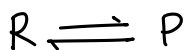


Chemical equilibrium



Le chatelier Principle \longrightarrow According to this principle if an eq. $R \rightleftharpoons P$ is subjected to change in conc or pressure or vol. or temp. etc. and causing some stress ($Q \neq K_{eq}$) then eq. $R \rightleftharpoons P$ proceeds spontaneously in that direction where it reduce or counteract the effect of change.

Case-1 Effect of conc. change



$$K_c = \frac{[P]_{eq}}{[R]_{eq}}$$

$$\text{If } [P] \downarrow \text{ at eq. } \Rightarrow Q_c = \frac{[P]_t}{[R]_{eq}}$$

$Q_c < K_c \Rightarrow R \rightleftharpoons P$ proceeds in forward direction to attain new eq.

If $[P] \uparrow$ at eq. \Rightarrow Rx^n Proceeds in BD
to attain new eq.

If $[R] \uparrow$ at eq. \Rightarrow Rx^n Proceeds in FD
to attain new eq.

If $[R] \downarrow$ at eq. \Rightarrow Rx^n Proceeds in BD
to attain new eq.

Case-2 Effect of temp. \rightarrow

(i) For endothermic Rx^n ($\Delta H^\circ > 0$)

$$\log \frac{K_2}{K_1} = \frac{\Delta H^\circ}{2.303 R} \left(\frac{T_2 - T_1}{T_1 T_2} \right)$$

on increasing temp, $T_2 > T_1$
 $\Rightarrow K_2 > K_1$

\Rightarrow Rx^n Proceeds in FD to attain
new eq.

on decreasing temp, $T_2 < T_1 \Rightarrow K_2 < K_1$

\Rightarrow Rx^n Proceeds in BD
to attain new eq.

(ii) For exothermic Rx^n ($\Delta H^\circ < 0$)

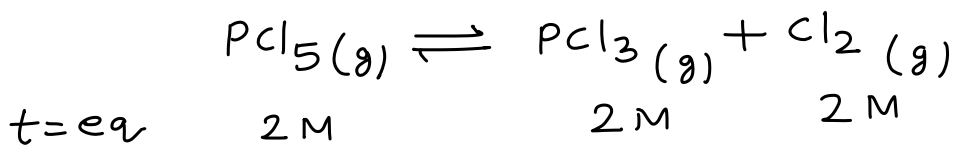
on increasing temp., $T_2 > T_1 \Rightarrow K_2 < K_1$

$\Rightarrow Rx^n$ Proceeds in BD
to attain new eq.

On decreasing temp., $T_2 < T_1 \Rightarrow K_2 > K_1$

$\Rightarrow Rx^n$ Proceeds in FD
to attain new eq.

Case-3 Effect of Pressure or vol. change



$$K_c = \frac{2 \times 2}{2} = 2M$$

Vol. is doubled at eq. \Rightarrow conc. of PCl_5 ,
 PCl_3 and Cl_2 becomes half.

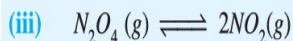
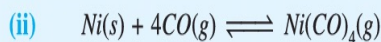
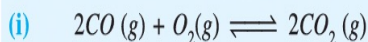
$$Q_c = \frac{1 \times 1}{1} = 1M$$

$Q_c < K_c \Rightarrow Rx^n$ Proceeds in FD to attain
new eq.

Note →

on Increasing vol. or decreasing pressure (at const. temp.), Rx^n proceeds in the direction of **more no. of gaseous moles**.

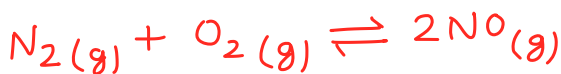
Illustration - 8 What would be the effect of increasing the volume of each of the following systems at equilibrium?



(i) Backward

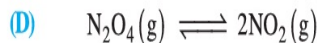
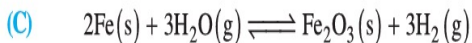
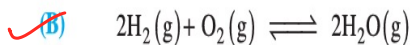
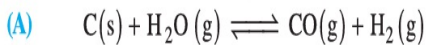
(ii) Backward

(iii) Forward



$V \uparrow \Rightarrow$ No effect on eq. Rx^n .

