

$$= \frac{(m \xi)^m (n \xi)^n p^{\Delta\nu}}{[a(1-\xi)^a [b(1-\xi)]^b [a+b+\Delta\nu\xi]^{\Delta\nu}} \quad (4)$$

Let us suppose that 'c' moles of an inert gas are added to the reaction mixture at equilibrium. It will increase the total no. of moles in the system and so mole fraction & partial pressures of each species will be changed. Total moles will be  $(a+b+c+\Delta\nu\xi')$  & then  $K_p$  is

$$K_p = \frac{(m \xi')^m (n \xi')^n p^{\Delta\nu}}{[a(1-\xi')^a [b(1-\xi')]^b [a+b+c+\Delta\nu\xi']^{\Delta\nu}} \quad (5)$$

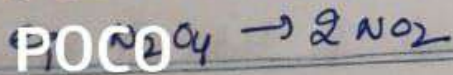
Since  $K_p$  is not depending on add<sup>n</sup> of inert gas amount hence  $\xi$  &  $\xi'$  will adjust in a such a way that eq (4) & (5) are same.  $\xi$  is extent of reaction before add<sup>n</sup> of inert gas &  $\xi'$  is " after add<sup>n</sup> of inert gas.  $\xi$  &  $\xi'$  can be same or different depending upon the nature of the reaction & the imposed conditions

(1) When the Pressure is kept constl.

a) When  $\Delta\nu = 0$ , then the last <sup>term</sup> in denominator of eq 4 & 5 are equal to 1 hence  $\xi = \xi'$  i.e. add<sup>n</sup> of inert gas have no effect on extent of reaction eg  $H_2 + I_2 \rightleftharpoons 2HI$

b) When  $\Delta\nu > 0$ , then the last term in the denominator of eq (5) will be lesser than eq. (4) so to have same value of  $K_p$  for eq. (4) & (5)  $\xi < \xi'$  (extent of reaction)

should increase with addition of an inert gas



c) When  $\Delta\nu < 0$ , the last term is less denominator of eq (5)  $K_p$  same for eq<sup>n</sup>, inert gas will



If eq (5) will be larger than eq (4) so to have same value of  $K_p$  for eq. (4) & (5)  $\xi < \xi'$  (extent of reaction)

should increase with addition of an inert gas  
 eg  $N_2O_4 \rightarrow 2NO_2$

(1) When  $\Delta U < 0$ , the last term is less denominator of eq (5) than (4) to keep  $K_p$  same for eq<sup>n</sup>, inert gas will decrease the extent of reaction.  $SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

(2) When volume is constant then the addition of inert gas will not cause any change in extent of reaction  $\xi = \xi'$  since they are ideal gases.

$$P(\text{before addition of inert gas}) = (a+b+\Delta U\xi) \frac{RT}{V}$$

$$P(\text{after " of "}) = (a+b+c+\Delta U\xi') \frac{RT}{V}$$

eq. (4) & (5) can be written as

$$K_p = \frac{(m\xi)^m (n\xi)^n [(a+b+\Delta U\xi) \frac{RT}{V}]^{\Delta U}}{[a(1-\xi)]^a [b(1-\xi)]^b [a+b+\Delta U\xi]^{\Delta U}}$$

$$= \frac{(m\xi)^m (n\xi)^n}{[a(1-\xi)]^a [b(1-\xi)]^b} \left(\frac{RT}{V}\right)^{\Delta U} \quad \text{--- (6)}$$

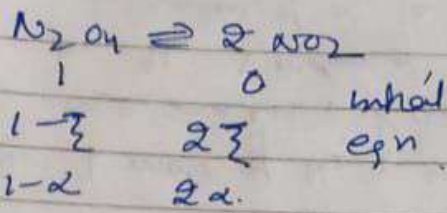
$$K_p = \frac{(m\xi')^m (n\xi')^n}{[a(1-\xi')]^a [b(1-\xi')]^b} \left(\frac{RT}{V}\right)^{\Delta U} \quad \text{--- (7)}$$

Since 6 & 7 eq. do not contain the amount of any substance other than those of reacting mixture, the addition of any non reacting substance at const<sup>n</sup> volume will not alter the eq<sup>n</sup> if T is not const<sup>n</sup>

Q. 1 mole of  $N_2O_4$  is confined in a vessel at  $25^\circ C$  and 1 atm  
 $N_2O_4 \rightleftharpoons 2NO_2$ .  $K_p = 0.1138$ . Calculate (a)  $\alpha$ ,  $\xi$

(b) If 5 moles of Argon is added, keeping 1 atm P what is value of  $\alpha$ . (c) When volume is kept const<sup>n</sup> what is  $\alpha$ .





$$\begin{aligned}
 \text{Total Moles} &= 1 - \xi + 2\xi = 1 + \xi \\
 &= 1 + \alpha
 \end{aligned}$$

$$K_p = \frac{4\xi^2 P}{1-\xi^2} = \frac{4\alpha^2 P}{1-\alpha^2}$$

$$\therefore P = 1 \text{ atm}$$

$$0.1138 = \frac{4\xi^2}{1-\xi^2} = \frac{4\alpha^2}{1-\alpha^2} = 0.166 = \alpha$$

