Thermodynamics-1 notes for II semester Geetha.S

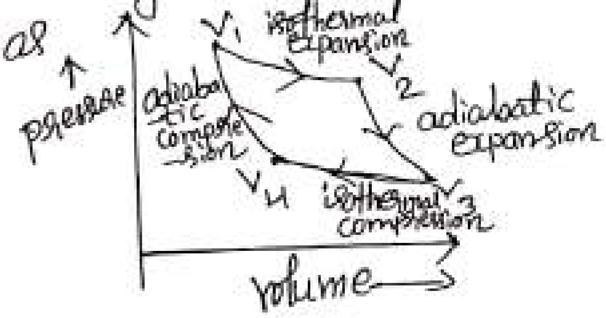
obtain the expression for the efficiency of Carnot's engine in terms of entropy.

French Engineer Sadi carnot imagined a hypothetical heat engine which works reversibly in cycles. It consists of a cylinder containing one mole of an ideal gas as the working substance and fitted with wightless, frictionless piston. All sides except the base of the cylinder are perfectly insulated. So that heat can flow to (or) from the system only through the base.

Further it is supposed that there are two heat reservoirs. one at a higher tempr (T_2) [called the source]. & the other at a lower tempr (T_1)

If some process is carried out by placing the cylinder in the source (or) the sink, it can exchange heat with it & hence the tempr remains constant. So that the process is isothermal. on the other hand, if the cylinder is placed on an insulating material, no heat exchange can takes place b/w the system & the surrounding & hence the process is adiabatic.

Carnot cycle consists of four different operations such as



1M

Isothermal Expansion:- The cylinder containing one mole of the ideal gas occupying a volume V_1, is placed in contact with the source. The gas absorbs q_2 Joules of heat from the source at tempr. T_2 & expands isothermally & reversibly till its volume has increased V_2.

$$\Delta S_1 = \frac{q_2}{T_2}$$

Adiabatic Expansion:- the gas is expanded adiabatically & reversibly from a volume V_2 to V_3. the tempr falls from T_2 to T_1. Since there is no heat transfer $q=0$

$$\therefore \Delta S_2 = 0$$

1M Isothermal compression:- The gas is isothermally & reversibly compressed from a V_3 to V_4 at temperature T_1.

$\therefore$ Heat q_1 is liberated in this step.

$$\therefore \Delta S_3 = \frac{-q_1}{T_1}$$

Adiabatic compression:- The gas is reversibly and adiabatically compressed from a volume $V_4 \rightarrow V_1$. The tempr. of the gas increases from $T_1 \rightarrow T_2$.

There is no heat transfer here

$$\therefore \Delta S_4 = 0.$$

The total entropy change for the four steps must be zero since this is a cyclic process & Entropy is a state function.

$$\Delta S_{total} = \Delta S_1 + \Delta S_2 + \Delta S_3 + \Delta S_4$$

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

$$\therefore \frac{q_2}{T_2} = \frac{q_1}{T_1}$$

(or) $$\frac{q_1}{q_2} = \frac{T_1}{T_2}$$

substracted on both side from 1

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

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

For a cyclic process $\Delta E = 0$

Hence from the I Law of thermodynamics.

$$\Delta E = q_r + w$$ [q_r is the heat absorbed reversibly]

$$0 = q_r + w$$

$$q_r = -w$$

$$\boxed{q_2 - q_1 = -w}$$

$$\text{Efficiency}(\eta) = \frac{\text{Heat converted into work}}{\text{Heat absorbed}}$$

$$(\eta) = \frac{-w}{q_2} = \frac{q_r}{q_2} = \frac{q_2 - q_1}{q_2} = \frac{T_2 - T_1}{T_2}.$$

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

Free energy:- Free energy is a measure of a system's ability to do work.

- * If reactants in a reaction have greater free energy than the products. the energy is released from the reactions which is called exergonic
- * If reactants in a reaction have lower free energy than the products. the energy is absorbed by the reaction which is called endergonic.

There are two free energy functions.

1) Helmholtz free energy (A) (or) work function
2) Gibb's free energy.

Helmholtz free energy:- [4 marks]

Helmholtz free energy is denoted by "A" & is defined by the equation.

$$A = U - TS \rightarrow ①$$

where $A \rightarrow$ Helmholtz free energy
$U -$ Internal energy
$T -$ Temperature
$S -$ Entropy.

In order to understand the physical significance of work function. consider an isothermal change takes place at temperature "T" then

$A_1 = U_1 - TS_1 \longrightarrow ②$ for the initial state

$A_2 = U_2 - TS_2 \longrightarrow ③$ for the final state

where A_1, U_1 & S_1. are respectively the values of work function, internal energy & entropy of system in

the initial state & A_2, U_2 & S_2 are the correspondi
values in the final state.

∴ Change in the work function "A" is given by

$$A_2 - A_1 = (U_2 - TS_2) - [U_1 - TS_1]$$

$$A_2 - A_1 = U_2 - TS_2 - U_1 + TS_1$$

$$A_2 - A_1 = U_2 - U_1 - T[S_2 - S]$$

$$\Delta A = \Delta U - T\Delta S \longrightarrow ④$$

A/c to the definition entropy

$$\Delta S = \frac{q_{rev}}{T} \longrightarrow ⑤$$

A/c to the I law of thermodynamics as applied to an isothermal reversible process. we have

$$\Delta U = q_{rev} - W_{max} \longrightarrow ⑥$$

Substituting the values of ΔS & ΔU from eqn. ⑤ & ⑥ in eqn. ④, we get

$$\Delta A = (\cancel{q_{rev}} - W_{max}) - \cancel{T}\left(\frac{\cancel{q_{rev}}}{\cancel{T}}\right)$$

$$\Delta A = -W_{max}$$

$$\boxed{-\Delta A = W_{max}}$$

Thus decrease in the work function "A" is equal to the maximum work done by the system. for this reason the Helmholtz free energy has been termed as work function.

Gibb's free energy:-

4 Marks.

It is denoted by "G" & is defined by the equation

$$G = H - TS \longrightarrow ①$$

where G - Gibb's free energy

H - Enthalpy (or) heat content

T - temp$\underset{..}{r}$

S - Entropy

change in Gibb's free energy Accuring at constant temperature "T"

$G_1 = H_1 - TS_1 \longrightarrow ②$ for the initial state

& $G_2 = H_2 - TS_2 \longrightarrow ③$ for the final state

$$\therefore \quad G_2 - G_1 = H_2 - TS_2 - (H_1 - TS_1)$$

$$= H_2 - H_1 - T(S_2 - S_1)$$

$$\Delta G = \Delta H - T\Delta S \longrightarrow ④$$

A/c to definition of entropy

$$\Delta S = \frac{q_{rev}}{T}$$

$$T\Delta S = q_{rev} \longrightarrow ⑤$$

From definition of enthalpy "H"

$$H = U + PV$$

The change in enthalpy at constant "p"

$$\Delta H = \Delta U + P\Delta V \longrightarrow ⑥$$

Substituting the values of $T\Delta S$ & ΔH from equation ⑤ & ⑥ in eq^n ④

$$\Delta G = \Delta U + P\Delta V - q_{rev}$$

$$\Delta G = (\Delta U - q_{rev}) + P\Delta V \longrightarrow ⑦$$

A/c to first law of the thermodynamics

$\Delta U = q_{rev} - W_{max}$ [workdone by a system carries negative sign]

$\boxed{\Delta U - q_{rev} = -W_{max}} \rightarrow ⑧$

substituting the values of ⑧ in eqn ⑦

$\Delta G = -W_{max} + P\Delta V$

$\boxed{-\Delta G = W_{max} - P\Delta V} \rightarrow ⑨$

Here W_{max} is the maximum work that can obtained from the system is the pressure volume work ($P\Delta V$) Thus decrease in Gibb's free energy is a measure of the useful work that can be obtained from the system.

