧ Only those collisions in which molecules have proper orientation and possess minimum amount of energy, can lead to the formation of products.
- ⑨ The minimum amount of energy required to form products is called threshold energy.
- ⑩ The energy possessed by a normal reactant at STP is called average energy.

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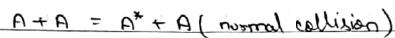
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$$\text{Activation Energy} = \text{Threshold Energy} - \text{Average Energy}$$

- (11) Some molecules will get energy greater than or equal to the threshold energy during collisions and are called activated molecules and is denoted by '\*'.

- (12) The collision taking place b/w activated molecules is called effective collisions or activated collisions.



$A$  = normal molecule

$A^*$  = activated molecule

Let us consider 2 gases denoted by 'A' and 'B'. For the reaction to occur, the molecules of A and B must collide. The reaction rate is given as -

$$V = Z_{AB} e^{-E_a/RT}$$

where  $Z_{AB}$  = no. of collisions / sec b/w A and B in one c.c. of gas

As per kinetic theory,

$$Z_{AB} = n_A \cdot n_B d_{AB}^2 \left[ \frac{8\pi kT}{m_A + m_B} \right]^{1/2}$$

where  $n_A, n_B$  = concentration of molecules A and B (unit :- molecules / cc)

$m_A, m_B$  = mass of molecules of A and B resp  
K is Boltzmann constant

$$d_{AB} = \text{average dist of A and B}$$

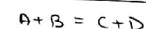
In many cases, observed state does not agree with the above equation. In order to account for the deviation, the equation is modified as -

$$V = Z_{AB} e^{-E_a/RT}$$

where  $V$  = probability factor / steric factor

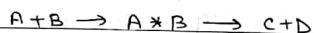
### Absolute Reaction Rate Theory -

For the reaction,



This theory assumed that before a chemical reaction takes place, the molecules A and B have to collide and then form an activated complex, which then decomposes to give the products.

So, the above reaction can be step-written as -



activated complex

### Purulates of Absolute Reaction Rate Theory -

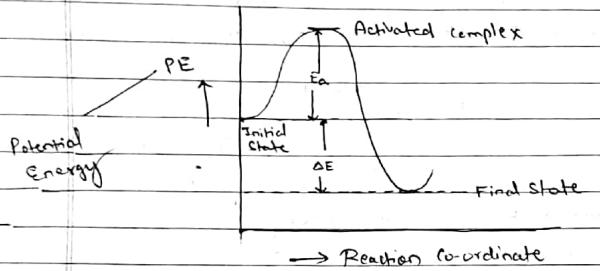
(1) The activated complex may be treated as any other chemical species and is in equilibrium with the reactants, although it has very short life span.

(2) The specific reaction rate of decomposition of activated complex into products is a universal

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vate, independent of the nature of the reactants and the form of activated complex.



The activation energy  $E_a$  is the additional energy which the reactant molecules must acquire to form the activated complex.

The reactants acquire the activation energy from the kinetic & vibrational energies of colliding molecules.

If in the above plot, free energy is plotted instead of PE,  $E_a$  will be substituted by  $\Delta G^*$  which is free energy of activation and  $\Delta E$  will be replaced by  $\Delta G$  which is change in free energy of the reaction.

$$\Delta G^* = -RT \ln K^* = \Delta H^* - T\Delta S^*$$

$$\text{Now, } A+B = A \cdot B$$

$$\text{For this reaction, } K^* = \frac{a^*}{a_A a_B}$$

$\Delta H^*$  = enthalpy of activation

$\Delta S^*$  = entropy of activation

$$K^* = \frac{\gamma^* c^*}{\gamma_A \gamma_B C_A C_B} \quad \text{--- (1)}$$

where  $c, \gamma$  = concentration & activity coefficient of respective molecules

Fewer Kinetic Theory,

Universal Rate of decomposition is given as -

$$V = \frac{kT}{h} C^*$$

where  $k$  = Boltzmann constant

$h$  = Planck's constant

$C^*$  = concentration of activated complex

$$\therefore k = \frac{R}{N} \rightarrow \text{Avogadro's No.}$$

$$\text{So, } V = \frac{RT}{Nh} C^* \quad \text{--- (2)}$$

$$\text{From eq.(1), } C^* = \frac{k^* \gamma_A \gamma_B C_A C_B}{\gamma^*}$$

Putting this value of  $C^*$  in eq.(2), we get-

$$V = \frac{RT}{Nh} \frac{k^* \gamma_A \gamma_B C_A C_B}{\gamma^*} \quad \text{--- (3)}$$

$$\therefore \Delta G^* = -RT \ln K^*$$

$$\therefore K^* = \exp\left(-\frac{\Delta G^*}{RT}\right)$$

$$K^* = \exp\left(-\frac{\Delta H^*}{RT}\right) \exp\left(\frac{\Delta S^*}{R}\right)$$



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Experimental data is now taken up and a plot is drawn. If the plot is linear then  $n=1$  is confirmed and if the plot is not linear then, the process may be repeated with some other values of  $n$ .