$\therefore \alpha = \xi$  for this reaction

(B) When 5 moles of Ar are added at const P  
 Total moles at eqn are  $= 1 - \alpha + 2\alpha + 5 = 6 + \alpha$

$$P_{\text{NO}_2} = \frac{2\alpha P}{6+\alpha}, \quad P_{\text{N}_2\text{O}_4} = \frac{1-\alpha P}{6+\alpha}$$

$$K_p = 0.1138 = \frac{(P_{\text{NO}_2})^2}{P_{\text{N}_2\text{O}_4}} = \frac{(4\alpha)^2 \times (6+\alpha)}{(6+\alpha)^2 \times (1-\alpha)} = \frac{16\alpha^2 P}{(6+\alpha)(1-\alpha)}$$

$$\therefore P = 1, \quad 0.1138 = \frac{16\alpha^2}{(6+\alpha)(1-\alpha)}, \quad \alpha = 0.343$$

When 5 moles of Ar are added at const volume  
 Gases are considered to be ideal then  $PV = (6+\alpha)RT$   
 $P = (6+\alpha)RT/V$

$$K_p = \frac{4\alpha^2}{1-\alpha} \frac{RT}{V}$$

$\therefore T, V, K_p$  are const  $\alpha$  would be const even though 5 moles of Ar are added.  $\alpha = 0.166$



## The Le Chatelier's Principle

This principle states that "If any of the reaction parameters  $T$ ,  $P$ , concentration be changed in a reaction at equilibrium then the reaction will be proceed in that direction where the change in the parameter is counteracted

(7)

(1) For eg. in a chemical reaction at eq<sup>n</sup>, temp. is raised, the reaction will proceed in that direction where heat will be absorbed so that rise of temp. can be prevented. i.e. eq<sup>n</sup> is shifted in the endothermic direction. If temp. is lowered, then reaction will proceed in a direction that heat is produced, lowering of temp. is prevented i.e. exothermic side

(2) If  $P$  is increased, the reaction will proceed in that direction, where Pressure is reduced i.e. no. of moles would be less or less volume side. If  $P$  is lowered, then reaction will proceed in a direction that there is an increase in no. of moles (high volume side)

(3) If conc<sup>n</sup> of any species is increased then reaction take place in a direction where that species is consumed.  $N_2 + 3H_2 \rightleftharpoons 2NH_3$   $\Delta H = -9$

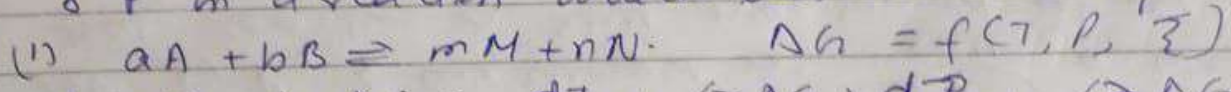
Reaction is exothermic &  $n_P < n_R$



- (1) Increase of temp will shift the reaction in reverse direction which is endothermic heat is absorbed  $\text{NH}_3 \downarrow$  &  $\text{conc}^n$  of  $\text{N}_2$  &  $\text{H}_2 \uparrow$
- (2) Decrease of temp will shift eq<sup>n</sup> reaction in forward direction,  $\text{conc}^n$  of  $\text{NH}_3 \uparrow$  &  $\text{N}_2$  &  $\text{H}_2 \downarrow$
- (3) Increase the P, the reaction proceed in forward direction  $n_p < n_r$   $\text{conc}^n$  of  $\text{NH}_3 \uparrow$  &  $\text{N}_2$  &  $\text{H}_2 \downarrow$
- (4) Increase of  $\text{conc}^n$  of  $\text{N}_2$  or  $\text{H}_2$  will make reaction to move in forward direction.

### Quantitative Treatment of Le Chatelier Principle

It explains how the extent of reaction  $\xi$  changes with  $T$  &  $P$  in a reaction which has attained eq<sup>n</sup>



$$d(\Delta G) = \left( \frac{\partial \Delta G}{\partial T} \right)_{P, \xi} dT + \left( \frac{\partial \Delta G}{\partial P} \right)_{T, \xi} dP + \left( \frac{\partial \Delta G}{\partial \xi} \right)_{T, P} d\xi$$

$$\therefore \Delta G = \left( \frac{\partial \Delta G}{\partial \xi} \right)_{T, P} \xi$$

$$\therefore d(\Delta G) = \frac{\partial}{\partial T} \left[ \left( \frac{\partial \Delta G}{\partial \xi} \right)_{T, P} \right]_{P, \xi} dT + \frac{\partial}{\partial P} \left[ \left( \frac{\partial \Delta G}{\partial \xi} \right)_{T, P} \right]_{T, \xi} dP + \frac{\partial}{\partial \xi} \left( \frac{\partial \Delta G}{\partial \xi} \right)_{T, P} d\xi \quad \text{--- (1)}$$

