G'' —— (4)

$\because G''$ is a +ve quantity, sign of $\left(\frac{\partial \xi_e}{\partial T}\right)_P$ depends on RHS (+⊙)

(1) For exothermic reactions, ΔH is −ve, $H_P < H_R$ RHS of eq(4) is −ve, therefore L.HS should also −ve.

If dT is +ve ie temp is ↑, then $d\xi_e$ should be −ve, ie ξ_e ↓ with ↑ of temp, Reactant conc will ↑ which high H

If dT is −ve that temp is lowered so $d\xi_e$ will be +ve, ξ will ↑ & more products will be formed. which have low enthalpy

(2) For endothermic ΔH is +ve $H_P > H_R$ RHS of eqn (4) is +ve, hence L.HS should be +ve

If dT is +ve, temp is ↑ed, $d\xi_e$ should be +ve, ξ should ↑, more Po with high enthalpy will be formed

If dT is −ve, T is lowered, $d\xi$ must be −ve ξ_e should ↓ with lowering of temp, reactants with lower enthalpy are formed

(3) In athermic reaction, $\Delta H = 0$, $H_P = H_R$, eq④ = 0 LHS = 0, ξ is independent of T at constt P

$\therefore$ An ↑ of temp shifts the eqn to high enthalpy side & lowering of temp " " " low " side.

Variation of ξ_e with P at constt T, $dT = 0$

$$\frac{\Delta H}{T}(\partial T)_P + (\Delta V)(\partial P)_T + G''(\partial \xi)_T = 0$$

$$\left(\frac{\partial \xi_e}{\partial P}\right)_T = -\frac{\Delta V}{G''} \quad -⑤$$

As G'' is +ve so sign of $\left(\frac{\partial \xi_e}{\partial P}\right)_T$ will depend on nature of ΔV

(1) If $V_P = V_R$, $\Delta V = 0$, ξ_e will be independent of P at Const T.

(2) If $V_P > V_R$, ΔV is +ve but RHS of eq^n (5) is −ve so LHS will be −ve.

Increase of P, $dP > 0$, ↓ ξ_e, & eq^n shifts toward reactant

↓ of P, $dP < 0$, ξ_e ↑, & eq^n " toward Product side

(3) If $V_R > V_P$, ΔV is −ve, RHS of eq(5) is +ve, & LHS +ve

Increase of P, $dP > 0$, ↑ ξ_e & eq^n shifts towards Product side & ↓ of P, $dP < 0$, ↓ ξ_e & eq^n " " reactant side

Free energy of Mixing & spontaniety of Reaction

A spontaneous reaction is one for which ΔG is negative & when ΔG is +ve, reaction is spontaneous in reverse direction

But there are many reactions for which ΔG is +ve but still they are spontaneous. eg $N_2O_4 \rightarrow 2NO_2$ $\Delta G^\circ = 5.39$ Reaction proceeds in forwards ie 16% of N_2O_4 is degree of dissociation (α) out of 6 molecules of N_2O_4, 1 dissociates while $2NO_2 \rightarrow N_2O_4$ has ΔG° −5.39 KJ/mole & still reaction doesn't go to completion

Reason / Explanation for this contribution of free energy of mixing to the total free energy of the system

Let us consider the dissociation of a dimer D into monomer M ($N_2O_4 \rightarrow 2NO_2$) or general reaction $A_2 \rightarrow 2A$. Let n_D be moles of the dimer & n_M is moles of monomer. The total free energy of the system in terms of chemical pot

$$G = n_D \mu_D + n_M \mu_M$$

$\mu_i = \mu_i^\circ + RT \ln P_i$ [illegible]

where x_i is mole fraction of species i & P is [illegible]

$\mu_D = \mu_D^\circ + RT \ln \frac{P}{P^\circ} + RT \ln x_D$, $\mu_M = \mu_M^\circ + RT \ln \frac{P}{P^\circ} + RT \ln x_M$

[illegible] given in terms of chemical pot

$G = n_D \mu_D + n_M \mu_M$

$\mu_i = \mu_i^\circ + RT \ln \frac{P_i}{P^\circ}$ For Ideal gas $P_i = x_i P$

where x_i is mole fraction of species i & P = total Pressure

$\mu_D = \mu_D^\circ + RT \ln \frac{P}{P^\circ} + RT \ln x_D$, $\mu_M = \mu_M^\circ + RT \ln \frac{P}{P^\circ} + RT \ln x_M$

$G = (n_D \mu_D^\circ + n_M \mu_M^\circ) + (n_D + n_D) RT \ln \frac{P_0}{P^\circ} + RT(n_D \ln x_D + n_M \ln x_M)$

The 1st two terms of R.H.S is sum of free energies of the two gases if each existed in a seperate vessel at P

$G_{pure} = (n_D \mu_D^\circ + n_M \mu_M^\circ) + (n_D + n_M) RT \ln \frac{P}{P^\circ}$ — ②

The third term is free energy mixing of dimer & monomer

$\Delta G_{mix} = RT(n_D \ln x_D + n_M \ln x_M)$ — ③

ΔG_{mix} is always negative since $\ln x$ is -ve quantities ie free energy in the mixed states is lower than unmixed state. Therefore dissociating the dimer is energetically unfavourable process nevertheless by dissociating some dimer into monomer a mixture is formed with -ve free energy of mixing. It is the free energy of mixing which makes the reaction spontaneous though the free energy of the unmixed state is positive. ∴ It is better to consider total free energy of the system rather than the free energy of the reaction.

