

Free Study Material from All Lab Experiments



**Thermodynamics Notes
for NET/GATE Physical Sciences
Thermodynamic Potentials #**

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⇒: GIBB'S FREE ENERGY :⇐

↓
const (T, P)

- It is an Extensive property.
- It is a State function.
- It is a form of Energy which can be used in any useful work
- ↓ in free Energy is use as a non-mechanical work
- Its unit is Joule
- mathematically it can be written as

$$G = H - TS$$

where H is a total Energy of a system

where TS is Unavailable Energy.

[or u can say that disorder can't be use as a work, becoz u used this energy the substance change their phase]

- Derivation of Maxwell Equation in term of G.

$$G = H - TS$$

$$G = U + PV - TS \quad [\because H = E + PV]$$

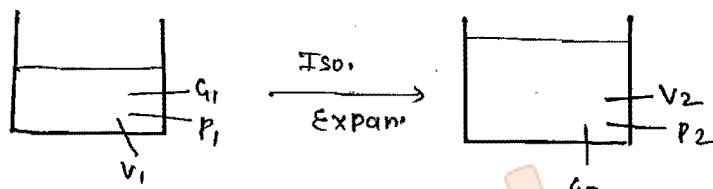
Diff. both side

$$dG = dE + PdV - Tds - SdT + VdP$$

$$\therefore dE = dq - pdv$$

$$dE = Tds - pdv$$

→ Calculation of change in free energy for an isothermal process in the case of ideal gas →



We know that -
from Maxwell Eqnⁿ

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

$$dG = V dP$$

$$[\because PV = RT]$$

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

$$\Delta G = RT \int_{P_1}^{P_2} \frac{dP}{P}$$

$$\Delta G = RT \ln \frac{P_2}{P_1}$$

(Ques-2009)

Ans. 10

Q1.32

$$\Delta G$$

$$n = 1$$

$$P_1 = 1 \text{ atm}$$

$$P_2 = 2 \text{ atm}$$

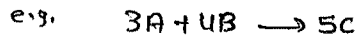
$$\Delta G = RT \ln \frac{2}{1}$$

$$\Delta G = RT \ln 2$$

⇒ calculation of ΔG for a reaction.

Imp!

$$\Delta G = \sum G_{\text{PRODUCT}} - \sum G_{\text{REACTANT}}$$



A $G_1 \Rightarrow J/\text{mole}$

B $G_2 \Rightarrow J/\text{mole}$

C $G_3 \Rightarrow J/\text{mole}$

$$\Delta G = 5G_3 - 4G_2 - 3G_1$$

For Spontaneous process ΔG always be -ive -

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

∴ ΔS always be positive

∴ ΔH ~~always~~ may be positive or negative

∴ $\Delta G \rightarrow \{\text{always Negative}\}$

[ΔG को -iv लाने के लिये

ΔH की value $T\Delta S$ से

छोटी होनी चाहिए

H

* Prove that for Spontaneous process ΔG is less than zero
(Iso-T, p, proc.)

We know that the heat change in a reversible process is more than the heat change in a irreversible process.

$$dq_{rev.} > dq_{isov.}$$

$$T ds > dq_{isov.}$$

$$\therefore \left(\Delta S = \frac{q_{rev.}}{T} \right)$$

$$0 > dq_{isov.} - T ds \quad \text{--- (1)}$$

$$(dq_{isov.})_p = dH \quad \text{--- (2)}$$

put the value of (2) in (1)

$$0 > dH - T ds$$

$$0 > (dG)_{T, p}$$

Gibbs Helmholtz Equation

we know that

$$G = H - TS$$

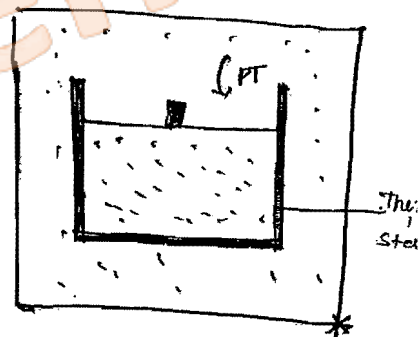
for initial \rightarrow

$$G_1 = H_1 - TS_1 \quad \text{--- (1)}$$

$$\text{for final, } G_2 = H_2 - TS_2 \quad \text{--- (2)}$$

at constant temp, p

$$\Delta G = \Delta H - T \Delta S \quad \text{--- (3)}$$



$$dG = V dp - S dT$$

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

for initial

$$\left(\frac{dG_1}{dT}\right)_P = -S_1 \quad \text{--- (4)}$$

for final

$$\left(\frac{dG_2}{dT}\right)_P = -S_2 \quad \text{--- (5)}$$

Substrate \rightarrow (5) - (4)