$$\therefore \frac{\partial}{\partial T} \left[ \left( \frac{\partial \Delta G}{\partial \xi} \right)_{T, P} \right]_{P, \xi} = \frac{\partial}{\partial \xi} \left[ \left( \frac{\partial \Delta G}{\partial T} \right)_{P, \xi} \right]_{T, P}$$

$$\frac{\partial}{\partial P} \left[ \left( \frac{\partial \Delta G}{\partial \xi} \right)_{T, P} \right]_{T, \xi} = \frac{\partial}{\partial \xi} \left[ \left( \frac{\partial \Delta G}{\partial P} \right)_{T, \xi} \right]_{T, P}$$

$$\frac{\partial}{\partial \xi} \left( \frac{\partial \Delta G}{\partial \xi} \right)_{T, P} = \frac{\partial^2 \Delta G}{\partial \xi^2}$$



$$\therefore \left(\frac{\partial G}{\partial T}\right)_{P, \xi} = -S, \quad \left(\frac{\partial G}{\partial P}\right)_{T, \xi} = V \quad (1)$$

\(\therefore\) eq (1) becomes,

$$d\Delta G = -\left(\frac{\partial S}{\partial \xi}\right)_{T, P} dT + \left(\frac{\partial V}{\partial \xi}\right)_{T, P} dP + \left(\frac{\partial^2 G}{\partial \xi^2}\right)_{T, P} d\xi \quad (2)$$

$\left(\frac{\partial S}{\partial \xi}\right)_{T, P}$  = Rate of change of entropy with extent of reaction  $\xi$  = Entropy change of reaction  
 $= \Delta S = \sum S_p - \sum S_r$

$\left(\frac{\partial V}{\partial \xi}\right)_{T, P}$  = Rate of change of volume with extent of reaction = Volume change of reaction  
 $= \Delta V = \sum V_p - \sum V_r$

$$d(\Delta G) = -\Delta S dT + \Delta V dP + \left(\frac{\partial^2 G}{\partial \xi^2}\right) d\xi \quad (3)$$

Let  $T, P, \xi$  are changed in such a way that reaction is still maintained at eqn then  $\Delta G = 0$ , &  $d\Delta G$  should be also equal to zero

$$-\Delta S dT + \Delta V dP + G'' d\xi = 0 \quad (4)$$

$G$  is min. at eqn  $\xi_e$  is extent of reaction

$$\Delta S = \frac{\Delta H}{T} \quad \text{of (4)}$$

$$-\frac{\Delta H}{T} dT + \Delta V dP + G'' d\xi = 0$$

Derivation of  $\xi_e$  with  $T$  at const  $P$

$$-\frac{\Delta H}{T} \left(\frac{\partial T}{\partial \xi}\right)_P + \left(\frac{\partial V}{\partial \xi}\right) \left(\frac{\partial P}{\partial \xi}\right) + G''(\xi_e)_P = 0 \quad (3)$$

$$\left(\frac{\partial T}{\partial \xi}\right)_P = \frac{\Delta H}{T G''} \quad (4)$$



(10)

$G^{\circ}$  is a +ve quantity, sign of  $(\frac{\partial \xi_e}{\partial T})_P$  depends on  $\Delta H$

(1) For exothermic reaction,  $\Delta H$  is -ve,  $H_P < H_R$   
RHS of eq (9) is -ve, therefore LHS should also be -ve.

If  $dT$  is +ve i.e. temp is  $\uparrow$ , then  $d\xi_e$  should be -ve i.e.  $\xi_e$   $\downarrow$  with  $\uparrow$  of temp, reactants which have high  $H$  will  $\uparrow$  which have high  $H$

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

(2) For endothermic  $\Delta H$  is +ve  $H_P > H_R$  RHS of eq (9) is +ve, hence LHS should be +ve

If  $dT$  is +ve, temp is  $\uparrow$   $d\xi_e$  should be +ve,  $\xi_e$  should  $\uparrow$ , more  $R$  with high enthalpy will be formed.

If  $dT$  is -ve,  $T$  is lowered,  $d\xi_e$  must be -ve  $\xi_e$  should  $\downarrow$  with lowering of temp, reactants with lower enthalpy are formed

(3) In athermic reaction,  $\Delta H = 0$ ,  $H_P = H_R$ ,  $eq(9) = 0$   
LHS = 0,  $\xi_e$  is independent of  $T$  at const  $P$

An  $\uparrow$  of temp shifts an eq<sup>n</sup> to high enthalpy side & lowering of temp " " " " low " side.

Variation of  $\xi_e$  with  $P$  at const  $T$ ,  $dT = 0$

$$\frac{\Delta H}{T} \left(\frac{\partial \xi_e}{\partial T}\right)_P + (\Delta V) \left(\frac{\partial \xi_e}{\partial P}\right)_T + G^{\circ} \left(\frac{\partial \xi_e}{\partial T}\right)_T = 0$$

$$\left(\frac{\partial \xi_e}{\partial P}\right)_T = -\frac{\Delta V}{G^{\circ}}$$