$G = G_{pure} + \Delta G_{mix}$

$$\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = \left(\frac{\partial G_{pure}}{\partial \xi}\right)_{T,P} + \left(\frac{\partial \Delta G_{mix}}{\partial \xi}\right)_{T,P}$$ — ④

Reaction is spontaneous when $\left(\frac{\partial G}{\partial \xi}\right)$ is negative but it when $\left(\frac{\partial \Delta G_{mix}}{\partial \xi}\right)_{T,P}$ should be more -ve than $\left(\frac{\partial G_{pure}}{\partial \xi}\right)_{T,P}$ when they are equal & opp then $\left(\frac{\partial G}{\partial \xi}\right)_{T,P} = 0$ & reaction attains equilibrium.

when $\left(\frac{\partial G}{\partial \xi}\right)_{T,P}$ is +ve mean reaction is spontaneous in reverse direction.

eg $N_2O_4 \rightarrow 2NO_2$ If 1mole N_2O_4 & at any moment ξ is extent of reaction (equal to α), then no. of moles of N_2O_4 & NO_2 are

$n_D = (1-\xi)$, $n_M = 2\xi$, Total moles $= 1-\xi+2\xi = 1+\xi$

$x_{D(N_2O_4)} = \frac{1-\xi}{1+\xi}$, $x_{M(NO_2)} = \frac{2\xi}{1+\xi}$

$G_{Pure} = (n_D \mu_D^\circ + n_M \mu_M^\circ) + RT (n_D + n_M) \ln \frac{P}{P^0}$ — ①

$= (1-\xi)(\mu_D^\circ) + (2\xi)(\mu_M^\circ) + (1+\xi) RT \ln \frac{P}{P^0}$ — ②

If eqn P ~~P~~ is same as P^0 then $\ln \frac{P}{P^0} = 0$

$G_{Pure} = (-\xi)\mu_D^\circ + 2\xi \mu_M^\circ = \mu_D^\circ + (2\mu_M^\circ - \mu_D^\circ)\xi$

③ → $G_{Pure} = \mu_D^\circ + \Delta G^\circ \xi$ where $\Delta G^\circ = 2\mu_M^\circ - \mu_D^\circ$

Value of μ° data from std. table can be substituted

$G_{Pure} = (98.28 + 5.39\xi)$ KJ. — ④

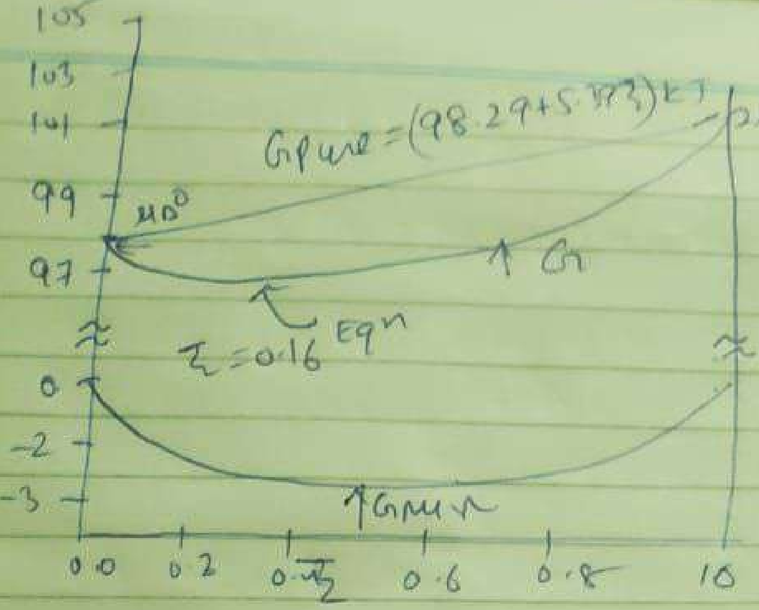
$\Delta G_{min} =$

$\Delta G_{mix} = RT(n_D \ln x_D + n_M \ln x_M)$

$= RT\left[(1-\xi)\ln\frac{(1-\xi)}{(1+\xi)} + 2\xi \ln \frac{2\xi}{1+\xi}\right]$ — ⑤

$= RT[(1-\xi)\ln(1-\xi) + 2\xi \ln 2\xi - (1+\xi)\ln(1+\xi)$

ξ	0	0.2	0.4	0.6	0.8	1.0
G_{Pure}	98.29	99.37	100.44	101.5	102.6	103.08
ΔG_{Pure}	0.0	−1.90	−2.38	−2.24	−1.57	0.0
G	98.29	97.47	98.06	99.26	101.03	103.08



From Graph it is concluded

(1) $\left(\frac{\partial G_{pure}}{\partial \xi}\right)$ is +ve for ξ between 0 to 1 ie free energy of the unmixed state favour pure dimer N_2O_4 or pure monomer NO_2 alone

(2) $\left(\frac{\partial \Delta G_{mix}}{\partial \xi}\right)$ is −ve for ξ between 0 to 0.5 ie ΔG_{mix} favours 50–50 mix of N_2O_4 & NO_2

(3) G first ↓ as ξ ↑ ie $\frac{\partial G}{\partial \xi}$ is −ve, attains a min value at $\xi = 0.16$, when eqn is attained. After this $\left(\frac{\partial G}{\partial \xi}\right)$ becomes +ve. −ve $\left(\frac{\partial G}{\partial \xi}\right)$ favour dissociation of N_2O_4 while +ve $\left(\frac{\partial G}{\partial \xi}\right)$ favour formation of N_2O_4

∴ starting with pure dimer N_2O_4 the free energy ↓ along the curve until 0.16 mole of N_2O_4 have been dissociated then monomer NO_2. total free energy ↓ until 0.84 moles of N_2O_4 have been formed. Although N_2O_4 has lower value of G, the system can achieve still a lower value of G having some NO_2 present at eqn with result of free energy of mixing. All reactions are reversible in nature