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CHEMISTRY
TARGET IIT JEE

CHEMICAL EQUILIBRIUM

THEORY AND EXERCISE BOOKLET

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CHEMICAL EQUILIBRIUM

1. The state at which concentrations of reactants or products do not change with time.
2. It is attained when rate of forward reaction becomes equal to rate of backward reaction.
3. A dynamic equilibrium, attained from either side.

IRREVERSIBLE AND REVERSIBLE REACTIONS

	Irreversible reactions	**Reversible reactions**
1.	Unidirectional	1. Both directional
2.	Go for completion	2. Never go for completion
3.	No equilibrium is attained	3. Attains equilibrium
4.	A reaction is said to be irreversible when either of the product is settled down as solid or escapes out as gas, e.g., $BaCl_2 + Na_2SO_4 \rightarrow BaSO_4$ (insoluble) $+ 2NaCl$ $CaCO_3 \rightarrow CaO + CO_2 \uparrow$	4. Otherwise the reaction is reversible e.g., $CaCO_3 \rightleftharpoons CaO + CO_2$ in closed container

HOMOGENEOUS SYSTEM

The system in which all the reactant and product have same physical state.

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$

$$CH_3COOC_2H_5(aq) + H_2O(aq) \rightleftharpoons CH_3COOH(aq) + C_2H_5OH(aq)$$

HETEROGENEOUS SYSTEM

The system in which atleast one reactant or product have different physical states from others. eg.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$$

$\Rightarrow$ This is three phase system

$$Salt + H_2O(aq) \rightarrow Salt(aq)$$

$\Rightarrow$ Three phase system.

RATE OF REACTION

The change in concentration per unit time of reactant or product is called rate of reaction
1. Average Rate
2. Instantaneous Rate

	A	$\longrightarrow$	B
t = 0	a		0
t = t	a – x		x

$$\text{Rate} = \frac{-\Delta A}{\Delta t} = \frac{\Delta B}{\Delta t}$$

$$\frac{\Delta A}{\Delta t} = \frac{a - x - a}{t} = \frac{-x}{t}$$

$$\frac{\Delta B}{\Delta t} = \frac{x - 0}{t} = \frac{x}{t}$$

	2A	$\longrightarrow$	B
t = 0	a		0
t = t	a – 2x		x

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$$\frac{\Delta A}{\Delta t} = \frac{a - 2x - a}{4t} = -\frac{2x}{\Delta t}$$

$$\frac{\Delta B}{\Delta t} = \frac{x}{t} \quad \Rightarrow \quad -\frac{1}{2}\frac{\Delta A}{\Delta t} = \frac{\Delta B}{\Delta t}$$

Instantaneous Rate :

$$\lim_{\Delta t \to 0} \frac{-\Delta A}{\Delta t} = \frac{-dA}{dt} \text{ (inst. Rate)}$$

☛

	3A +	2B ⟶	5C +	7D
t=0	a	b	0	0
	a – 3x	b – 2x	5x	7x

$$\frac{\Delta A}{\Delta t} = -\frac{3x}{t} \; ; \quad \frac{\Delta B}{\Delta t} = -\frac{2x}{t}$$

$$\frac{\Delta C}{\Delta t} = \frac{5x}{t} \; ; \quad \frac{\Delta D}{\Delta t} = \frac{7x}{t}$$

$$\Rightarrow \quad -\frac{1}{3}\frac{\Delta A}{\Delta t} = -\frac{1}{2}\frac{\Delta B}{\Delta t} = \frac{1}{5}\frac{\Delta C}{\Delta t} = \frac{1}{7}\frac{\Delta D}{\Delta t}$$

LAW OF MASS ACTION

A ⟶ B

Ex.1 ***Is this a one step reaction or more than one step reaction ?***

Sol. By merely seeing the reaction we can not predict the step of the reaction.
The above reaction can also be written as

A ⟶ C

C ⟶ D

D ⟶ B

Adding A ⟶ B

☛ Law of mass action is only valid for elementary reaction.
According ***"The rate of a chemical reaction is directly proportional to active mass of the reactants"***

A ⟶ Product

rate ∝ Active mass of A

where Active mass = Activity coefficient × molar concentration

when active coefficient = 1

Active mass = Molar concentration

ACTIVITY COEFFICIENT

The fraction of molecules taking part in effective collision is called activity coefficient. It is always less than 1.