3. Pressure is doubled in each of the following equilibria. In which case yield is maximum?



(A) Backward

(B) Forward

(C) No effect

(D) Backward

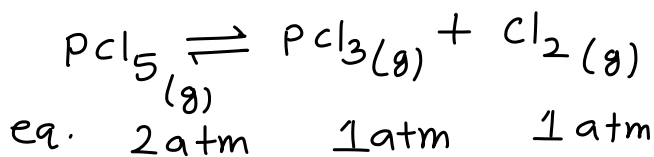
Case-4

Addition of Inert gas

(i) At const. V, T \rightarrow

eq. Mix.

2mol He \rightarrow	PCl_5	2 atm
	PCl_3	1 atm
	Cl_2	1 atm



$$Q_p = K_p$$

\Rightarrow No effect on state of eq.

\Downarrow

Total moles of gaseous mix. \uparrow

\Rightarrow Mole fraction of $\text{PCl}_5, \text{PCl}_3, \text{Cl}_2 \downarrow$

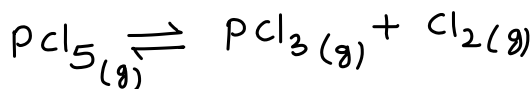
\Rightarrow Total Pressure of system \uparrow

\Rightarrow Partial pressure of $\text{PCl}_5, \text{PCl}_3, \text{Cl}_2$ will be unchanged.

(ii) At const P, T \rightarrow

eq. Mix.

2mol He \rightarrow	PCl_5	2 atm
	PCl_3	1 atm
	Cl_2	1 atm



\Rightarrow Total moles \uparrow

\Rightarrow Mole fraction of $\text{PCl}_5, \text{PCl}_3, \text{Cl}_2 \downarrow$

\Rightarrow Partial Pressure of $\text{PCl}_5, \text{PCl}_3, \text{Cl}_2 \downarrow$

* Eq. Rxⁿ proceeds in the direction of more no. of gaseous moles.

Illustration - 9

What happens when an inert gas is added to



at equilibrium at : (a) constant pressure and temperature, (b) constant volume and temperature.

(i) (a) Forward (b) No change

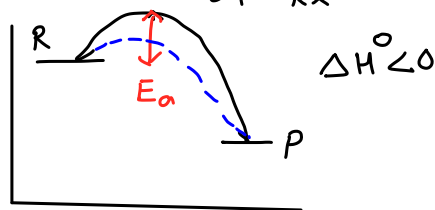
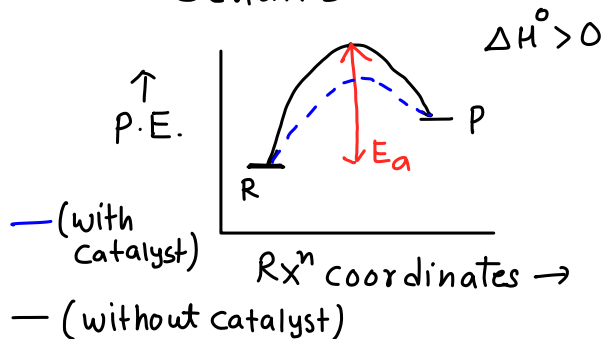
(ii) (a) Backward (b) No change

Case-5 Effect of catalyst

\Rightarrow No effect on eq. Rxn^n

* Catalyst provides an alternative path for mechanism.

$E_a \rightarrow$ activation energy of Rxn^n



68. For the reaction, $\text{PCl}_3(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons \text{PCl}_5(\text{g})$ the position of equilibrium can be shifted to the right by:

- (A) Doubling the volume
- (B) Increasing the temperature
- (C) Addition of inert gas at constant volume
- ✓ (D) Addition of Cl_2 at constant volume

$\Delta H < 0 \Rightarrow T \uparrow \Rightarrow$ Backward dirⁿ.