$$\left(\frac{d(\Delta G)}{dT}\right)_P = -\Delta S \quad \text{--- (6)}$$

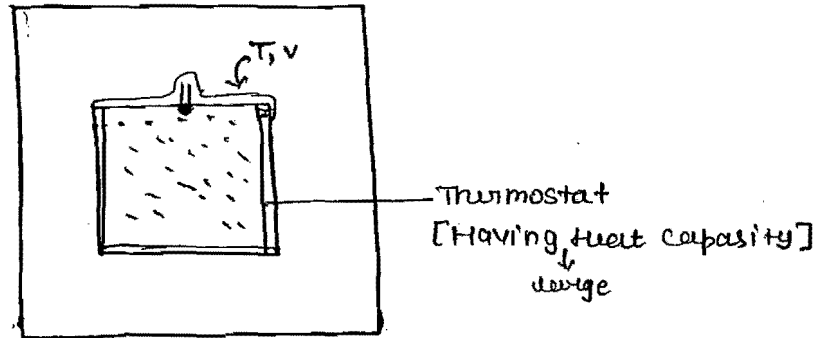
Put the value of (3) in (6)

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

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

\downarrow
 \leftarrow Gibbs Helmholtz Equation \rightarrow

Helmholtz function



for (T, V)

Work-Function

or

Helmholtz Function or 'A'

$$A = \underbrace{E}_{\text{Energy}} - \underbrace{TS}_{\text{disorder}}$$

- ⇒ It is a Energy function
- ⇒ It is also Extensive property
- ⇒ Its Unit Expresses in Joule
- ⇒ It is also called work function and represented by 'A'
- ⇒ When a system undergoing change at a const. volume then their Energy Express in internal Energy & when you subtract disorder from total Energy, we get Helmholtz free Energy or work function:

⇒ for Spontaneous $(dA)_{T,V} < 0$

⇒ Comparison b/w Helmholtz free Energy and Gibbs free Energy
* For an Isothermal process, for an ideal gas ($\Delta Q = \Delta A$)

$$Q = H - TS$$

$$Q = E + PV - TS$$

$$dQ = dE + PdV + VdP - Tds - sdT \quad [\because dT=0]$$

$$dQ = dA + \cancel{Tds} + \cancel{sdT} + PdV - VdT - \cancel{Tds} - \cancel{sdT} \quad A = E - TS$$

$$\therefore dA = dE - Tds - sdT$$

$$dQ = dA + \partial(PV)$$

$$[\because PV = RT]$$

$$\partial Q = dA + \partial CRT$$

$$\partial Q = dA + R \partial T \quad [\because \partial T = 0]$$

$$\boxed{dQ = dA}$$

To prove ⇒

$$\boxed{\Delta A = \Delta E + T \left(\frac{\partial (\Delta A)}{\partial T} \right)_V} *$$

Partial Molar Property : \Rightarrow

Suppose Z is a function of \rightarrow

$$Z = f(T, P, n_1, n_2, n_3, \dots, n_i)$$

= where system having different mole of gases
($n_1, n_2, n_3, \dots, n_i$)

\rightarrow The total diff. of Z is \rightarrow

$$dz = \left(\frac{dz}{dT} \right)_{P, n_1, n_2, n_3, \dots, n_i} dT + \left(\frac{dz}{dP} \right)_{T, n_1, n_2, n_3, \dots, n_i} dP$$

$$+ \left(\frac{dz}{dn_1} \right)_{P, T, n_2, \dots, n_i} dn_1 + \left(\frac{dz}{dn_2} \right)_{T, P, n_1, n_3, \dots, n_i} dn_2$$

at const. $T, \& P$

$$dz = \left(\frac{dz}{dn_1} \right)_{T, P, n_2, n_3, \dots, n_i} dn_1 + \left(\frac{dz}{dn_2} \right)_{T, P, n_1, n_3, \dots, n_i} dn_2 + \left(\frac{dz}{dn_3} \right)_{T, P, n_1, n_2, n_4, \dots, n_i} dn_3$$

$$dz = \left(\frac{dz}{dn_i} \right)_{T, P, n_1, n_2, \dots, (n_i-1)}$$

\downarrow
Partial molar property

this is called P.M.P. because $\Delta Z [G, E, A]$ ^(with change in i th) \uparrow component of the system where all other component are constant.