### (2) Half-life period Method

This is the time elapsed during which the mass of a substance is reduced to ~~its original~~ half of its original mass. This is denoted by  $t_{1/2}$  or  $t_{0.5}$ .

In this process, 2 sets of data are required for mass & half-life period.

$$\text{For } n=2, \quad k = \frac{1}{t} \left[ \frac{x}{c_0(c_0-x)} \right]$$

$$\Rightarrow t = \frac{1}{k} \left[ \frac{x}{c_0(c_0-x)} \right]$$

$$\text{Now, } t_{0.5} = \frac{1}{k} \left[ \frac{c_0/2}{c_0(c_0-c_0/2)} \right]$$

$$t_{0.5} = \frac{1}{k c_0}$$

So, in general formula for half-life period is -

$$t_{0.5} = \frac{1}{k c_0^{n-1}}$$

$$\ln t_{0.5} = -\ln k - (n-1) \ln c_0$$

$$1^{\text{st}} \text{ set: } \ln t_{0.5,1} = -\ln k - (n-1) \ln c_{0,1}$$

$$2^{\text{nd}} \text{ set: } \ln t_{0.5,2} = -\ln k - (n-1) \ln c_{0,2}$$

$$\ln t_{0.5,1} - \ln t_{0.5,2} = (n-1) [\ln c_{0,2} - \ln c_{0,1}]$$

$$\Rightarrow n-1 = \frac{\ln t_{0.5,1} - \ln t_{0.5,2}}{\ln c_{0,2} - \ln c_{0,1}}$$

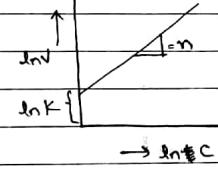
do,	$n = 1 + \frac{(\ln t_{0.5,1} - \ln t_{0.5,2})}{(\ln c_{0,2} - \ln c_{0,1})}$
-----	---

### (3) Van't Hoff differential Method

$$V = kC^n$$

$$\text{do, } \ln V = \ln k + n \ln C$$

$$y = c + m x$$



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Prob-2

For the reaction  $A + B = C$ , following data were obtained -

Experiment No.	Initial Concentration (mole/litre)			Half-decaying time (hrs)
	A	B		
1	2.0	2.0		2.5
2	5.0	5.0		1.0

Calculate the order of Reaction & specific reaction rate.