If ΔG is negative, the process will be spontaneous
ΔG is positive, the process will be non-spontaneous
$\Delta G = 0$ the process is at equilibrium.

* Variation of free energy with pressure [3 marks]

The free energy is given by the equation

$G = H - TS \rightarrow ①$

But $H = U + PV \rightarrow ②$

Substituting equation ② in eqn. ① we get

$G = U + PV - TS \rightarrow ③$

complete differentiation of this equation gives

$dG = dU + PdV + VdP - TdS - SdT \rightarrow ④$

$\Delta G = nRT \ln\left(\frac{P_2}{P_1}\right)$ $\quad [\because \ln a - \ln b = \ln(a/b)$

$\Delta G = nRT\, 2.303 \log\left(\frac{P_2}{P_1}\right)$

$\Delta G = 2.303 nRT \log(P_2/P_1)$

At standard condition.

$P_1 = 1 atm \quad T = 298K$ then

$G - G^0 = 2.303 nRT \log P$

$$\boxed{G = G^0 + 2.303 nRT \log P}$$

Here G^0 is the standard free energy. The above equation is useful in deriving van't Hoff isotherm.

Variation of free energy with temperature [3 Marks].

Gibb's free energy is defined by equation.

$G = H - TS \rightarrow ①$

from defination of enthalpy

$H = U + PV \rightarrow ②$

Substitute eqn ② in eqn ①

$G = U + PV - TS \rightarrow ③$

complete differentiation ~~of~~ this equation gives.

$dG = dU + pdV + Vdp - Tds - sdT \rightarrow ④$

From defination of Entropy. $ds = \frac{q}{T} \Rightarrow q = Tds \rightarrow ⑤$

From I law of Thermodynamics.

$dU = q + w$

$q = dU - w \rightarrow ⑥$

W.K.T $\quad w = -pdV \rightarrow ⑦$

From definition of enthalpy

$$\Delta S = \frac{q}{T} \Rightarrow T\Delta S = q \rightarrow ⑤$$

A/c to I law of thermodynamics

$$du = q + w$$

$$q = du - w \longrightarrow ⑥$$

we know that $w = -pdv \longrightarrow ⑦$

$$q = du - (-pdv)$$

$$q = du + pdv \longrightarrow ⑧$$

Substitute equation ⑧ & equation ⑤ in equation ④

$$dG = \cancel{q} + vdp - \cancel{q} - sdT$$

$$dG = vdp - sdT$$

At constant temper., $dT = 0$

$$dG = vdp$$

$$\boxed{\left(\frac{dG}{dp}\right)_T = V}$$

W.K.T $pV = nRT \Rightarrow V = \frac{nRT}{p}$

$$\frac{dG}{dp} = \frac{nRT}{p}$$

$$dG = \frac{nRT}{p} dp$$

$$\therefore \int_{G_1}^{G_2} dG = nRT \int_{P_1}^{P_2} \frac{dp}{p}$$

$$G_2 - G_1 = nRT[\ln P]_{P_1}^{P_2}$$

$$G_2 - G_1 = nRT \ln P_2 - \ln P_1$$

Substitute eqn. ⑦ in equation ⑥

$$q = du + pdV \rightarrow ⑧$$

Substitute equation ⑧ & eqn. ⑤ in equation ④

$$dG = q + vdp - q - sdT$$

$$dG = vdp - sdT$$

At constant pressure, dp=0

$$\boxed{\left(\frac{dG}{dT}\right)_P = -S}$$

Relation ship b/w free energy & work function:-

Free energy is defined as $G = H - TS$

where H- enthalphy & T= temperatur

S= Entropy

G= free energy

Now Let us consider a system which undergoes a change in free energy of a state from ① to ② at constant temperature

$$G_2 - G_1 = (H_2 - H_1) - T(S_2 - S_1)$$

(or) $\Delta G = \Delta H - T\Delta S \rightarrow$ ①

W.K.T $\Delta H = \Delta U + P\Delta V \rightarrow$ ②

substitute eqn ② in eqn ①

$\Delta G = \Delta U + P\Delta V - T\Delta S \rightarrow$ ③

But Helmholtz free energy is defined by equation $\Delta A = \Delta U - T\Delta S \rightarrow$ ④

There fore eqn ③ becomes

$$\boxed{\Delta G = \Delta A + P\Delta V}$$

Thus it is clear that decrease in free energy $(-\Delta G)$ taking place at constant temperature & pressure is maximum work obtained from the system other than of expansion.

The value of ΔH & ΔS for a chemical reac are -94.47 KJ mol^{-1} & $-188.94 \, JK^{-1}$ respectively the change in free energy of the reac at 300K. predict the spontaneity of the reac

Solution:-

Given data:

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$$\Delta H = -94.47 \, kJ mol^{-1}$$

$$\Delta S = -188.94 JK^{-1} = \frac{188.94}{1000} \text{ (or) } 188.94 \times 10^{-3} kJK^{-1}$$

$$T = 300K$$

$$\Delta G = ?$$

we know that $\Delta G = \Delta H - T\Delta S$

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

$$\Delta G = -94.47 \, kJ mol^{-1} - 300K(-188.94 \times 10^{-3} kJK^{-1})$$

$$\Delta G = -37.79 \, kJ$$

Since free energy Charge for the reaction is negative at 300K. It is a spontaneous reaction

2) calculate the standard free energy change of the reaction

$$NO_{(g)} + \frac{1}{2} O_{2(g)} \rightarrow NO_{2(g)}$$

standard free energies of formation $NO_{(g)}$ & $NO_2(g)$ are 87 kJ & 52 $kJ mol^{-1}$.

solution:-

$$\Delta_f G^0 = \Sigma \Delta_f G^0 (\text{products}) - \Sigma \Delta_f G^0 (\text{Reactants})$$

$$\Delta_f G^0 = \Delta_f G^0(NO_2) - [\Delta_f G^0(NO) + \frac{1}{2} \Delta_f G^0(O_2)]$$

$$\Delta_f G^0 = 52 - [87 + \frac{1}{2} \times (0)$$

$$\Delta_f G^0 = \underline{-35 \, kJ}$$

alculate the standard free energy charge for the reaction
$CO + \frac{1}{2} O_{2(g)} \longrightarrow CO_{2(g)}$, $\Delta H^\circ = -270$ kJ
Standard entropies of CO_2, CO & O_2 are 205, 190 & 200 J/degree/mole respectively. predict whether the reaction is feasible (or) not (spont 3

solution:-

Given data
$\Delta H^\circ = 270$ kJ
$S^\circ(CO_2) = 205$ J/degree/mole
$S^\circ(CO) = 190$ -||-
$S^\circ(O_2) = 200$ -||-
$\Delta G^\circ = ?$

$\Delta S^\circ = \Sigma S^\circ_{products} - \Sigma S^\circ_{reactants}$.

$\Delta S^\circ = S^\circ(CO_2) - [S^\circ(CO) + \frac{1}{2} S^\circ(O_2)]$

$\Delta S^\circ = 205 - [190 + \frac{1}{2} 200]$

$\Delta S^\circ = -85$ J/degree/mole.

Apply the relation

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

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

$\Delta H^\circ = -270 \times 1000$ J $= 270000$ J

$T = 25 + 273 = 298$ K.

$\Delta S^\circ = -85$ J/degree/mol.

$\Delta G^\circ = -270000 - 298(-85)$

$\Delta G^\circ = -244670$ J

$\boxed{\Delta G^\circ = -244.67 \text{ kJ}}$

Since ΔG is negative hence the reaction is spontaneous.

Variation **Derive Gibb's - Helmoltz equation:-**

HM *

we know that (a) The Gibb's free energy defined by the equation

$G = H - TS \rightarrow ①$

(b) $\Delta G = \Delta H - T\Delta S$.

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But Enthalpy is defined by the equation

$H = U + PV \rightarrow ②$

Substitute the value of H from ② in eqn ①

$G = U + PV - TS \rightarrow ③$

complete differentiation of eqn ③ is given by

$dG = dU + PdV + VdP - TdS - SdT \rightarrow ④$

From Ist Law of T.D.