Rate ∝ [A]

Rate = k [A]

k = Rate constant

A → product (complex Reaction)

Rate = K $[A]^x$ where x = order of Reaction w.r.t. A

• 2A ⟶ product

Rate = K $[A]^2$ [for elementory Reaction]

Rate = k $[A]^x$ [for complex Reaction]

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☛ ***"If there are more than one reactant then the rate of reaction is directly proportional to product of Active masses of substances."***

Rate $\propto$ Active mass of A × Active mass of B

Rate = k [A] [B]

and if any reaction is of the type

$aA + bB \longrightarrow$ product

Rate = $k[A]^a [B]^b$

$aA + bB \rightleftharpoons cC + dD$

Rate of forward Reaction (R_f) = $k_f [A]^a [B]^b$

Rate of backward Reation (R_b) = $k_b[C]^c [D]^d$

At equilibrium

$R_f = R_b$

$k_f[A]^a [B]^b = k_b[C]^c [D]^d \Rightarrow \frac{k_f}{k_b} = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

☛ $\mathbf{k_c = \frac{k_f}{k_b}}$

$K_c \rightarrow$ equilibrium constant in terms of concentration

$K_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b}$ (K_p = eq. constant in terms of partial pressure)

- Consider the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

then $K_C = \frac{[NH_3]^2}{[N_2][H_2]^3}$

☛ $\boldsymbol{K_p = \frac{p_{NH_3}^2}{p_{N_2} \times p_{H_2}^3}}$

RELATION BETWEEN K_P AND K_C

PV = nRT

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

P = CRT

$P_A = [A] RT$ ...(1)

$P_B = [B] RT$ ...(2)

$P_c = [C] RT$ ...(3)

$P_D = [D] RT$ ...(4)

We know that for a reaction of the type

$aA + bB \rightleftharpoons cC + dD$

$k_p = \frac{p_C^c \times p_D^d}{p_A^a \times p_B^b}$

$k_p = \frac{[C]^c[D]^d}{[A]^a[B]^b} \frac{(RT)^{C+d}}{(RT)^{a+b}}$ (from eq. (1), (2), (3) & (4))

$\boldsymbol{k_p = k_c(RT)^{\Delta n}}$

where $\Delta n = (c + d) – (a + b)$

Δn = no. of moles of gaseous Reactants – no. of moles of gaseous products

if $\Delta n = 0$

$\Rightarrow$ $K_p = K_c$

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EQUILIBRIUM CONSTANT IN TERMS OF MOLE FRACTION

$$k_x = \frac{x_C^c \times x_D^d}{x_B^b \times x_A^a}$$

Partial pressure = mole fraction × total pressure

Ex.2 ***Find the relation between K_p and K_x for the reaction***

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

Sol. $$k_p = \frac{p_{NH_3}^2}{p_{N_2} \times p_{H_2}^3} = \frac{(x_{NH_3} \times p)^2}{(x_{N_2} \times p) \times (x_{H_2} \times p)^3} = \frac{x_{NH_3}}{x_{N_2} \times (x_{H_2})^3} \frac{p^2}{p^4} \Rightarrow k_p = \frac{k_x}{p^2}$$

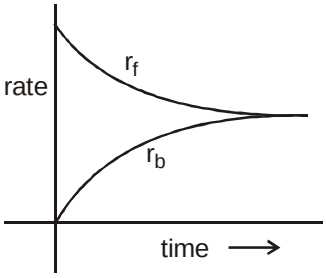
Ex.3 ***What is the relation between k_c and k_x for the same reaction ?***