V ↑ ⇒ Backward

(C) No effect

(D) Forward direction

115. For the gaseous reaction, $C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$, $\Delta H^\circ = -130 \text{ kJ mol}^{-1}$ carried in a closed vessel, the equilibrium concentration of the C_2H_6 can definitely be increased by :

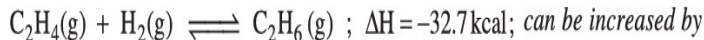


- (A) Increasing temperature and decreasing pressure
(B) Decreasing temperature and pressure both
(C) Increasing temperature and pressure both
(D) Decreasing temperature and increasing pressure

T ↓ ⇒ Forward dirⁿ.

p ↑ ⇒ Forward dirⁿ

15. The equilibrium concentration of C_2H_4 in the gas phase reaction



- I. removal of C_2H_6 II. removal of H_2 III. decreasing temperature IV. increasing pressure

The correct choice is :

- (A) I, II (B) I, III (C) II, III (D) None of these

(I) $[C_2H_6] \downarrow \Rightarrow$ Forward

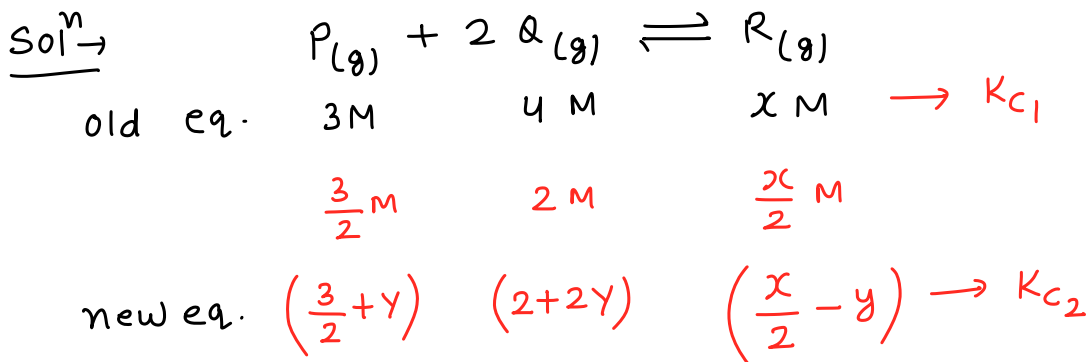
(II) $[H_2] \downarrow \Rightarrow$ Backward

(III) T ↓ ⇒ Forward (IV) Forward

Example - 6

Consider the equilibrium : $P(g) + 2Q(g) \rightleftharpoons R(g)$. When the reaction between P and Q is carried out at a certain temperature, the equilibrium concentrations of P and Q are 3 M and 4 M respectively. When the volume of the vessel is doubled and equilibrium is allowed to re-established, the concentration of Q is found to be 3 M. Find the :

- (a) value of K_c
(b) concentration of R at two equilibrium stages.



$$2 + 2y = 3$$

$$\Rightarrow y = \frac{1}{2} = 0.5$$

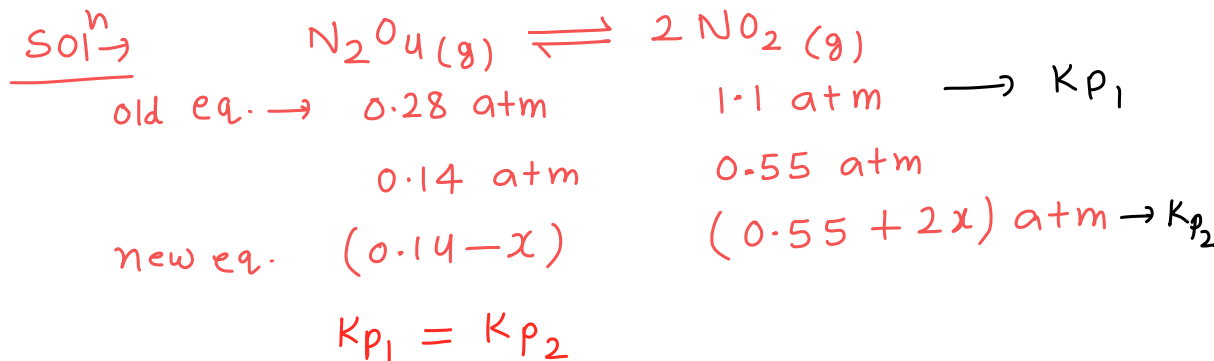
$$K_{c1} = K_{c2}$$

$$\frac{x}{3 \times 4^2} = \frac{\left(\frac{x}{2} - \frac{1}{2} \right)}{2 \times 3^2} \Rightarrow x = 4$$

$$(i) \quad K_c = \frac{x}{48} = \frac{1}{12} \text{ M}^{-2}$$

$$(ii) \quad [R]_{\text{old eq.}} = x = 4 \text{ M}, \quad [R]_{\text{new eq.}} = 1.5 \text{ M}$$