$dU = dq + w \rightarrow ⑤$

But $w = -PdV \rightarrow ⑥$

Substitute eqn ⑥ in eqn ⑤

$dU = dq - PdV$

$dq = dU + PdV \rightarrow ⑦$

From Entropy definition

$dS = \frac{dq}{T}$

$\therefore dq = TdS \rightarrow ⑧$

compare eqn ⑧ & eqn ⑦

$TdS = dU + PdV \rightarrow ⑨$

Substitute values TdS from ⑨ in eqn ④

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

$dG = VdP - SdT \rightarrow ⑩$

At constant pressure

$\Rightarrow dP = 0$

$dG = -SdT \rightarrow ⑪$ $\Longrightarrow$

Therefore equation ⑪ is also written as

$$\left(\frac{dG}{dT}\right)_p = -S \longrightarrow ⑫$$

Therefore for the initial state of the system.

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$$\left(\frac{dG_1}{dT}\right)_p = -S_1 \longrightarrow ⑬$$

For the final state of the system

$$\left(\frac{dG_2}{dT}\right)_p = -S_2 \rightarrow ⑬$$

∴ Change in Gibb's free energy at constant pressure.

$$\left(\frac{dG_2}{dT}\right)_p - \left(\frac{dG_1}{dT}\right)_p = -S_2-(S_1)$$

$$\therefore \left[\frac{d(G_2-G_1)}{dT}\right]_p = -(S_2-S_1)$$

$$\left(\frac{d(\Delta G)}{dT}\right)_p = -\Delta S \rightarrow ⑭$$

multiply negative sign on both sides.

$$\Delta S = \left[-\frac{d(\Delta G)}{dT}\right]_p \longrightarrow ⑮$$

W.K.T. $\Delta G = \Delta H - T\Delta S \rightarrow ⑯$

Substitute value of ΔS from eqn ⑮ in eqn ⑰

$$\therefore \boxed{\Delta G = \Delta H + T\left(\frac{d(\Delta G)}{dT}\right)_p}$$

The above equation is called Gibb's Helmoltz equation

1) The free energy change involved in a process is -1
300K and -1200J at 310K. calculate the change in
~~of~~ the process at 306K

Solution:-

$\Delta G_1 = -1235J$ at $T_1 = 300K$

6 $\Delta G_2 = -1200J$ at $T_2 = 310K$

$\Delta H = ?$

using Gibb's Helmholtz equation.

$$\Delta G = \Delta H + T\left(\frac{\partial(\Delta G)}{\partial T}\right)_P$$

$$\text{where } \left(\frac{\partial(\Delta G)}{\partial T}\right)_P = \frac{\Delta G_2 - \Delta G_1}{T_2 - T_1}$$

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = \frac{-1200 - (-1235)}{310 - 300}$$

$$= \frac{35}{10}$$

$$\left(\frac{\partial(\Delta G)}{\partial T}\right)_P = 3.5JK^{-1}$$

The free energy change at 306K can be taken as the average values of free energy at 300K & 310K

$$\therefore \Delta G(\text{at } 306K) = \frac{1}{2}\left[\cancel{\frac{G_2 + G_1}{T_2 - T_1}}\right] = \frac{G_2 + G_1}{2}$$

$$= \frac{1}{2}\left[\cancel{\frac{-1200 + (-1235)}{310 - 300}}\right] = \frac{-1200 + (-1235)}{2}$$

~~= −121.75~~

~~= −0.1217 kJ~~

$$\Delta G = \frac{-2435}{2}$$

$$\Delta G = -1217.5\,J$$

$$\Delta G = -1.217\,kJ$$

Gibb's Helmholtz equation can be written as

$$\Delta H = \Delta G - T\left[\frac{\partial(\Delta G)}{\partial T}\right]_p$$

Substituting values

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$\Delta H = ~~-0.1217~~ - 306 \times 3.5$

$\Delta H = 1071.12$ kJ

$\Delta H = -1.2017 - 1306 \times [3.5/1000]$

$\Delta H = -1217.5 - 306 \times 3.5$

$\Delta H = -2288.5$ J

$\Delta H = \underline{-2.288 \text{ kJ}}$

* Applications of Gibb's Helmholtz equation:-

- * Gibb's - helmoltz equation is useful in calculating **ΔH when ΔG is known at two different temperature**
- * Gibb's helmholtz equation is used in deriving Van't Hoff reaction isochore.

* Derive Van't Hoff reaction isotherm

Consider a general reversible reaction.

② Let us assume a reaction involving four gases A, B, C & D

$$A + B \rightleftharpoons C + D$$

In this reaction amounts of A & B are decreasing C, D are increasing. Free energy of A & B are decreasing while these C & D are increasing.

Free energy of substance A per mole at te
'T' is given as follows

$$G_A = G_A^\circ + RT \ln P_A$$

S

where P_A is the pressure of A

G_A° is the free energy at standard condition

Similarly the free energy of B, C & D are as follows

$$G_B = G_B^\circ + RT \ln P_B$$

$$G_C = G_C^\circ + RT \ln P_C$$

$$G_D = G_D^\circ + RT \ln P_D$$

The free energies of the reaction

$$\Delta G = G_P - G_R$$

$$\Delta G = (G_C + G_D) - (G_A + G_B)$$

$$\Delta G = G_C^\circ + RT \ln P_C + G_D^\circ + RT \ln P_D - [G_A^\circ + RT \ln P_A + G_B^\circ + RT \ln P_B]$$

$$= G_C^\circ + RT \ln P_C + G_D^\circ + RT \ln P_D - G_A^\circ - RT \ln P_A - G_B^\circ - RT \ln P_B$$

$$= G_C^\circ + G_D^\circ - G_B^\circ - G_A^\circ + RT \ln P_C + RT \ln P_D - RT \ln P_A - RT \ln P_B$$

$$= \Delta G^\circ + RT \ln P_C + RT \ln P_D - RT \ln P_A - RT \ln P_B$$

$$= \Delta G^\circ + RT [\ln P_C + \ln P_D - (\ln P_A - \ln P_B]$$

$$= \Delta G^\circ + RT [\ln P_C + \ln P_D - (\ln P_A + \ln P_B)]$$

$$= \Delta G^\circ + RT \ln \left[\frac{P_C \cdot P_D}{P_A \cdot P_B}\right]$$

$\Downarrow$

$$\Delta G = \Delta G^\circ + RT \ln(P_C \cdot P_D) - \ln(P_A \cdot P_B)$$

$\ln(a) + \ln(b) = \ln(ab)$

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

$$\Delta G = \Delta G^\circ + RT \ln \left[\frac{P_C \cdot P_D}{P_A \cdot P_B}\right] \rightarrow ①$$

$$\Rightarrow \Delta G = \Delta G^\circ + RT \ln[(P_C \cdot P_D) \div P_A \cdot P_B)$$

If the system is at equilibrium

$$\Delta G = 0$$

$$0 = \Delta G^\circ + RT \ln \frac{P_C \times P_D}{P_A \times P_B}$$

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$$\Delta G^\circ = -RT \ln \frac{P_C \times P_D}{P_A \times P_B}$$

For general equation

$$aA + bB + \text{------} \rightleftharpoons cC + dD + \text{-----}$$

$$\Delta G^\circ = -RT \ln \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \Rightarrow \Delta G^\circ = -RT \ln K_p$$

$$\Delta G^\circ = -2.303\, RT \log \left[\frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^b} \right]$$

$$\boxed{\Delta G^\circ = -2.303\, RT \log K_p}$$

where $K_p = \frac{P_C^c \cdot P_D^d}{P_A^a \cdot P_B^c}$

- The above equation is called Van't Hoff reaction isotherm.

* This is useful in calculating ΔG° for reaction.