Sol. $$k_c(RT)^{-2} = \frac{k_x}{p^2} \Rightarrow k_c = \frac{k_x R^2 T^2}{p^2}$$

CHEMICAL EQUILIBRIUM WITH GRAPH

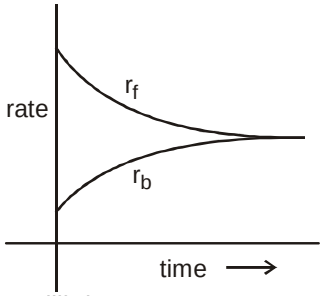
$$N_2O_4(g) \underset{r_b}{\overset{r_f}{\rightleftharpoons}} 2NO_2(g)$$

(a)



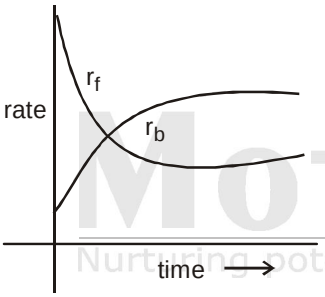
equilibrium as $r_f = r_b$

(b)



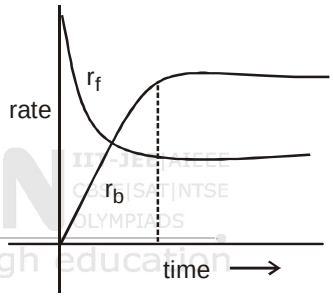
equilibrium as $r_f = r_b$

(c)



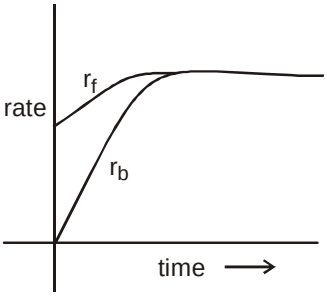
Not equilibrium as $r_f \neq r_b$

(d)



Not equilibrium as $r_f \neq r_b$

(e)



Same reason as below.

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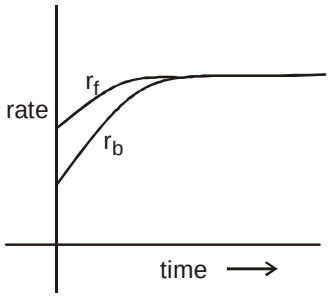
(f)



(not equilibrium rate of forward reaction and backward reaction can not increase together)

☛ If we consider concentration and time for the above plot then only e and f will not show the state of equilibrium.

EXPRESSION FOR K_P AND K_C FOR A GIVEN REACTION

$$\begin{array}{lccc} & N_{2(g)} + & 3H_{2(g)} & \rightleftharpoons & 2NH_{3(g)} \\ t = 0 & a & b & & 0 \\ \text{At eq.} & \frac{a-x}{v} & \frac{b-3x}{v} & & \frac{2x}{v} \end{array}$$

$$k_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right)^3}$$

$$k_c = \frac{4x^2}{(a-x)(b-3x)^3 v^2} \Rightarrow k_p = \frac{p_{NH_3}^2}{p_{N_2} \times p_{H_2}^3}$$

$$\Rightarrow \quad k_p = \frac{\left(\frac{2x}{a+b-2x} \times p\right)^2}{\left(\frac{a-x}{a+b-2x} \times p\right) \times \left(\frac{b-3x}{a+b-2x} \times p\right)^3} \Rightarrow k_p = \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3 p^2}$$

DEGREE OF DISSOCIATION

$$2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$$

$a - 2x \qquad x \qquad 3x$

It is the no. of moles dissociated from 1 mole of reactant.

OR

Fraction of moles dissociated from one mole of reactant.