Note: \Rightarrow [1] The properties which is occur in the pure state of the system is different for the impure system

(Pure state)
e.g. When we adding one mole of water 100 cm^3 of pure water
when we get $\Delta V = 18 \text{ cm}^3$. because (one mole of water = 18 cm^3)

... in the impure state when we adding a 1 mole of H_2O in

2) the change in property in impure state is arises due to bcz of different interaction take place.

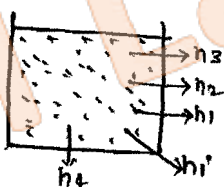
CHEMICAL POTENTIAL



$$\mu_i^0 = \frac{G}{n}$$

$\mu_i \Rightarrow$ (temp. dependent)

$$Z = G$$



$$\mu_i = \left(\frac{\partial G}{\partial n_i} \right)_{T, P, n_1, n_2, \dots, (n_i - 1)}$$

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

$$\mu_2 = \left(\frac{\partial G}{\partial n_2} \right)_{T, P, n_1, n_3, \dots, n_i}$$

$$\mu_3 = \left(\frac{\partial G}{\partial n_3} \right)_{T, P, n_1, n_2, \dots, n_i}$$

⋮

⇒ change in free energy with change in particular component in a system which containing diff. no. of moles where all other moles are constant

⇒ Gibbs free energy changes with the change in particular component at constant T & P where all other component are constant that is represented by chemical potential.

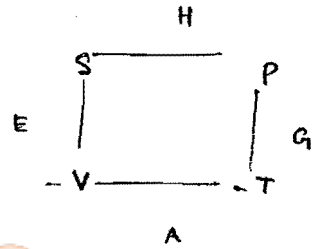
⇒ for a pure state free energy per mole is called chemical potential. Standard chemical potential can be defined for a pure state of a compound, amount 1 mole, 1 atm pressure at any temp. then it is called standard chemical potential.

$$[\mu^\circ] = \frac{G}{n}$$

⇒ Standard chemical potential only depends upon temp. where chemical potential of a particular component in a pure state depends upon T & P both.

$\mu = \mu^\circ + RT \ln P_i$	⇒ in terms of partial pressure
$\mu = \mu^\circ + RT \ln X_i$	⇒ in terms of mole fraction

Chemical potential can also be represented in different thermodynamically.



$$\left(\frac{\partial A}{\partial n_i} \right)_{V,T} = \mu_i$$

$$\left(\frac{\partial H}{\partial n_i} \right)_{S,P} = \mu_i$$

$$\left(\frac{\partial G}{\partial n_i} \right)_{P,T} = \mu_i$$

$$\left(\frac{\partial E}{\partial n_i} \right)_{S,V} = \mu_i$$

⇒ Variation of chemical potential with temperature

{ ∵ G decreases with temp. } $\left(\frac{\partial G}{\partial T} \right) < 0$

∴ μ also be ↓ with temp.

⇒ [जैसे Phase transfer वैसे μ_i same रहेगा]

we know that ⇒

$$\left(\frac{\partial G}{\partial n_i} \right)_{T,P} = \mu_i$$

$$\frac{d}{dT} \left(\frac{\partial G}{\partial n_i} \right) = \frac{\partial \mu_i}{\partial T}$$

$$\frac{\partial^2 G}{\partial T \partial n_i} = \frac{\partial \mu_i}{\partial T} \quad \text{--- (1)}$$