1) At 2000K, the standard state free energy change (ΔG°) for the reaction $N_2 + O_2 \rightleftharpoons 2NO$ is given by $\Delta G^\circ = 92048 - 10.46T$ J. Calculate K_p for the reaction at 2000K ($R = 8.314\ JK^{-1} mol^{-1}$]

Solution:- W.K.T $\Delta G^\circ = -RT \ln K_p$

$$\Delta G^\circ = -2.303 RT \log K_p$$

$$\log K_p = -\left[\frac{\Delta G^\circ}{2.303 \times R \times T} \right]$$

$$\log K_p = -\left[\frac{92048-10.246\times 2000\ J\,mol^{-1}}{(2.303)(8.314\ JK^{-1}mol^{-1})\ (2000K)}\right]$$

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$= -\left[\frac{12,40769098}{}\right.$

$\log K_p = -246.8068.8$

$K_p =$ ③ $\Delta G^0 = -RT\ln K_p$

$\Delta G^0 = -2.303RT\log K_p$

$(92048-10.246\times 2000) = -[2.303\times 8.314\times 2000\log K_p]$

$(92048-20,920) = -38,294.284\log K_p$

$71,128 = -38,294.284\log K_p$

$\log K_p = -\frac{71,128}{38294.284}$

$\log K_p = -1.8574$

$K_p = \text{antilog}(-1.8574) = 0.01389$

$K_p = 1.39\times 10^{-2}$ atm

2) The value of K_p for the water gas reaction $CO + H_2O \rightleftharpoons CO_2 + H_2$ is 1.06×10^5 at 25°C calculate the standard state free energy change ΔG^0 of the reaction at 25°C [$R = 8.314\ JK^{-1}mol^{-1}$]

Solution:-

$K_p = 1.06\times 10^5$

$T = 25+273 = 298K$

$\Delta G^0 = ?$

$\Delta G^0 = -RT\ln K_p$

$\Delta G^0 = -2.303RT\log K_p$

$\Delta G^0 = -2.303\times 8.314\times 298\log(1.06\times 10^5)$

$\Delta G^0 = -28,673.633$

e Van't Hoff Reaction Isochore:- 4 Marks

From Gibbs Helmholtz equation

$$\Delta G = \Delta H + T\left[\frac{d(\Delta G)}{dT}\right]_P \longrightarrow ①$$

$$\Delta H = \Delta G - T\left[\frac{d(\Delta G)}{dT}\right]_P \longrightarrow ②$$

equation ② is divided by T^2 on both side

$$\frac{\Delta H}{T^2} = \frac{\Delta G \quad - T\left[\frac{d(\Delta G)}{dT}\right]_P}{T^2}$$

$$\frac{\Delta H}{T^2} = \frac{\Delta G - T\left[\frac{d(\Delta G)}{dT}\right]_P}{T^2} \longrightarrow ③$$

W.K.T $$\left[\frac{d\left(\frac{\Delta G}{T}\right)}{dT}\right]_P = \frac{T\cdot\frac{d(\Delta G)}{dT} - \Delta G \ (1)}{T^2}$$

$$\left[\frac{d\left(\frac{\Delta G}{T}\right)}{dT}\right]_P = \frac{T\frac{d(\Delta G)}{dT} - \Delta G}{T^2} \longrightarrow ④$$

multiply negative sign on. Both side of equation ④

$$-\left[\frac{d\left(\frac{\Delta G}{T}\right)}{dT}\right]_P = \frac{\Delta G - T\frac{d(\Delta G)}{dT}}{T^2} \longrightarrow ⑤$$

comparing equation ③ & ⑤

$$\frac{\Delta H}{T^2} = -\left[\frac{d(\Delta G/T)}{dT}\right]_P \longrightarrow ⑥$$

$$-\frac{d\left(\frac{\Delta G}{T}\right)}{dT} = \frac{\Delta H}{T^2}$$

equation (8) is multiplied with negative sign

$$\frac{d\left(\frac{\Delta G}{T}\right)}{dT} = -\frac{\Delta H}{T^2}$$

At standard condition

$$\frac{d\left(\frac{\Delta G^0}{T}\right)}{dT} = -\frac{\Delta H^0}{T^2} \longrightarrow (9)$$

w.k.t $\Delta G^0 = -RT\ln K_p$ —(8) [Van't Hoff reaction Isotherm]

Substitude the value of ΔG^0 from eqn (8) in equation (9)

$$\frac{d\left(\frac{-RT\ln K_p}{T}\right)}{dT} = -\frac{\Delta H^0}{T^2}$$

$$\frac{d(-R\ln K_p)}{dT} = -\frac{\Delta H^0}{T^2}$$

$$\frac{d(-R\ln K_p)}{dT} = -\frac{\Delta H^0}{T^2}$$

$$d(R\ln K_p) = \frac{\Delta H^0}{T^2}\cdot dT$$

Integrate on Both side

$$\int_{K_1}^{K_2} d(R\ln K_p) = \Delta H^0 \int_{T_1}^{T_2} \frac{1}{T^2}\, dT$$

$$R[\ln K_p]_{K_1}^{K_2} = \Delta H^0 \left[\frac{-1}{T}\right]_{T_1}^{T_2}$$

$$[\ln K_p]_{K_1}^{K_2} = \frac{\Delta H^0}{R}\left[\frac{-1}{T^2} - \left[\frac{-1}{T_1}\right]\right]$$

13 $$\ln[K_2 - K_1] = \frac{\Delta H^0}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$\ln\left[\frac{K_2}{K_1}\right] = \frac{\Delta H^0}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\boxed{\log\left[\frac{K_2}{K_1}\right] = \frac{\Delta H^0}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]}$$

This is known as Van't Hoff reaction isochore.

1) The equilibrium constant K_p, for the reaction $H_2(g) + S(g) \rightleftharpoons H_2S(g)$ is 20.2 atm at 945°c & 9.21 atm 1065°c calculate the heat ~~of~~ reaction.

Solution:-

$K_2 = 9.21$ atm at $T_1 = 945 + 273 = 1218K$

$K_1 = 20.2$ atm at $T_2 = 1065 + 273 = 1338K$

$\Delta H = ?$

we know that,

$$\log\left[\frac{K_2}{K_1}\right] = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\log\left[\frac{9.21}{20.2}\right] = \frac{\Delta H}{2.303 \times 8.314}\left[\frac{1338 - 1218}{1338 \times 1218}\right]$$

$$\log(0.4559) = \frac{\Delta H}{19.147}\left[7.3633 \times 10^{-5}\right]$$

$$-0.34113 = \frac{\Delta H}{19.147} \times 7.3633 \times 10^{-5}$$

$$\Delta H = \frac{-0.34113}{7.3633\times10^{-5}} \times 19.147$$

$$\Delta H = -88705.117\,J$$

$$\boxed{\Delta H = -88.705\,kJ}$$

2) The equilibrium constant K_p for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.64×10^{-4} atm at 400°C what will b the equilibrium constant at 500°C if the heat of reacti in this temperature range is −105185.8J ?

Solution:-

$K_1 = 1.64\times10^{-4}$ atm at $T_1 = 400°C + 273 = 673K$

14 $K_2 = ?$ at $T_2 = 500 + 273 = 773K$

$\Delta H = -105185.8J$

w.k.T $$\log\left(\frac{K_2}{K_1}\right) = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log K_2 - \log K_1 = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log K_2 = \log K_1 + \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log K_2 = \log(1.64\times10^{-4}) + \left[\frac{-105185}{2.303\times8.314}\right]\left[\frac{773-673}{773\times673}\right]$$

$$\log K_2 = (-3.7851) - (5493.509)(1.9222\times10^{-4})$$

$$\log K_2 = -3.7851 - 1.0559$$

$$\log K_2 = -4.84107$$

$$K_2 = \text{antilog}(-4.84107) = 1.441\times10^{-5}\ \text{atm}$$

$$K_2 = 0.144\times10^{-4}\ \text{atm}$$

Clausius-clapeyron Equation

4 Marks

Consider a liquid in equilibrium with its vapour at tempr. T & pressure P.