129. An equilibrium mixture at 300 K contains N_2O_4 and NO_2 at 0.28 and 1.1 atmosphere respectively. If the volume of container is doubled, calculate the new equilibrium pressure of NO_2 .



$$\frac{(1.1)^2}{0.28} = \frac{(0.55 + 2x)^2}{0.14 - x}$$

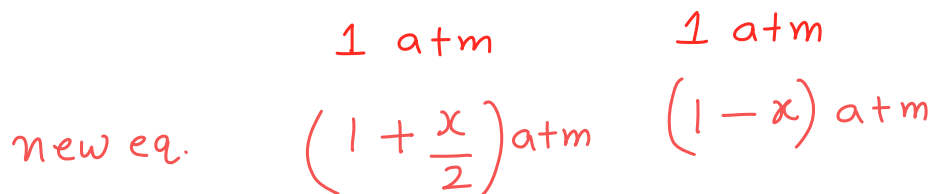
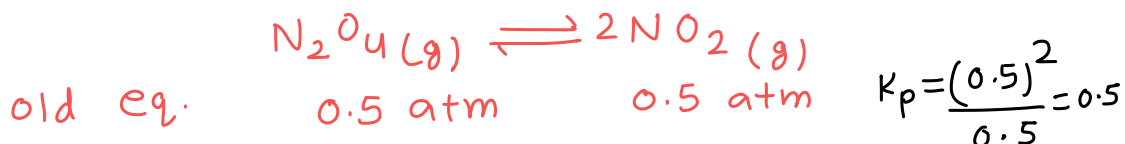
Solve for $x \Rightarrow$ calculate $(0.55 + 2x)$

Illustration - 12 At a given temperature and a total pressure of 1.0 atm for the homogenous gaseous reaction

$N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the partial pressure of NO_2 is 0.5 atm.

(a) Find the value of K_p .

(b) If the volume of the vessel is decreased to half of its original volume, at constant temperature, what are the partial pressures of the components of the equilibrium mixture?



$$0.5 = \frac{(1-x)^2}{1 + \frac{x}{2}}$$

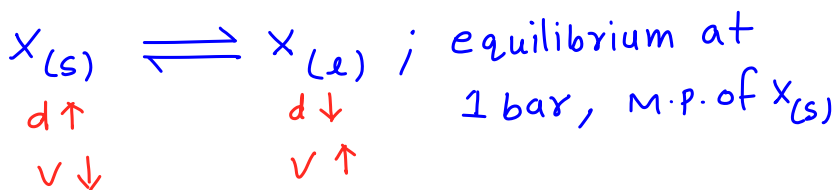
$$x = \frac{1}{4}, \text{ } \cancel{x}$$

$$P_{N_2O_4} = 1 + \frac{x}{2} = \frac{9}{8} \text{ atm}$$

$$P_{NO_2} = 1 - x = \frac{3}{4} \text{ atm}$$

Physical equilibrium \rightarrow

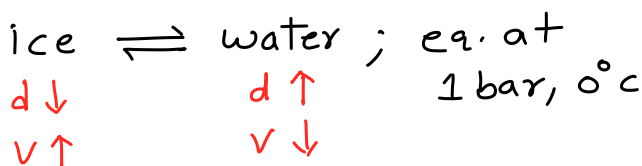
Case-1



$\Delta_r H^\circ > 0 \Rightarrow$ High temp. is favourable for forward direction

Low pressure is favourable for forward dirⁿ.