$$dG = vdp - SdT$$

$$\left(\frac{\partial G}{\partial T}\right)_P = -S$$

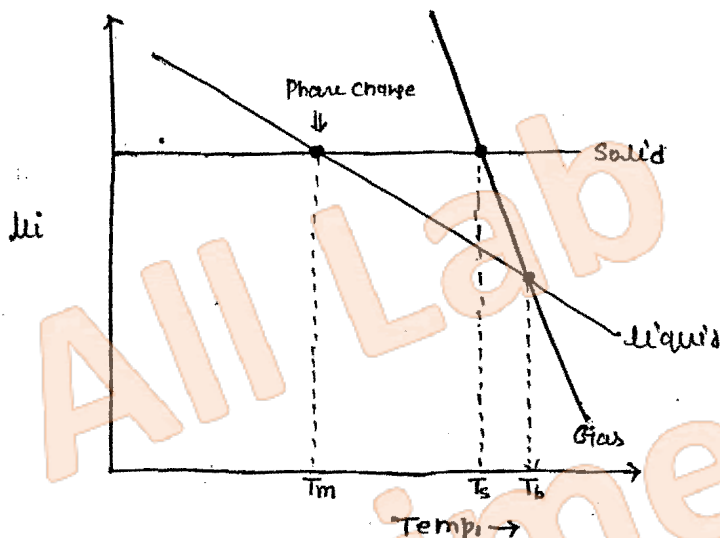
by (I) and (II)

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

$$\frac{\partial^2 G}{\partial n_i \partial T} = -\bar{S}_i \quad \text{--- (II)}$$

$$\boxed{\left(\frac{\partial \mu_i}{\partial T}\right)_P = -\bar{S}_i}$$

Q.44-2010



T_s = Sublimation temp.

T_b = Boiling temp.

T_m = Melting temp.

Graph: \Rightarrow Variation of chemical potential with change in temp.

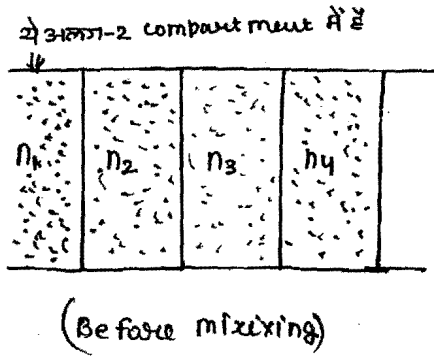
\Rightarrow during phase transformation, chemical potential remains same for both the phases. [where $T, v, \&$ all other component are constant],

\Rightarrow Since we know that G is state function so it must follow Euler's theorem.

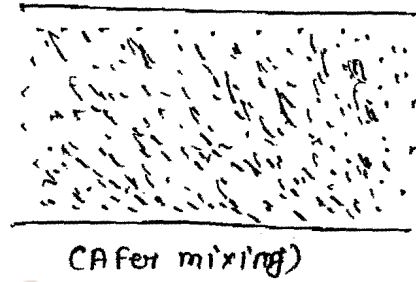
$$\boxed{\left(\frac{\partial (\mu_i)}{\partial T}\right)_P = -\bar{S}_i} *$$

Calculation of thermodynamic parameter [ΔH^{mixing} , ΔV^{mix} , ΔS^{mix} , ΔA^{mix}]

In the case of ideal gases



(After removing compartment)
[सारे compartment को open कर दिया जाएगा]



<https://alllabexperiments.com> n_1 [Pure state] *

$$\mu_1^0 = \frac{G_1}{n_1}$$

$$n_2, \mu_2^0 = \frac{G_2}{n_2}$$

$$n_3, \mu_3^0 = \frac{G_3}{n_3}$$

$$n_4, \mu_4^0 = \frac{G_4}{n_4}$$

$$G_{Total} = n_1 \mu_1^0 + n_2 \mu_2^0 + n_3 \mu_3^0 + n_4 \mu_4^0$$

[Before mixing]

$$\mu_1 = \mu_1^0 + RT \ln X_1$$

$$\mu_2 = \mu_2^0 + RT \ln X_2$$

$$\mu_3 = \mu_3^0 + RT \ln X_3$$

$$\mu_4 = \mu_4^0 + RT \ln X_4$$

$$G_{Total} = n_1 \mu_1 + n_2 \mu_2 + n_3 \mu_3 + n_4 \mu_4$$

[After mixing]

$$\Delta G_{mixing} = G_{Total} \text{ (After mixing)} - G_{Total} \text{ (Before mixing)}$$

$$= (n_1 \mu_1 + n_2 \mu_2 + n_3 \mu_3 + \dots) - (n_1 \mu_1^0 + n_2 \mu_2^0 + n_3 \mu_3^0 + \dots)$$

$$= n_1 (\mu_1^0 + RT \ln X_1) + n_2 (\mu_2^0 + RT \ln X_2) + n_3 (\mu_3^0 + RT \ln X_3) + \dots - (n_1 \mu_1^0 + n_2 \mu_2^0 + \dots)$$