(or) consider a system in which liquid & its vapour are in equilibrium at tempr T & pressure P.

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

is

Let the tempr. of the system is changed from T to T+dT and pressure from P to P+dP at equilibrium. dT & dp are infinitesimal changes in tempr & pressure respectively.

We know that $dG = Vdp - SdT \longrightarrow ①$

For evaporisation of liquid, $dG_1 = V_1dp - S_1dT \longrightarrow ②$

For condensation of gases $dG_2 = V_2dp - S_2dT \longrightarrow ③$

When liquid & vapours are in equilibrium

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

From equation ① & ②

$$V_1dp - S_1dT = V_2dp - S_2dT$$

$$(V_1 - V_2)dp = (S_1 - S_2)dT$$

$$\frac{dP}{dT} = \frac{S_1 - S_2}{V_1 - V_2}$$

(or) $$\frac{dP}{dT} = \frac{\Delta S_{(vap)}}{\Delta V_{(vap)}} \longrightarrow ④$$

where ΔS – change in Entropy
ΔV – change in volume

But At equilibrium $dG = 0$

$$\therefore \Delta G_{(vap)} = \Delta H_{(vap)} - T\Delta S_{(vap)}$$

$$0 = \Delta H_{(vap)} - T\Delta S_{(vap)}$$

$$\Delta H_{(vap)} = T\Delta S_{(vap)}$$

$$\Delta S_{vap} = \frac{\Delta H(vap)}{T} \longrightarrow ⑤$$

Substituting the value of $\Delta S_{(vap)}$ in ④

16 $$\boxed{\frac{dP}{dT} = \frac{\Delta H(vap)}{T \cdot \Delta V}} \longrightarrow ⑥$$

Equation ⑥ is called clapeyron equation

clapeyron equation ⑥ can be apply to vaparisation & Sublimation equilibrium in which one of the two phases is gaseous.

$$\Delta V(vap) = V_{(g)} - V_{(l)} \longrightarrow ⑦$$

We know that, the volume of the liquid is very small compared to volume of the gas. hence $V_{(l)}$ can be neglected in comparision to $V_{(g)}$

∴ eqn. ⑦ becomes

$$\Delta V_{(vap)} = V_{(g)} \longrightarrow ⑧$$

But $PV_{g} = RT \Rightarrow V_{(g)} = \frac{RT}{P}$

$$\Delta V_{(vap)} = V_{g} = \frac{RT}{P} \longrightarrow ⑨$$

Substitute equation ⑨ in equation ⑥

$$\frac{dP}{dT} = \frac{\Delta H(vap)}{T \cdot \frac{RT}{P}}$$

$$\frac{dP}{dT} = \frac{\Delta H \times P}{RT^2} \longrightarrow ⑩$$

rearranging eqn. ⑩

$$\frac{dP}{P} = \frac{\Delta H}{R} \frac{dT}{T^2} \longrightarrow ⑪$$

Integrating equation ⑪ b/w limits P_1 & P_2 and T_1 & T_2

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H_{(vap)}}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\left[\ln P\right]_{P_1}^{P_2} = \frac{\Delta H_{(vap)}}{R} \left[\frac{-1}{T}\right]_{T_1}^{T_2}$$

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$$\ln P_2 - \ln P_1 = \frac{\Delta H_{(vap)}}{R} \left[-\frac{1}{T_2} - \left(-\frac{1}{T_1}\right)\right]$$

$$\ln\left[\frac{P_2}{P_1}\right] = \frac{\Delta H_{(vap)}}{R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

$$2.303 \log\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{(vap)}}{R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]$$

$$\boxed{\log\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_{(vap)}}{2.303R}\left[\frac{T_2 - T_1}{T_1 T_2}\right]} \longrightarrow 12$$

The equation ⑫ is called clausius-clapeyron equation.

1) The normal boiling point of water is 100°C. It vapour pressure at 80°C is 0.4672 atm. Calculate the Enthalpy of vaporisation per mole of water.

$T_1 = 100°C = 100 + 273 = 373\,K$

$P_1 = 1\,atm$

$T_2 = 80°C = 80 + 273 = 353\,K$

$P_2 = 0.4672\,atm$

$\Delta H_{vap} = ?$

we know that

$$\log\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_V}{2.303R}\left[\frac{T_2-T_1}{T_1 \times T_2}\right]$$

$$\log\left(\frac{0.4672}{1}\right) = \frac{\Delta H_V}{2.303 \times 8.314}\left[\frac{353-373}{353 \times 373}\right]$$

$$-0.3305 = \frac{\Delta H_V}{2.303 \times 8.314}\left[\frac{-20}{353 \times 373}\right]$$

$$-0.3305 = \frac{\Delta H_V}{19.1147}\left[-1.5189 \times 10^{-4}\right]$$

∴

$$\Delta H_V = \frac{0.3305 \times 19.1147}{1.5189 \times 10^{-4}}$$

$$\Delta H_V = 41668.275$$

$$\Delta H_V = 41.668\ kJ\ mol^{-1}$$

2) water boils at 373K at one atmospheric pressure. At what temperature will it boil when atmospheric pressure becomes 528 mm of Hg at some space station. Latent heat of H_2O = 2.28 kJg^{-1}, R = 8.314 $JK^{-1}mol^{-1}$

Solution:-

$T_1 = 373K$

$P_1 = 1atm = 760mm$ ⇒ A millimetre of mercury is a manometric unit of pressure.

$P_2 = 528mm$

$T_2 = ?$

$\Delta H_V = 2.28\ kJ\ g^{-1}$

$= 2.28 \times 18\ kJ\ mol^{-1}$

$= 41.04\ kJ\ mol^{-1}$

$= 41040\ J\ mol^{-1}$

$R = 8.314\ JK^{-1}\ mol^{-1}$

We know that

$$\log\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_v}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$\log\left(\frac{521}{760}\right) = \frac{41440}{2.303\times 8.314}\left[\frac{T_2-373}{373T_2}\right]$$

$$-0.1582 = 2143.4 \times \left[\frac{T_2-373}{373T_2}\right]$$

19 $$-50.0T_2 = 2143.4T_2 - 799488.2$$

$$2202.4T_2 = 799488.2$$

$$\boxed{T_2 = 363K}$$

3) water boils at 100°c at a pressure of 1atm. Calculate the Vapour pressure of water at 90°c. The heat of vaporisation of water is 9.80 kcal mol^{-1}

$T_1 = 100+273 = 373K$

$P_1 = 1atm$

$T_2 = 90+273 = 363K$

$P_2 = ?$

$\Delta H_v = 9.80\, kcal\, mol^{-1}$

$= 9.50\times 1000\ cal\, mol^{-1}$

$\Delta H_v = 9500\ cal\, mol^{-1}$

$R = 1.987\ cal\, deg^{-1} mol^{-1}$

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

$R = 1.987\ cal\, deg^{-1} mol^{-1}$

w.k.T $$\log\left(\frac{P_2}{P_1}\right) = \frac{\Delta H_v}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$\log\left(\frac{P_2}{1}\right) = \frac{9800}{2.303\times 1.987}\left[\frac{363-373}{373\times 363}\right]$$

$$\log P_2 - \log(1) = -2141.57 \times 7.385\times 10^{-5}$$

$$\log P_2 = -0.15816$$

$$P_2 = \text{antilog}(-0.15816) \Rightarrow \underline{P_2 = 0.6938\, atm}$$

Nernst Heat Theorem:-

This theorem Explain the variation of enthalpy cl
& free energy charge of a system with decrease of temperature.

A/c to Gibb's-Helmholtz equation.

$$\Delta G = \Delta H + T\left(\frac{\partial \Delta G}{\partial T}\right)_p \longrightarrow ①$$

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From this equation, it is evident that at the absolute zero i.e. when T=0, $\Delta G = \Delta H$.