$\Rightarrow$ a moles NH_3 gives 2x mole

$\therefore$ 1 mole $NH_3 \longrightarrow \frac{2x}{a}$

degree of dissociation (α) = $\frac{2x}{a}$

☛ $2NH_3 \rightleftharpoons N_2 + 3H_2$

$a(1-\alpha) \qquad \frac{a\alpha}{2} \qquad \frac{3a\alpha}{2}$

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DEGREE OF DISSOCIATION FROM VAPOUR DENSITY

Ex.4 ***The V.D. of mixture of PCl_5, PCl_3 and Cl_2 is 92. Find the degree of dissociation of PCl_5.***

Sol.

$$\underset{1}{PCl_5} \rightleftharpoons \underset{0}{PCl_3} + \underset{0}{Cl_2}$$
$$\underset{1-x}{} \qquad \underset{x}{} \qquad \underset{x}{}$$

☛ If initial concentration is not given in the question then we suppose initial mole = 1 mole
molecular wt. of mixture. = 2 × 92 = 184
total moles of mix = 1 – x + x + x = 1 + x
wt. of the mixture = (1 + x) × 184
wt. of initial mixture = 1 × 208.5
$\Rightarrow$ 1 × 208.5 = (1 + x) × 184 (according to law of mass conservation)
$\Rightarrow$ 208.5 = 184 + 184 x $\Rightarrow$ x = 0.13
% dissociation = 13 %

Ex.5 $nA \rightleftharpoons A_n$
V.D. of A = d
V.D. of mix = D
find the degree of polymerisation.

Sol.

$$\underset{1}{nA} \rightleftharpoons \underset{0}{A_n}$$
$$\underset{1-x}{} \qquad \underset{\frac{x}{n}}{}$$

moles of mix = $1 - x + \frac{x}{n}$

wt. of mix = $(1 - x + \frac{x}{n}) \times 2D$

1 × 2d = $(1 - x + \frac{x}{n}) \times 2D$ (According to law of mass conservation)

$$\frac{d}{D} = 1 + x\left(\frac{1}{n} - 1\right) \Rightarrow \frac{d}{D} - 1 = x\left(\frac{1}{n} - 1\right) \Rightarrow x = \frac{(d-D)n}{D(1-n)} \Rightarrow x = \frac{(D-d)n}{D(n-1)}$$

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

1. $A + B \underset{}{\overset{k_1}{\rightleftharpoons}} C + D$

$$k_1 = \frac{[C][D]}{[A][B]}$$

After reversing the reaction

$C + D \overset{k_2}{\rightleftharpoons} A + B$

$$k_2 = \frac{[A][B]}{[C][D]} = \frac{1}{k_1}$$

After reversing the reaction the equilibrium constant get reversed.

2. $E + F \overset{k_2}{\rightleftharpoons} G$ and $A + B \overset{k_1}{\rightleftharpoons} C + D$

After adding the reaction $\rightarrow A + B + E + F \overset{k_3}{\rightleftharpoons} C + D + G$

$$k_3 = \frac{[C][D][G]}{[A][B][E][F]} \Rightarrow K_3 = K_1 \times K_2$$

when the two reaction are added there equilibrium constant get multiplied.

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3. $A + B \underset{}{\overset{k_1}{\rightleftharpoons}} C + D$

$$k_1 = \frac{[C][D]}{[A][B]}$$

After multiplying by n

$nA + nB \overset{k_2}{\rightleftharpoons} nC + nD$

$$k_2 = \frac{[C]^n[D]^n}{[A]^n[B]^n} = k_1^{\,n} \Rightarrow k_2 = k_1^{\,n}$$

When the reaction is multiplied by any number then eq. constant gets the same number in its power.