$$= n_1 RT \ln X_1 + n_2 RT \ln X_2 + \dots$$

$$\Delta G_{mix} = RT \sum n_i \ln x_i$$

$$\frac{\Delta G_{mix}}{T} = R \sum n_i \ln x_i$$

$$\frac{\partial}{\partial T} \left[\frac{\Delta G_{mix}}{T} \right]_P = \frac{R}{T} \sum (n_i \ln x_i)_P$$

$$-\frac{\Delta G_{mix}}{T^2} + \frac{1}{T} \left(\frac{\partial (\Delta G_{mix})}{\partial T} \right)_P = 0 \quad \text{--- (1)}$$

$$\therefore \Delta G_{mix} = \Delta H_{mix} + T \left(\frac{\partial (\Delta G_{mix})}{\partial T} \right)_P$$

Divide both side by T^2 then,

$$\frac{\Delta G_{mix}}{T^2} = \frac{\Delta H_{mix}}{T^2} + \frac{1}{T} \left(\frac{\partial (\Delta G_{mix})}{\partial T} \right)_P$$

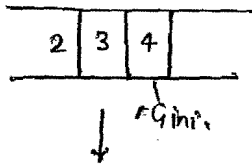
$$-\frac{\Delta H_{mix}}{T^2} = -\frac{\Delta G_{mix}}{T^2} + \frac{1}{T} \left(\frac{\partial (\Delta G_{mix})}{\partial T} \right)_P \quad \text{--- (2)}$$

By Eqn- (1) + (ii)

$$-\frac{\Delta H_{mix}}{T^2} = 0$$

$$\boxed{\Delta H_{mix} = 0}^*$$

e.g. 2 mol O_2 , 3 mol N_2 , 4 mol H_2



$$n_{Total} = 9$$

Q_{if}

$$\Delta G = Q_f - Q_i$$

$$\Delta G_{mix} = RT \left(2 \ln \frac{2}{9} + 3 \ln \frac{3}{9} + 4 \ln \frac{4}{9} \right)$$

(Per mole)

$$= RT \left[\left(\frac{2}{9} \right) \ln \left(\frac{2}{9} \right) + \frac{3}{9} \ln \left(\frac{3}{9} \right) + \frac{4}{9} \ln \left(\frac{4}{9} \right) \right]$$

Rxn of kinetic energy \rightarrow \uparrow temp, \uparrow $K.E.$, $P.E.$ \Rightarrow

$$\Delta G_{mix} = \frac{RT \sum n_i \ln x_i}{n_{total}}$$

$$\Delta G_{mix} = RT \sum x_i \ln x_i$$

(Per mole)

Q4.8

2 mole of N_2

3 mole of H_2

2 mole of NH_3

$$\begin{aligned} \Delta S_{\text{mixing}} &= 8.314 \times \left[\left(\frac{2}{7}\right) \ln\left(\frac{2}{7}\right) + \left(\frac{3}{7}\right) \ln\left(\frac{3}{7}\right) + \left(\frac{2}{7}\right) \ln\left(\frac{2}{7}\right) \right] \\ &= 8.314 \times 2.303 \left[2 \log \frac{2}{7} + 3 \log \frac{3}{7} + 2 \log \frac{2}{7} \right] \\ &= 8.314 \times 2.303 \times \left[4 \log \frac{2}{7} + 3 \log \frac{3}{7} \right] \\ &= -8.314 \times 2.303 \times \left[-2.4784 + (-0.36 \times 3) \right] \\ &= -8.314 \times 2.303 \times \left[-2.4782 - 1.1039 \right] \\ &= -8.314 \times 2.303 \times (-3.5821) \\ &= 62.80 \text{ J K}^{-1} \end{aligned}$$

<https://alllabexperiments.com>

Q4.9

□ Monatomic

adia. Expn. → $\gamma = 1.67$

→ lose energy very much

□ diatomic
↓

adia. Expn. → $\gamma = 1.4$

No. of atom \propto Rotation, \propto Vibration
No. of atom \propto Heat capacity *

$\Rightarrow T_m < T_p < T_r$

monatomic \Rightarrow Temp. independent.