Soln

$$n = 1 + \frac{(ln c_{0.5} - ln c_0)}{(ln c_0 - ln c_2)}$$

$$n = 1 + \frac{(ln c_2 - ln c_1)}{(ln c_1 - ln c_0)}$$

~~n = 2~~

$$t_{0.5} = \frac{1}{k C_0^{0.5}}$$

$$\therefore K = \frac{1}{t_{0.5} C_0} = \frac{1}{2 \times 5} = \frac{1}{10}$$

$$k = 0.2 \text{ mole/litre}^{-0.5} \text{ hr}^{-1}$$

$$k = 0.2 \text{ mole/litre}^{-0.5} \text{ hr}^{-1}$$

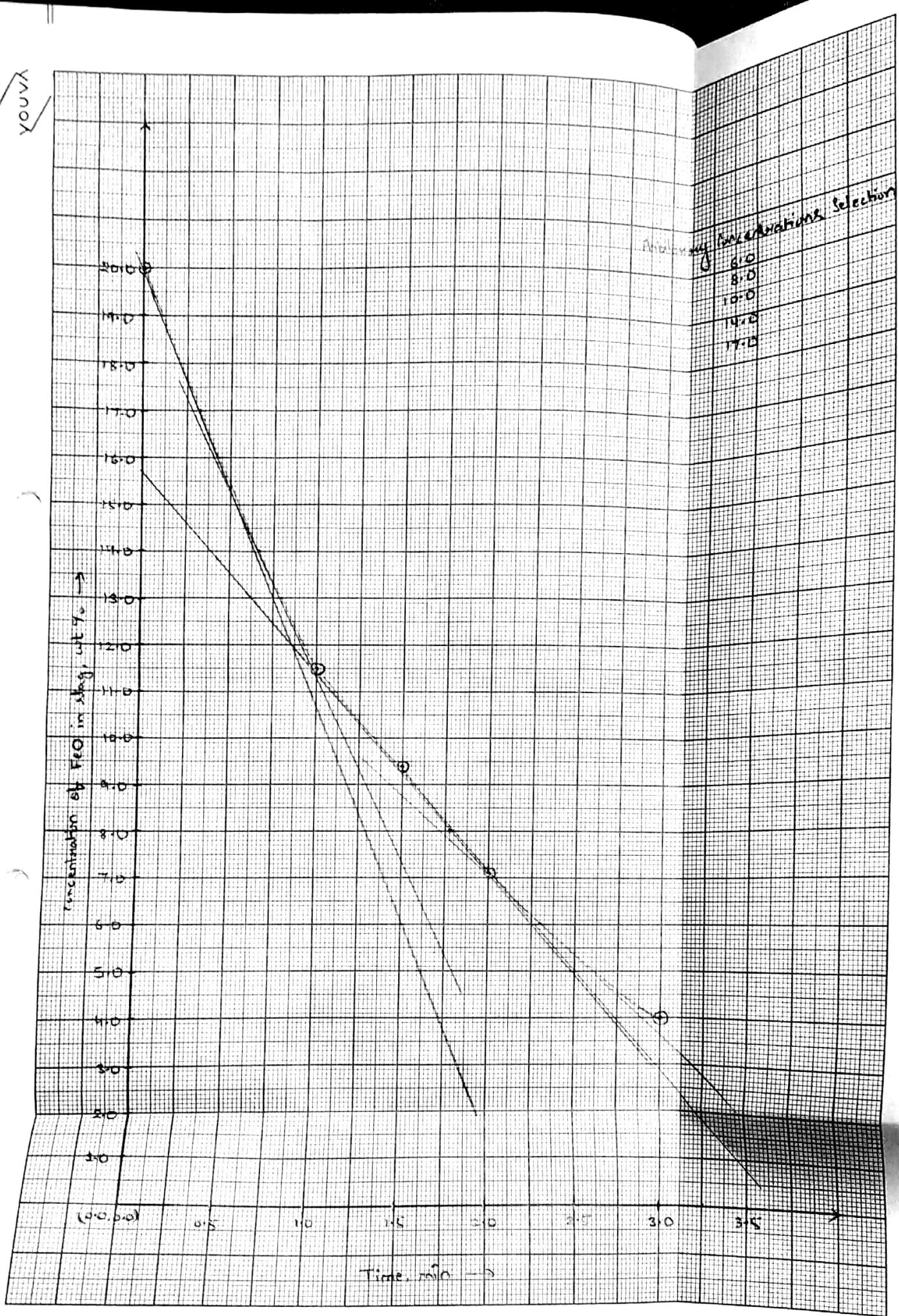
Prob-2 The following data were obtained for the kinetics of reduction of FeO in slag by carbon in molten pig iron at a certain temperature -