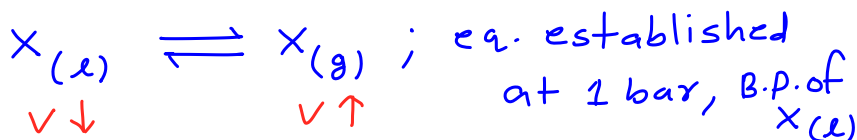
Special case \rightarrow



$\Delta_r H^\circ > 0 \Rightarrow$ High temp. is favourable for forward direction.

High pressure is favourable for forward direction.

Case-2



$\Delta_r H^\circ > 0 \Rightarrow$ High temp. is favourable for forward direction.

Low pressure is favourable for forward direction

4. Increase in the pressure for the equilibrium : $\text{H}_2\text{O}(\ell) \rightleftharpoons \text{H}_2\text{O}(\text{g})$ results in the :

I : formation of more $\text{H}_2\text{O}(\ell)$

II : formation of more $\text{H}_2\text{O}(\text{g})$

III : increase in b.p. of $\text{H}_2\text{O}(\ell)$

IV : decrease in b.p. of $\text{H}_2\text{O}(\ell)$

Hence, correct choice is :

(A) I, II

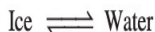
(B) II, III

☒ (C) I, III

(D) I, IV

$P \uparrow \Rightarrow$ Backward direction

10. When pressure is applied to the equilibrium system



Which of the following phenomenon will happen ?

(A) More ice will be formed

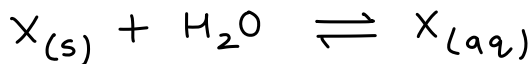
(B) Water will evaporate

☒ (C) More water will be formed

(D) Equilibrium will not be shifted

Effect on solubility in water by Le-chatelier

Principle \rightarrow



If $\Delta_r H^\circ > 0 \Rightarrow T \uparrow \Rightarrow \text{eq. Rxn proceeds in forward direction}$

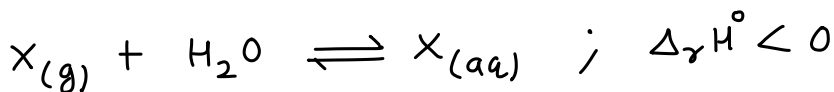
\Rightarrow more amount of $X_{(s)}$ dissolve in H_2O

\Rightarrow solubility \uparrow

Ex. NaCl, KCl, KI, $NaNO_3$ etc.

If $\Delta_r H^\circ < 0 \Rightarrow \text{if } T \uparrow \Rightarrow \text{solubility } \downarrow$

Ex. Li_2CO_3 , $CaCO_3$, KOH etc.



$T \uparrow \Rightarrow \text{solubility of gas in } H_2O \downarrow$

16. When KOH is dissolved in water, heat is evolved. If the temperature is raised, the solubility of KOH.

(A) Increases

☒ (B)

Decreases

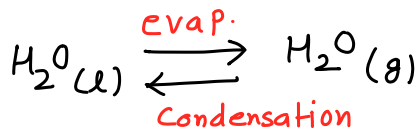
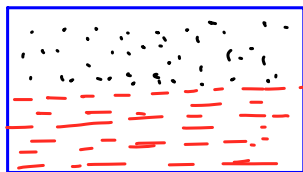
(C)

Remains the same

(D)

Cannot be predicted

Vapour Pressure \rightarrow It is the pressure exerted by vapours of a substance at the surface of same substance at equilibrium.



at eq. \rightarrow rate of evaporation = rate of condensation

$$(P_{H_2O(g)})_{eq.} = \text{v.p. of } H_2O$$

$$K_p = (P_{H_2O(g)})_{eq.} = \text{v.p. of } H_2O$$

Factors affecting v.p. \rightarrow

(1) $\text{v.p.} \propto \text{Temp.}$

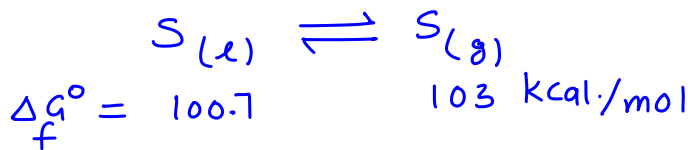
(2) $\text{v.p.} \propto \frac{1}{\text{Strength of Intermolecular forces}}$

(3) v.p. doesn't depend on size, shape, vol. of container and surface area of substance.