HETEROGENEOUS EQUILIBRIUM

$CaCO_3(s) \rightleftharpoons CaO_{(s)} + CO_{2(g)}$

☛ The density of the solid at constant temp. remains constant.

$$d = \frac{m}{V}$$

$$\frac{d}{M} = \frac{m}{v} \times \frac{1}{M} = \frac{n}{V}$$

$$\text{constant} = \frac{n}{v}$$

$\Rightarrow$ concentration = constant

Here m = mass of solid

M = molecular weight of solid

n = moles of solid.

$$k = \frac{[CaO(s)][CO_2(g)]}{[CaCO_3(s)]} \Rightarrow k \times \frac{[CaCO_3(s)]}{[CaO(s)]} = [CO_2(g)]$$

$\Rightarrow$ $K_c = [CO_2(g)]$

PREDICTION OF THE DIRECTION OF THE REACTION

$2A + B \underset{}{\overset{K_C = 10}{\rightleftharpoons}} C + D$

conc. at t time 2 mol 3 mol 5 mol 4 mol [volume of container = 1 litre]

$$k_C = \frac{[C][D]}{[A]^2[B]}$$ $\Rightarrow$ All concentration at eq.

Reaction quotient $Q_C = \frac{[C][D]}{[A]^2[B]}$ Here concentration is at any time 't'

$$Q_C = \frac{5 \times 4}{4 \times 3} = \frac{5}{3}$$

If $Q_C > K_c \Rightarrow$ backward Reaction

$Q_C < K_C \Rightarrow$ forward Reaction

$Q_C = K_C \Rightarrow$ Equilibrium condition

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LE CHATELIER'S PRINCIPLE

When the equilibrium is disturbed by changing pressure, temp, volume and concentration of the reactants or products then reaction proceeds in that direction where the applied change is nullified"

1. Effect of Temperature :

(i) Endothermic Reaction

$A + B \rightleftharpoons$ product $\quad \Delta H > 0$

or $A + B + \text{heat} \rightleftharpoons$ product

In case of endothermic reaction on increasing the temp, reaction proceeds in the forward direction and vice versa.

On increasing temp, the value of eq. constant increasing.

$$\log\frac{k_2}{k_1} = \frac{\Delta H}{2.303R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

If temp is increased

$$T_1 < T_2$$

for endothermic reaction, $\Delta H > 0$ i.e. +ve

Also $\quad \frac{1}{T_1} - \frac{1}{T_2} = +ve$

$\Rightarrow \quad \log\frac{k_2}{k_1} > 0 \quad \Rightarrow \quad \log\frac{k_2}{k_1} > \log 1$

$\Rightarrow \quad \frac{k_2}{k_1} > 1 \quad \Rightarrow K_2 > K_1$

if $\quad T_1 > T_2$

$\Rightarrow \quad \log\frac{k_2}{k_1} < 0 \Rightarrow \log\frac{k_2}{k_1} < \log 1 \quad \Rightarrow k_2 < k_1$

Thus it can be conclude that

$\Delta H > 0$	$T\uparrow$	$k\uparrow$
(endothermic)	$T\downarrow$	$k\downarrow$
$\Delta H < 0$	$T\uparrow$	$k\downarrow$
(exothermic reaction)	$T\downarrow$	$k\uparrow$

(ii) Exothermic Reaction($\Delta H < 0$)

On increasing temperature, the reaction proceeds in backward direction.

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2. Effect of Pressure :

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

At eq. $\quad n_1 \qquad n_2 \qquad n_3$

$$k_p = \frac{\left(\frac{n_2}{n_1+n_2+n_3}\times P\right)\left(\frac{n_3}{n_1+n_2+n_3}\times P\right)}{\frac{n_1}{n_1+n_2+n_3}\times P}$$

$$\Rightarrow \quad k_p = \frac{n_2 n_3 \times P}{n_1(n_1+n_2+n_3)}$$

On increasing P, eq. will be disturbed $\therefore$ k_p will not defined at that pressure Hence Qp will be defined

$$Q_p = \frac{n_2 n_3}{n_1(n_2+n_1+n_3)} \times p^1$$

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$\Rightarrow$ value of Q_p > value of k_p
$\Rightarrow$ backward reaction

$\Rightarrow$ On increasing Pressure the reaction shift in direction where the number of moles are less.
$\Rightarrow$ If no. of moles at reactant side and product side are equal then there will be no effect of changing pressure at equilibrium.