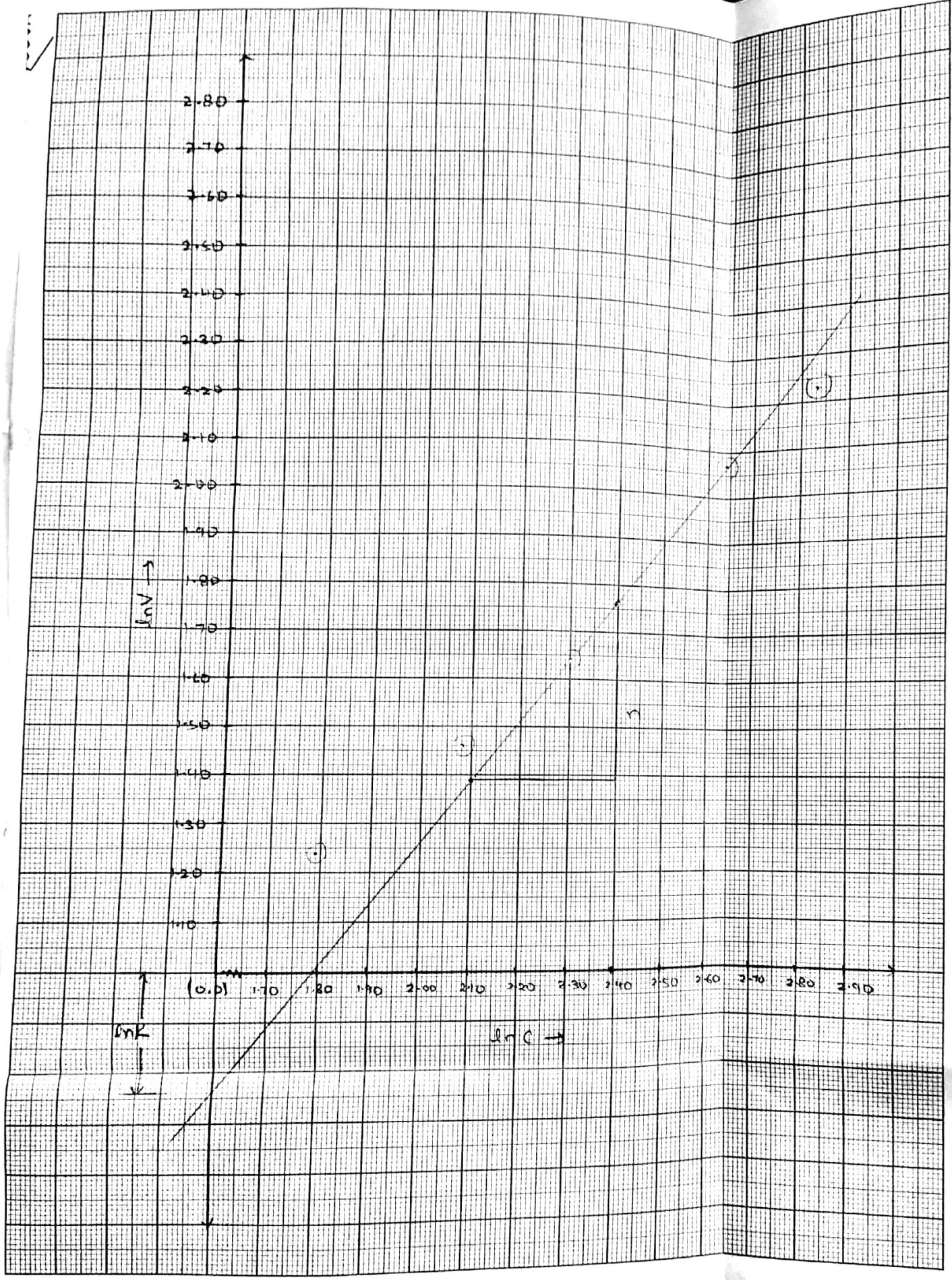
Time, min.	Conc. of FeO in slag, wt-%	20.00	11.50	9.35	7.10	4.00
	0.00	1.0	1.5	2.0	3.0	

Calculate order of R w.r.t. FeO by Van't Hoff differential Method. Also calculate specific reaction rate

Ambiguous concentrations selection	$\frac{dc}{dt}$	$v = -\frac{dc}{dt}$	$\Delta v$
7.0	-1.10	1.10	0.095
8.5	-0.45	0.45	-0.799
10.0	-0.20	0.20	-1.609
12.5	-0.52	0.52	-0.654
14.5	-0.07	0.07	-2.659
<u>In C</u>			
1.95			
2.14			
2.40			
2.53			
2.67			

YUVV





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Arbitrary Concentrations
 $\ln C \quad \frac{dc}{dt} \quad V = -\frac{dc}{dt}$ 

6.0

~~-1.79~~

-3.47

3.47

1.24

8.0

2.08

-4.30

4.30

~~-1.46~~

10.0

2.30

~~-5.13~~

5.13

1.64

14.0

2.64

-7.90

7.90

2.07

17.0

2.83

-9.27

9.27

2.23

So, we have

 $\ln C \quad \ln V$ 
~~-1.79~~ 1.24

~~2.08~~ ~~1.46~~
~~2.30~~ 1.64

~~2.64~~ 2.07

~~2.83~~ 2.23

☞ We have two points on best fit line as (2.10, 1.39) and (2.40, 1.76)

$$\text{So, } n = \frac{1.76 - 1.39}{2.40 - 2.10} = 1.2 \approx 1$$

So, order of the Reaction is 1. (Ans)

and  $\ln K = -1.24$

$$\text{So, } K = 0.3 \text{ (Ans)}$$