26. $\Delta_f G^\circ$ at 500 K for substance 'S' in liquid state and gaseous state are $+100.7 \text{ kcal mol}^{-1}$ and $+103 \text{ kcal mol}^{-1}$, respectively. Vapour pressure of liquid 'S' at 500 K is approximately equal to: (2018)

- ✓ (A) 0.1 atm (B) 1 atm (C) 10 atm (D) 100 atm

Solⁿ \rightarrow



$$(\Delta G^\circ)_{Rxn} = 103 - 100.7 = 2.3 \text{ kcal/mol}$$

$$\Delta G^\circ = -2.3 RT \log_{10} K_p$$

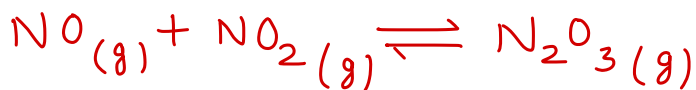
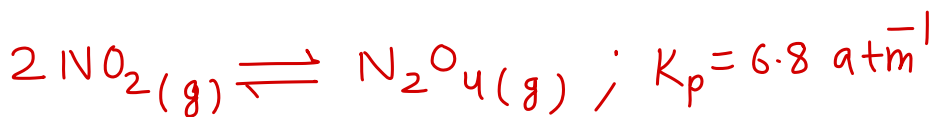
$$(\cancel{2.3} \times \cancel{1000}) = -\cancel{2.3} \times \cancel{2} \times \cancel{500} \log_{10} K_p$$

$$K_p = 0.1$$

$$K_p = (P_{S(g)})_{eq.} = \text{v.p. of } S_{(l)} = 0.1 \text{ atm}$$

Simultaneous equilibrium \rightarrow When two or more equilibria are established in a same vessel simultaneously then it is called simultaneous equilibrium.

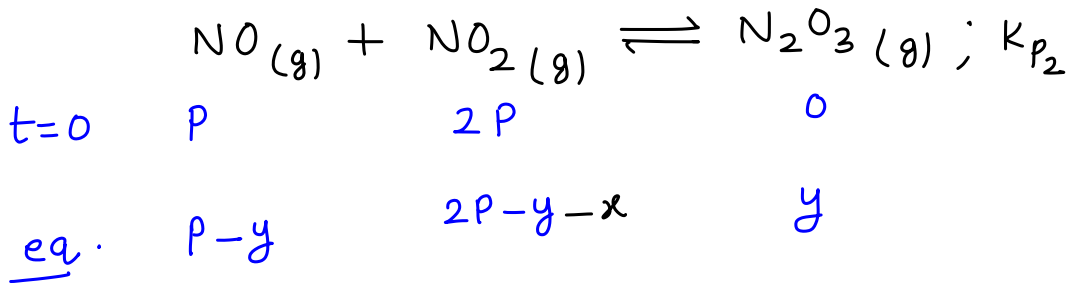
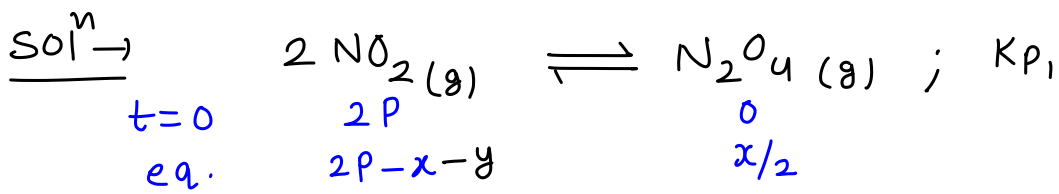
Q. When NO(g) and $\text{NO}_2(\text{g})$ are mixed, the following equilibria are established simultaneously:



When NO and NO_2 are mixed in the ratio of 1:2, the final pressure at eq. is 5.05 atm and the partial pressure of $\text{N}_2\text{O}_4(\text{g})$ is 1.7 atm then calculate:

(i) Partial pressure of NO at eq.