Thus ΔG & ΔH approach each other as temper approaches zero.

Statement of Nernst's heat theorem:-

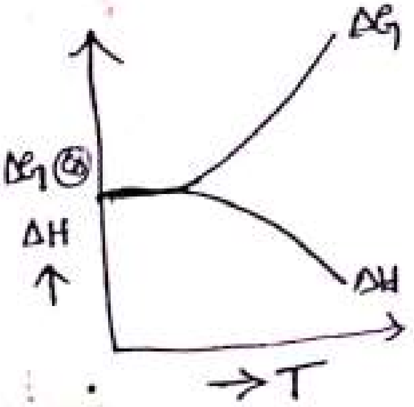
Nernst heat theorem states that "At zero kelvin. ΔG & ΔH not only become equal but also approaches each other gradually at temperature close to absolute zero."

This theorem is mathematically expressed as.

$$\lim_{T\to 0} \frac{d(\Delta G)}{dT} = \lim_{T\to 0} \frac{d(\Delta H)}{dT} = 0 \longrightarrow ①$$

This means that Nernst observed that as the temps. is lowered towards absolute zero. the value of $\frac{\partial(\Delta G)}{\partial T}$ decreases and then approaches zero asymptotically.

graphically represented by



Further $$\left[\frac{\partial(\Delta G)}{\partial T}\right]_p = -\Delta S \rightarrow ②$$

$$\left(\frac{\partial(\Delta H)}{\partial T}\right)_p = \Delta C_p \rightarrow ③$$

from equations ①, ② & ③, as $T \rightarrow 0$

$\Delta S = 0$ & $\Delta C_p = 0$.

i.e as the temper is lowered towards absolute zero, the entropy change of the reaction & difference in the heat capacities of products & reactants also tends to be zero

=> Nernst heat theorem is applicable only to pure crystalline solids as no gas exists at absolute zero
2) and is not applicable to liquids.

Third law of thermodynamics :-

Third law of thermodynamics states that "the entropy of all perfectly crystalline solids is zero at the absolute zero temperature."

Residual entropy :-

[Residual entropy conclude that entropies of substance are not zero at 0K

3marks 2019 Absolute entropy of substance can be calculated from (i) III law of thermodynamics & ii) stastical methods.

* The entropy possessed by a substance even at absolute zero is known as residual entropy

$S = k \ln W$

S = statistical entropy

W = Number of possible arrangement of atoms, molecules (or) ions in a crystal [thermodynamic probability]

k = Boltzman constant.

In many cases the above two method give same values from entropy.

In few cases like H_2, CO, NO etc absolute values of entropy calculated from statistical method gives higher value.

The difference b/w entropy calculated from statistical method & using III law of T.D is called residual entropy.

Residual entropy in hydrogen is due to ~~exis~~ existence of ortho & para hydrogens.

In CO & NO, in the solid state, the arrangement can be like CO & OC, NO & ON. Due to these different possibilities residual entropy is observed.

Residual entropy of CO :-

A sample of CO contains N molecules. Each molecule of CO can have two orientations.

CO (or) OC

Let there be N molecules in one mole of the substance. Therefore N molecules can have 2^N orientations

i.e. $W = 2^N$

The residual entropy can be calculated as

$S = k \ln W$

$S = k \ln 2^N$

$S = k.N \ln(2)$

$S = R \ln(2)$

$S = 8.314 \ln(2)$

$S = 8.314 \times 0.693$

$S = 5.762 \ JK^{-1} mol^{-1}$

$S = k \ln w$

$S = 2.303 k \log w$

$S = 2.303 k \log(2)^N$

$S = 2.303 (k.N) \log(2)$

$S = 2.303 R \log 2$

$S = 2.303 \times 8.314 \times \log(2)$

$S = 5.762 \ JK^{-1} mol^{-1}$

$R = K.N$

$R = 8.314 \ JK^{-1} mol^{-1}$

hemical potential @ partial molar free energy

* The most important partial molar property in physical chemistry is the partial molar free energy, designated as chemical potential & represented as.

$$\left(\frac{\partial G}{\partial n_i}\right)_{T,P,n_1\cdots n_j} = \overline{G_i} = \mu_i$$

* Magnitude of an extensive property like G, H, E etc depends on temperature pressure & also on the number of moles of different components in case of an open system.

If n_1 & n_2 are the number of moles of two components in an open system.

$$G = f(P, T, n_1, n_2 \cdots)$$

dG corresponds to a small change in all variables of the system is given by

$$dG = \left(\frac{\partial G}{\partial T}\right)_{P,n_1,n_2} dT + \left(\frac{\partial G}{\partial P}\right)_{T,n_1,n_2} dP + \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1} + \cdots$$

At constant pressure & temperature

$$dG = \left(\frac{\partial G}{\partial n_1}\right)_{T,P,n_2\cdots} dn_1 + \left(\frac{\partial G}{\partial n_2}\right)_{T,P,n_1\cdots} dn_2$$

$$dG = \mu_1 dn_1 + \mu_2 dn_2$$

where $\mu_1 = \left(\frac{\partial G}{\partial n_1}\right)_{P,T,n_2}$

$$\mu_2 = \left(\frac{\partial G}{\partial n_2}\right)_{P,T,n_1}$$

μ_1 & μ_2 are called partial molar free energy @ chemical potential.

Adsorption.

- Adsorption is a surface phenamenon.
- The solid surface is able to attract the molecula to gas Ⓡ liquid & accumalates them on it surface. the adsorption is defined as,
- ∴ The process of adhearing (accumulation) of the molecules of gas Ⓡ liquid on the surface of solid is known as <u>adsorption</u>.

- <u>examples</u> :

i) A small amount of finely powdered charcoal is added to the solution of blue ink. intensity of blue colour decreases molecula of dye (ink) holds on the surface of activated charcoal, hence colour decreases.

- ii) A small quantity of finely powdered Nickel is added to hydrogen gas in a vessel. the pressure of H_2 gas decreases. i.e. the gas molecula are held on the solid surface. hence pressure of gas decreases.

iii) A small quantity of silica gel is placed in humid chamber, water molecules are held on silica-gel & there is a decrease in concentration of H_2O.

Adsorbent :- The solid which adsorbs the molecules of gas Ⓡ liquid. here the solid is called <u>adsorbent</u>

Adsorbate :- The substance (gas Ⓡ liquid) which adsorbs on the solid. The substance is called adsorbate.

sorption:- Absorption is the penetration of gas (or) liquid molecules into the interior of the solid, the molecules are spread throwout the solid & its concentration is uniform.

Ex:- * Sponge soaked in water
* absorption hydrogen chloride in water.

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3marks difference b/w adsorption & absorption

Adsorption	absorption.
* Accumulation of the molecules of gas (or) Liquid on the surface of solid	* molecules penetrate into interior of solid
* concentration of adsorbed molecules is high on surface	* absorbed molecules uniformly distributed through out the solid by capillary forces.
* magnitude of adsorption depends on T, P & concen. & surface area	* Magnitude does not depend on T, P & concen.
* Heat is released	* Heat may be released (or) absorbed.

Mechanism of adsorption:-

* Mechanism of adsorption can be explained as, In terms of chemical bonding. The atoms of solid in the interior part are different from atoms of the same solid on its surface.

* In the interior part each atom is bounded to otheratom and all the valencies are satisfied. But on the surface of solid the situation is different that is at the surface atoms are not bounded to any

other atoms. and this leads to unsatified valenc due to this reason the surface of solid can hold the atoms of gases & liquids.

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Types of adsorption:- * There are two types of adsorp

Types of adsorptions are classified on the basis of force by which the molecules of adsorbate are held to the surface of adsorbent.