3. Effect of volume :
If the concentration of reactant increases or that of concentration product decreases then reaction proceeds in forward direction.

3. Addition of Inert Gas
(1) At constant volume
(2) At constant pressure

(i) At constant volume.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

At eq. $\frac{n_1}{v}$ $\frac{n_2}{v}$ $\frac{n_3}{v}$

$$k_c = \frac{\frac{n_2}{v} \times \frac{n_3}{v}}{\frac{n_1}{v}} = \frac{n_2 n_3}{n_1 v}$$

$PV = nRT$
$P \propto n$ (V, T constant)
After the Adding of inert gas

$$Q_c = \frac{n_2 n_3}{n_1 v} \quad \Rightarrow \quad Q_c = K_c$$

$\Rightarrow$ there is no effect of adding inert gas on the state of equilibrium at constant volume.

$$k_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}} = \frac{\left(\frac{n_2}{n_1+n_2+n_3} \times p\right)\left(\frac{n_3 p}{n_1+n_2+n_3}\right)}{\left(\frac{n_1}{n_1+n_2+n_3} \times P\right)} = \frac{n_2 n_3 p}{n_1(n_1+n_2+n_3)}$$

If we n_4 moles of inert gas is added

$$Q_p = \frac{n_2 n_3 p'}{(n_1+n_2+n_3+n_4)} \Rightarrow \frac{P}{n} = \text{constant}$$

$\Rightarrow$ $Q_P = K_p$
$\Rightarrow$ there will be no effect of adding inert gas on equilibrium at constant volume.

(ii) At constant pressure

$PV = nRT$
$V \propto n$

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

At eq. $\frac{n_1}{v}$ $\frac{n_2}{v}$ $\frac{n_3}{v}$

$\Rightarrow$ $k_c = \frac{n_2 n_3}{n_1 v}$

After the Adding of inert gas

$$Q_c = \frac{n_2 n_3}{n_1(v+\Delta v)}$$

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$\Rightarrow Q_c < K_C \Rightarrow$ forward direction

- On Adding of inert gas At constant pressure, the reaction proceeds in that direction where the sum of stoichiometric coefficient is greater.

SIMULTANEOUS EQUILIBRIUM

$$A_{(s)} \rightleftharpoons B_{(g)} + C_{(g)}$$
$$D_{(s)} \rightleftharpoons B_{(g)} + E_{(g)}$$

☛ Applicable only when at least one of the product is common in both the reaction.

Ex.6 ***The pressure at equilibrium over solid A is 50 atm and over solid D is 68 atm if both solid A and D are heated simultaneously then find the total pressure over the solids.***

Sol. At 1st equilibrium

$$k_{p_1} = (25)^2;\ k_{p_2} = (34)^2$$

At IInd equilibrium

$$A_{(s)} \rightleftharpoons \underset{x+y}{B_{(g)}} + \underset{x}{C_{(g)}}$$
$$D_{(s)} \rightleftharpoons \underset{x+y}{B_{(g)}} + \underset{y}{E_{(g)}}$$

$K_{p_1} = (x+y)\times x$ ...(i)

$K_{p_2} = (x+y)\times y$ ...(ii)

total pressure = $p_B + p_C + p_E = x + y + x + y = 2\,(x + y)$

Also $k_{p_1} + k_{p_2} = (x+y)^2$

$\Rightarrow \quad x + y = \sqrt{k_{p_1} + k_{p_2}}$

$\Rightarrow$ Total pressure = $2\,(x + y) = 2\sqrt{k_{p_1} + k_{p_2}}$

(i) In the above question find the mole ratio of C and B

(ii) mole fraction of C

Sol. At constant temp and volume

$P \propto n$

$\Rightarrow$ pressure Ratio will their mole ratio

by eq. (i)/(ii)