(ii) K_p of N_2O_3 .



$$K_{p_1} = 6.8 = \frac{P_{\text{N}_2\text{O}_4}}{P_{\text{NO}_2}^2} = \frac{1.7}{P_{\text{NO}_2}^2}$$

$$P_{\text{NO}_2} = 0.5 \text{ atm}$$

$$\begin{aligned}
 P_T &= P_{\text{NO}_2} + P_{\text{NO}} + P_{\text{N}_2\text{O}_4} + P_{\text{N}_2\text{O}_3} \\
 &= 0.5 + P-y + 1.7 + y = 5.05 \\
 P &= 2.85
 \end{aligned}$$

$$P_{\text{N}_2\text{O}_4} = 1.7 = \frac{x}{2} \Rightarrow x = 3.4$$

$$\begin{aligned}
 P_{\text{NO}_2} &= 0.5 = 2P-x-y \\
 \Rightarrow y &= 1.8
 \end{aligned}$$

$$(P_{\text{NO}})_{\text{eq.}} = P-y = 1.05 \text{ atm}$$

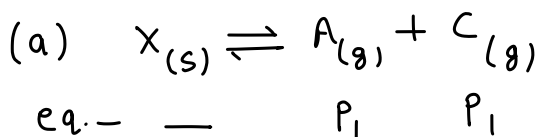
$$K_{p_2} = \frac{P_{\text{N}_2\text{O}_3}}{P_{\text{NO}} \cdot P_{\text{NO}_2}} = \frac{1.8}{1.05 \times 0.5} = 3.43 \text{ atm}^{-1}$$

Example - 5

Two solids X and Y dissociates into gaseous products at a certain temperature as follows :

$X(s) \rightleftharpoons A(g) + C(g)$, and $Y(s) \rightleftharpoons B(g) + C(g)$. At a given temperature, pressure over excess solid X is 40 mm and total pressure over solid Y is 80 mm. Calculate :

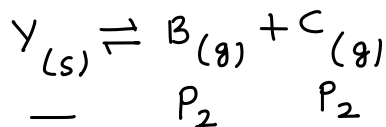
- (a) the values of K_p for two reactions.
- (b) the ratio of moles of A and B in the vapour state over a mixture of X and Y.
- (c) the total pressure of gases over a mixture of X and Y.



$$P_1 + P_1 = 40$$

$$\Rightarrow P_1 = 20$$

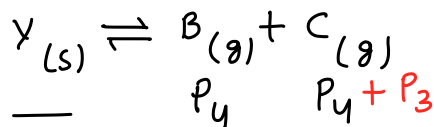
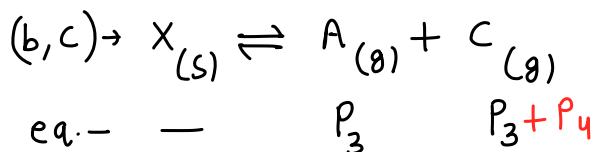
$$K_{p_1} = P_1 \cdot P_1 = 400 \text{ atm}^2$$



$$P_2 + P_2 = 80$$

$$P_2 = 40$$

$$K_{p_2} = P_2 \cdot P_2 = 1600 \text{ atm}^2$$



$$K_{p_1} = P_3 (P_3 + P_4) \text{ ———— ①}$$

$$K_{p_2} = P_4 (P_3 + P_4) \text{ ———— ②}$$

$$\text{①} \div \text{②} \Rightarrow \frac{P_3}{P_4} = \frac{K_{p_1}}{K_{p_2}} = \frac{400}{1600} = \frac{1}{4}$$

Ans.

$$\text{①} + \text{②} \Rightarrow K_{p_1} + K_{p_2} = (P_3 + P_4)^2$$

$$(P_3 + P_4) = \sqrt{K_{p_1} + K_{p_2}}$$

$$P_{\text{Total}} = P_A + P_B + P_C = P_3 + P_4 + P_3 + P_4$$

$$= 2(P_3 + P_4)$$

$$= 2 \sqrt{K_{P_1} + K_{P_2}}$$

$$= 2 \sqrt{400 + 1600}$$

$$= 89.44 \text{ atm}$$