1) physisorption or physical adsorption

* physisorption or physical adsorption occurs when the molecules of a gas are held on the surface of a solid by weak Vanderwaals force.
* physical adsorption depends on the surface area of solid & nature of gas. nature of gas means readily adsorbed & it is reversible. Increase in pressure increases physical adsorption.
* The adsorbed molecules can be desorbed by decreasing pressure. physiccal adsorption is favored at low tempr.
* the adsorbed molecule of gas can be desorbed by increasing tempr.
* The enthalpy (heat liberated) in physical adsorption is low & it is of the order of $\Delta H = -20kJ$ to $\Delta H = -40kJ$.
* the adsorption is multilayer.

2) Chemisorption or chemical adsorption:-

* Chemical adsorption takes place through chemical bond formed b/w adsorbate molecules & the surface of adsorbent.
* chemical adsorption takes place at higher tempr.
* chemical adsorption results in breaking of bonds & formation of new bonds

The enthalpies of chemisorption are high [ΔH = -200 to -400 kJ] mol

* The adsorbed molecules are tightly held. it is difficult to desorb them by raising temp.

* In this adsorption single layer adsorption takes place.

Imp * Difference b/w physisorption & chemisorption. [3 marks question.

27	physisorption (or) physical adsorption	chemisorption (or) chemical adsorption
1)	physical adsorption is a very fast process	chemical adsorption is a slow process.
2)	Adsorbate molecules are held to surface by weak vanderwaals forces.	Adsorbate molecules are held to surface by strong chemical bonds
3)	Adsorption is multilayer	Adsorption is single layer.
4)	Enthalpy of adsorption is low [ΔH = -20 to -40 kJ]	4) Enthalpy of adsorption is high [ΔH = -200 to -400 kJ]
5)	Reversible [adsorbate molecules are removed]	5) Not reversible [adsorbate molecules are not removed]
6)	Depends on nature of gas, Easily liquifiable gases are readily adsorbed	6) Much more specific than physical adsorption.

Factors influencing adsorption :-

solids (adsorbent) have a tendency to adsorp gases due to unsaturated valencies on their surface. the Imp factors that influence adsorption of gases on solid are the following.

→ 1) surface area of adsorbent:-

The capacity of adsorption of a solid depends on the state of subdivision of the solid. A more finely divided solid has a large surface area, hence finely divided solids can adsorb more quantities of substance and also solids with porous can have large surface & they are also good adsorbents.

→ 2) Nature of adsorbate & adsorbent:-

Physical adsorption is general phenomenon & does not depends on nature of adsorbate & adsorbent. But chemical adsorption is specific & it depends on nature of both adsorbent & adsorbate.

for eg:- Ni, pt, Fe adsorbs only H_2 but not O_2
silicagel adsorbs only moisture.
tungsten adsorbs only oxygen (O_2)

3) Temperature:-

physical adsorption occurs rapidly at low temp^r and decreases with increasing temp^r.

(or) Both physical adsorption and chemical adsorption are takes place with the liberation of heat (or) exothermic process. This shows that with increase in T, adsorption decreases.

4) Pressure:- For both physical adsorption & chemical adsorption the amount of gas adsorbed at a given temp^r increases initially with increase in pressure & becomes const at high pressure.

Adsorption Isotherm :-

An adsorption isotherm is graphical representation ⓞⓡ mathematical expression. which relates the amount of gas adsorbed by the solid (adsorbent) and the equilibrium pressure at constant temperature

There are 2 types of isotherms

1) Freundlich Isotherm ✗ Freundlich isotherm is emperical.

Imp If 'x' is the mass of the gas adsorbed on a mass 'm' of the solid (adsorbent) at a pressure 'p' of the adsorbate (gas) at constant temperature

[ⓞⓡ Freundlich isotherm gives the relationship b/w mass of gas (x), mass of solid (m) and pressure "p" of the gas (adsorbate) at constant temperature].

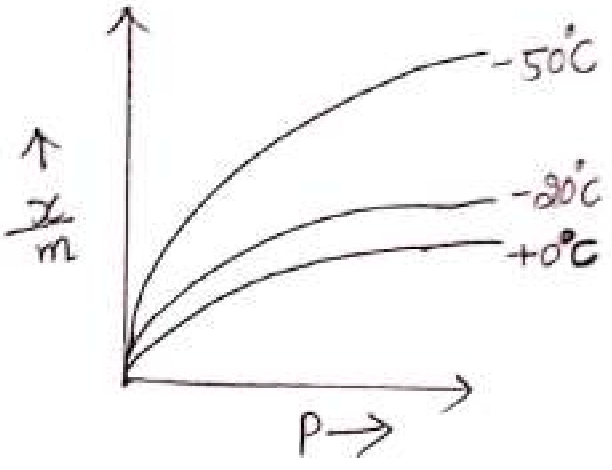
This isotherm is mathematically represented as

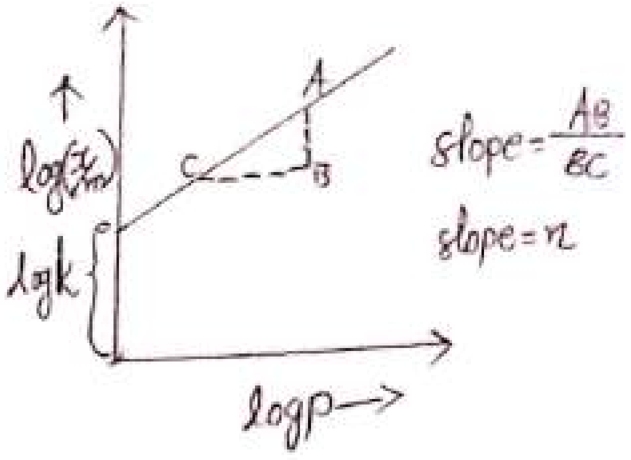
$$\frac{x}{m} = k.p^{n} \longrightarrow ①$$

where x – mass of gas (adsorbate)
m – mass of solid (adsorbent)
p – pressure of gas
k & n are constant, depends on nature of adsorbent & adsorbate and the temperature.

on taking log on both side of equation ① we get

$$\log\left(\frac{x}{m}\right) = \log k + n.\log p \longrightarrow ②$$





Equation ② is of the form $y = mx + c$, gives a straight line, if the values of $\log \frac{x}{m}$ v/s logp a straight line is obtained. The slope of this line gives the value of 'n', the intercept of the line is equal to logk. From this we come to know that the values of constants n & k can be evaluated.

2) Langmuir adsorption isotherm

Vimp

* Langmuir's model was a theoretical construct. Following are the Imp postulates of langmuirs adsorption isotherm.

1) only one molecule of a gas (adsorbate) can adsorbs at each site of solid (adsorbent)
2) There is no interaction b/w the adjacent adsorbed molecules.
3) The adsorbed gas molecules continuously evaporate from the surface of solid & passes into gas phase after sometime an equilibrium is established b/w condensing & evaporating gas molecules. The equilibrium is dynamic in nature. [Rate of adsorption is equal to rate of desorption]

Deduce Langmuir adsorption isotherm

Derivation

If 'θ' is the fraction of the surface covered by the molecules, the $(1-\theta)$ is the fraction of the surface not covered by molecules.

Rate of adsorption depends on
1) pressure of the gas - P
2) surface uncovered [number of sites not covered by molecules → $1-\theta$]

∴ Rate of adsorption $\propto P(1-\theta)$

Rate of adsorption $= K_a P(1-\theta) \longrightarrow ①$

where K_a → rate constant for adsorption process

∴ Rate of desorption $\propto \theta$

Rate of desorption $= K_d\theta$

where K_d → rate constant for desorption process.