$$\frac{k_{p_1}}{k_{p_2}} = \frac{x}{y}$$

(iii) Mole fraction of C

$$C = \frac{x}{2(x+y)}$$

As we know $\frac{k_{p_1}}{k_{p_2}} = \frac{x}{y}$

$$\Rightarrow \quad \frac{y}{x} = \frac{k_{p_2}}{k_{p_1}} \quad \Rightarrow \quad \frac{x+y}{x} = \frac{k_{p_2} + k_{p_1}}{k_{p_1}}$$

$$\Rightarrow \quad \frac{2(x+y)}{x} = \frac{2(k_{p_2} + k_{p_1})}{k_{p_1}} \quad \Rightarrow \quad \frac{x}{2(x+y)} = \frac{k_{p_1}}{2(k_{p_2} + k_{p_1})}$$

$\Rightarrow$ mole fraction of C = $\frac{k_{p_1}}{2(k_{p_2} + k_{p_1})}$

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Ex.7 ***A(s)*** $\rightleftharpoons$ $H_2S(g)$ + B(g) ***At eq., pressure = 18 atm***

C(s) $\rightleftharpoons$ $H_2S(g)$ + D(g) ***At eq., pressure = 36 atm***

Calculation

(i) total pressure at new equilibrium when both the solids are heated simultaneously.

(ii) mole ratio of B and D

(iii) mole fraction of B in the mixture.

Sol. $kp_1 = (9)^2 = 81$

$kp_2 = (18)^2 = 324$

After

A(s) $\rightleftharpoons$ $H_2S(g)$ + B(g)

x + y x

C(s) $\rightleftharpoons$ $H_2S(g)$ + D(g)

x + y y

total pressure = x + y + x + y = 2 (x + y)

$kp_1 = x(x + y)$

$kp_2 = y(x + y)$

$\Rightarrow kp_1 + kp_2 = (x+ y)^2 \Rightarrow x + y = \sqrt{kp_1 + kp_2}$

$\Rightarrow$ total pressure = 2 (x + y) = $2\sqrt{kp_1 + kp_2}$

$= 2\sqrt{81+ 324} = 2\sqrt{405}$ atm

(ii) mole ratio of B & D = $\frac{x}{y} = \frac{81}{324} = \frac{9}{108} = \frac{1}{12}$

(iii) mole fraction of B in mixture = $\frac{x}{2(x+y)} = \frac{kp_1}{2(kp_1 + kp_2)}$

PHYSICAL EQUILIBRIUM

Let us consider the following physical equilibrium

$H_2O(\ell) \rightleftharpoons H_2O(g)$

1. Effect of temperature

Since it is an endothermic reaction therefore reaction will proceed in forward direction on increasing temp. (Le Chatelier's principle)

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2. Effect of pressure :

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

for the above equilibrium $\Delta H > 0$

ΔV ie $V_g - V_\ell$ = +ve

$\Rightarrow$ $\frac{dP}{dT}$ = +ve

$\Rightarrow$ on increasing P, T increases

But As reaction is to complete at the initial temp, therefore temperature must be lowered. This will make the reaction go to direction as suggested by Le-chatelior (endothermic reaction)

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Ex.8 ***A(s) (d = 1.14 gm/cc)***
B(s) (d = 1.5 gm/cc)
A(s) $\rightleftharpoons$ ***B(s) + Heat***
If mass of A and B are equal, on increasing the pressure, will for formation of B ↑or ↓?

Sol. A(s) $\rightleftharpoons$ B(s)

As density of solid B > solid A

$\Rightarrow V_B < V_A \quad \Rightarrow V_B - V_A = -ve$

since reaction is exothermic

$\therefore \Delta H = -ve$

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

$$\Rightarrow \frac{dP}{dT} = +ve$$

$\Rightarrow$ on ↑ing P, T also ↑es

To achieve initial temp. i.e., reaction temp. The temp. must lowered and lowering.
the temp. in an exothermic reaction clearly indicates forward reaction.

$\Rightarrow$ On increasing pressure, the rate of formation of B will be enhanced.

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