$$\Delta G_{\text{mixing}} = \Delta H_{\text{mixing}}^{\circ} - T \Delta S_{\text{mixing}}$$

$$\Delta G_{\text{mixing}} = - T \Delta S_{\text{mixing}}$$

$$\Delta S_{\text{mixing}} = \frac{- \Delta G_{\text{mixing}}}{T}$$

$$\Delta S_{\text{mixing}} = - R \sum n_i \ln x_i$$

$$\Delta S_{\text{mixing, permole}} = - R \sum x_i \ln x_i$$

$$\Delta G_{\text{mixing}} = \Delta A_{\text{mixing}}$$

[beoz isotherm] \Rightarrow ideal working substance

\Rightarrow When ideal gases mixing with each other since there is no interaction b/w the molecules so there is no absorption or rejection of heat take place so that $\Delta H = 0$

$$\Delta H_{\text{mixing}} = 0$$

(अज्ञात आना ला-11 है
No Interaction
No waste Energy)

Ques One mole of CO_2 , one mole of NO_2 & two mole of O_2 when mixed at 300K calculate the Entropy of mixi, ΔH_{mixing} , ΔV_{mixi} , ΔA_{mixi} .

1 mole of CO_2

1 mole of NO_2

2 mole of O_2

$$\Delta G = RT \left[1 \ln \frac{1}{4} + 1 \ln \frac{1}{4} + 2 \ln \frac{2}{4} \right]$$

$$\Delta G = RT \left[2 \ln \frac{1}{4} + 2 \ln \frac{1}{2} \right]$$

$$\Delta G = RT \times 2.303 \left[2 \log \frac{1}{4} + 2 \log \frac{1}{2} \right]$$

$$\Delta G = 8.314 \times 300 \times 2.303 \times [-2 \times (0.60) - 2 \times (0.30)]$$

$$= 8.314 \times 300 \times 2.303 \times [-1.2 - 0.6]$$

$$= 8.314 \times 300 \times 2.303 \times [-1.8]$$

$$= -10,374$$

$$\boxed{\Delta H_{\text{mix}} = 0}$$

$$\Delta G = \Delta A = -10,374$$

$$= -10.374 \text{ KJ}$$

$$\Delta S = -\frac{\Delta G}{T} = +34.58 \text{ J}$$

$$\boxed{\Delta V_{\text{mixing}} = 0}$$

OR

$$\Delta S = 6R \ln 2$$

$$\ln \frac{k_2}{k_1} = \frac{E_a}{R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right] \quad \text{Arrhenius Eq}^n$$

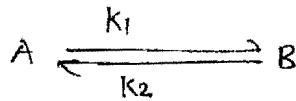
[in term of rate constant]

$$\ln \frac{k_{p1}}{k_{p2}} = \frac{\Delta H^\circ}{R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right] \quad \text{in term of } k_p \text{ [Equi. constt]}$$

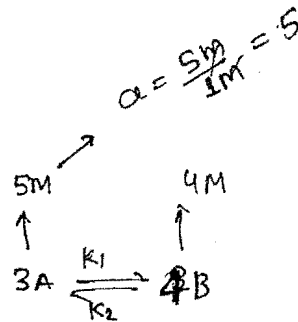
$$\ln \frac{k_{c1}}{k_{c2}} = \frac{\Delta F^\circ}{R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right] \quad \text{[in term of } k_c]$$

Vant-Hoff Relation

⇒ For Chemical Equilibrium first condition system must be close. [It is dynamic in nature]



- k ⇒
- k_x ⇒
- k_p ⇒
- k_c ⇒



unitless (mole fraction)
(always)

$$K_x = \frac{[X_B]^4}{[X_A]^3}$$

$$\frac{k_1}{k_2} = K_c = \frac{[C_D]^4}{[C_A]^3}$$

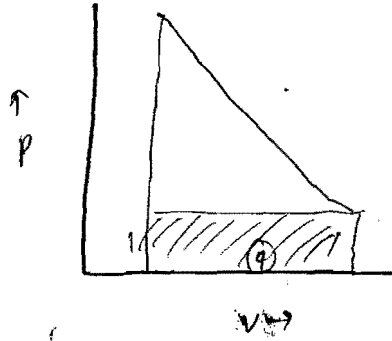
K = thermodynamic equl. (unitless)
= (unitless)
always

$$K_p = \frac{[P_B]^4}{[P_A]^3} \quad (\text{pure mixture})$$

(k_p & k_c ⇒ may or may not unitless)
means depends upon
stoichiometry)

Issu:

Q4.21



$$\begin{aligned} \text{Rev:} &= \frac{1}{2} \times 4 \times 4 + 4 \times 1 \\ &= 8 + 4 = 12 \text{ [X]} \end{aligned}$$

$$\text{Issu} = 1 \times 4 = 4 \text{ L.atm}$$

All Lab Experiments

$$\frac{\partial (\ln k_p)}{\partial T} = \frac{\Delta H^\circ}{RT^2}$$

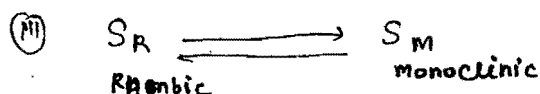
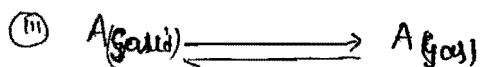
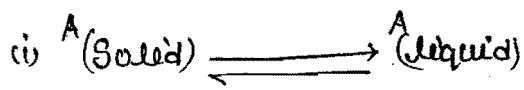
$$\frac{\partial (\ln k_c)}{\partial T} = \frac{\Delta E^\circ}{RT^2}$$

-: CLASSICUS - CLAYPERON RELATION

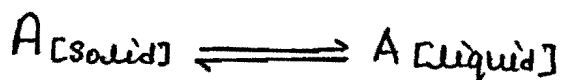
[Phase-transformation]
 chemical potential = 0
 $\Delta G = 0$] (beoz at Equi.)
 $\therefore \Delta G = 0$ [at Equilibrium]

Clavicus Clayperon Equation is applying for any phase transformation a phase transformation which is a immediate process, during this the temp, pressure, Equilibrium conc., free Energy of two different phases Etc. are Equal.

For eg. \Rightarrow There is a lot of phase transfer



for Solid \rightleftharpoons liquid Equi.



~~for~~ Solid changes into liquid at their melting point during this they absorb heat at a const. pressure from the surrounding. during this phase transformation the sign of heat absorb is +ve.
[अगर liquid से solid जाता तो -ive]



At a slight increase of temp. ($T+dT$, $P+dP$)



from (I) & (II)

$$dG(s) \rightleftharpoons dG(l)$$

applying Maxwell Equation \rightarrow

~~dG(s)~~

$$V_G dP - S_G dT = V_L dP - S_L dT$$

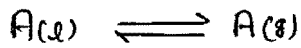
$$\frac{dP}{dT} = \frac{\Delta S}{V_L - V_G} \quad \text{--- (III)}$$

$$\therefore \Delta S = \frac{\Delta H}{T} \quad \text{--- (IV)}$$

Here Integrated form not possible coz we neglect V_G &

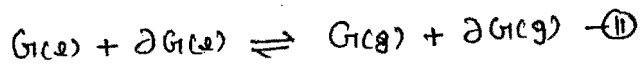
$$\boxed{\frac{dP}{dT} = \frac{\Delta H}{T \Delta V}}$$

Differential form of

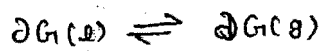


$$\therefore G(l) \rightleftharpoons G(g) \quad [\text{at const. } T, P] \quad \text{--- (I)}$$

When you slightly increases the $(T+\Delta T, P+\Delta P)$ then,



from I & II Ind-



$$\therefore \partial G = V dp - S dT \quad [\text{maxwell equation}]$$

$$V(l) dp - S(l) dT = V(g) dp - S(g) dT$$

$$\frac{dp}{dT} = \frac{\Delta S}{V(g) - V(l)}$$

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

$$\boxed{\frac{dp}{dT} = \frac{\Delta H}{T (V(g) - V(l))}}$$

↓
diff. form of Clausius-Clayperon Eqⁿ

$$\therefore V_g \gg \gg \gg V_l$$

$$\frac{dp}{dT} = \frac{\Delta H}{T \times V_g}$$

$$\frac{\partial p}{\partial T} = \frac{\Delta H \times p}{T \times RT} \quad [\because PV=RT], \quad V = \frac{RT}{P}$$

$$\frac{\partial p}{\partial T} = \frac{\Delta H \cdot p}{RT^2}$$

Integrated on both side

$$\int_{P_1}^{P_2} \frac{dP}{P} = \frac{\Delta H}{R} \int_{T_1}^{T_2} \frac{dT}{T^2}$$

$$\ln \frac{P_2}{P_1} = \frac{\Delta H^\circ}{R} \left[\frac{T_2 - T_1}{T_1 \cdot T_2} \right]$$