At equilibrium

Rate of adsorption = Rate of desorption

$$K_aP(1-\theta) = K_d\theta$$

$$K_aP - K_aP\theta = K_d\theta$$

$$K_aP = K_d\theta + K_aP\theta$$

$$K_aP = [K_d + K_aP]\theta$$

$$\theta = \frac{K_aP}{K_d + K_aP} \longrightarrow ③$$

÷ equn.③ by K_d only on righ side

$$\theta = \frac{\left(\frac{K_a}{K_d}\right)P}{\left(\frac{K_d}{K_d}\right) + \left(\frac{K_a}{K_d}\right)P}$$

$$\boxed{\theta = \frac{bp}{1+bp}} \longrightarrow Ⓗ$$ where $\frac{K_a}{K_d}$ is equal to 'b' and "b" is called adsorption co-efficien

This equation is called langmuir's isotherm.

case-1: At low pressure: bp<<1 hence bp in Denominator is neglected in equation Ⓗ

$$\boxed{\theta = bp}$$

Means, fraction of total sites (θ) covered is directly proportional to pressure of the gas & follows first order kinetic.

case-2: At high pressure.

$bp >> 1$

∴ Indinaminator; $1+bp = bp$

$$\theta = \frac{bp}{bp} = 1$$

$$\theta = P^0$$

This follows zero order kinetics.

BET Multilayer theory :- [2M]

[Brunauer, Emmet & Teller]

BET theory assuming multilayer adsorption they derived the equation

$$\frac{P}{V(P_0 - P)} = \frac{1}{V_m C} + \frac{C-1}{V_m C}\left(\frac{P}{P_0}\right)$$

where V- volume of the adsorbed gas at pressure "p"

V_m- volume of the gas when surface is completely covered.

P_0 - standard pressure

c - constant depends on nature of gas

P - pressure

Industrial applications of adsorption

1) Animal charcoal is used in sugar industry to adsorb colouring matter from cane sugar solution.

2) Silicagel (SiO_2) can be used as an adsorbent to remove moisture.

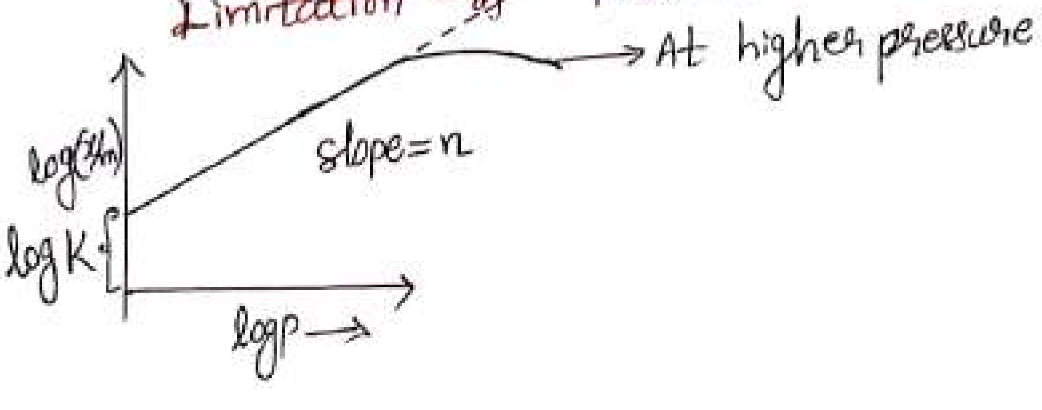
3) Activated charcoal is used in purification of air which is used in gas mask to adsorb toxic gases.

4) In softening hard water, zeolite adsorbs Ca^{2+} & Mg^{2+} ions present in hard water.

5) In Dewar flasks activated charcoal is placed b/w the walls of the flask, to adsorb the gas b/w annulds space & preserves vaccum.

6) The solid catalysts adsorbs the gaseous reactants on its surface and increases concen of reactants on its surface of the catalyst & increases rate of reaction.

Limitation of Freundlich adsorption isotherm.



It is clear from the above figure that at higher pressure, $\log(x/m)$ is not linearly dependent on $\log P$. as there is a slight deviation from linearity. Therefore Freundlich adsorption is not applicable at high pressure. This is the limitation of Freundlich's adsorption isotherm.

2017

1) Using thermodynamic parameters explain why adsorption process is spontaneous.

Ans:- Adsorption is always an exothermic process. i.e, heat of adsorption (ΔH) will have negative sign. Also adsorption is accompained by decrease in entropy of the system (ΔS is negative). Since ΔS & ΔH are both negative, it means negative value of ΔH must be very high, in order to make ΔG negative according to $\Delta G = \Delta H - T\Delta S$, For adsorption process to spontaneous, ΔG (free energy charge) must be negative.

2017

2) Using the signs of ΔH & ΔS, predict the spontanety of a process.

Ans: We have $\Delta G = \Delta H - T\Delta S \rightarrow$ ①

For a reaction to be spontaneous, ΔG should be negative i.e., $\Delta G = \Delta H - T\Delta S < 0 \rightarrow$ ②

This means that $\Delta H < 0$ & $\Delta S > 0$ will favours a charge in reaction.

A/c to equation ① & ②, the sign of ΔG depends on sign & magnitude of ΔH &

ΔS. Let us consider different cases.

1) when $\Delta H<0$ & $\Delta S>0$: Reactions with these change can be carried out any temp? since ΔG will be negative
e.g:-

$$2H_2O_{2(g)} \longrightarrow 2H_2O_{(g)} + O_{2(g)}$$

At 298K, $\Delta H = -211.29$ KJ mol^{-1},
$T\Delta S = 39.33$ KJ mol^{-1}
& $\Delta G = -250.62$ KJ mol^{-1}

2) when $\Delta H<0$ & $\Delta S<0$: when $\Delta S<0$, $-T\Delta S>0$ ∴ Reaction will be spontaneous only when $|T\Delta S| < |\Delta H|$ because in this case ΔG will be negative. ∴ Reaction must be strongly exothermic. However at very high temperature $-T\Delta S$ will be greater than ΔH & (therefore $\Delta G>0$) therefore reaction cannot proceed.

example: $3H_{2(g)} + N_{2(g)} \longrightarrow 2NH_{3(g)}$

At 298K $\Delta H = -92.22$ KJ mol^{-1}
$-T\Delta S = -59.23$ KJ mol^{-1}
$\Delta G = -32.99$ KJ mol^{-1}

3) when $\Delta H > 0$ & $\Delta S > 0$: In this case, reaction will proceed only if $T\Delta S > \Delta H$ i.e. temp^r of the reaction should be high enough such that $T\Delta S$ exceeds ΔH However the reaction will not proceed at lower temp^r when $T\Delta S < \Delta H$

eg:- $N_2O_{4(g)} \longrightarrow 2NO_{2(g)}$

at 298K $\Delta H = 57.20\ KJmol^{-1}$

$T\Delta S = 52.40\ KJmol^{-1}$

$\Delta G = 4.80\ KJmol^{-1}$

Hence for a spontaneous reac^n, ΔG should be negative, the composition of $N_2O_{4(g)}$ to $NO_{2(g)}$ will not be spontaneous at 298K, However at higher temp^r $T\Delta S$ becomes larger than ΔH which makes ΔG negative & thus makes reac^n spontaneous.

4) when $\Delta H > 0$ & $\Delta S < 0$: Both the factors make ΔG more & more positive & therefore reac^{n}s will be non-spontaneous at all temps.

eg:- $N_{2(g)} + 2O_{2(g)} \longrightarrow 2NO_{2(g)}$

At 298K $\Delta H = 66.36\ KJmol^{-1}$

$T\Delta S = -36.29\ KJmol^{-1}$

$\Delta G = 102.65\ KJmol^{-1}$

Ⓗ

Imp using the signs of ΔH & ΔS, predict the Spontaneity of a process

Enthalpy (ΔH)	Entropy (ΔS)	Free energe Charge $\Delta G = \Delta H - T\Delta S$	conclusion
Negative (exothermic)	positive	Negative	spontaneous Charge.
Negative (exothermic)	Negative	→ Negative - at low tempr → positive - at higher tempr.	Spontaneous Non-spontaneous
positive (Endothermic)	positive	positive at low tempr. Negative at higher tempr.	Non-spontaneous spontaneous
positive (endothermic)	negative	positive	Forbidden in forward direction.