SUBJECTIVE SOLVED EXAMPLES

Example - 1 *H_2 and I_2 are mixed at 400°C in a 1.0 L container and when equilibrium is established, the following concentrations are present : [HI] = 0.8 M, $[H_2]$ = 0.08 M and $[I_2]$ = 0.08 M. If now an additional 0.4 mol of HI are added, what are the new equilibrium concentrations, when the new equilibrium $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is re-established ?*

SOLUTION :

First determine the equilibrium constant

$$K_c \text{ for } H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.8)^2}{0.08 \times 0.08} = 100$$

When 0.4 mol of HI are added, equilibrium is disturbed.

At that instant, $[HI] = 0.8 + 0.4 = 1.2\ M$

$\Rightarrow$ $Q > K_c$ since $Q = \dfrac{(1.2)^2}{0.08 \times 0.08} = 225$

$\Rightarrow$ Backward reaction dominates and the equilibrium shifts to the left.

Let $2x$ = concentration of HI consumed (*while going left*)

then concentration of each of H_2 and I_2 formed $= x$

$\Rightarrow$ $[HI] = 1.2 - 2x$, $[H_2] = 0.08 + x$,
$[I_2] = 0.08 + x$ and $K_c = 100$

$$\Rightarrow \quad K_c = \frac{(1.2 - 2x)^2}{(0.08 + x)(0.08 + x)} = 100$$

$\Rightarrow$ Take square root on both side to get :

$x = 0.033$

Finally, the equilibrium concentrations are :

$[HI] = 1.2 - 2x = 1.2 - 0.033 \times 2 = 1.13\ M$

$[H_2] = 0.08 + x = 0.08 + 0.033 = 0.11\ M$

$[I_2] = 0.08 + x = 0.08 + 0.033 = 0.11\ M$

Example - 2 *0.25 mol of CO taken in a 1.5 L flask is maintained at 500 K along with a catalyst so that the following reaction can take place ; $CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$. Hydrogen is introduced until the total pressure of the system is 8.2 atm. at equilibrium and 0.1 mol of methanol is formed. Calculate :*

(i) *K_p and K_c*

(ii) *The final pressure if the same amount of CO and H_2 as before are used but no catalyst so that the reaction does not take place.*

SOLUTION :

First balance the equation as :

$$CO(g) + 2H_2(g) \rightleftharpoons CH_3OH(g)$$

$$K_C = \frac{[CH_3OH]}{[CO][H_2]^2}$$

Let y moles of H_2 were present initially.

Moles	CO	H_2	CH_3OH
Initially	0.25	y	0
At equilibrium	$0.25 - x$	$y - 2x$	x

$x = 0.10$ (*given*)

$\Rightarrow$ moles of $CO = 0.25 - 0.10 = 0.15$,
moles of $H_2 = y - 0.2$ and
moles of $CH_3OH = 0.10$

$\Rightarrow$ Total moles $= n_T = 0.15 + (y - 0.2) + 0.10 = 0.05 + y$

Equilibrium pressure $(P) = 8.2$ atm

Volume of vessel $(V) = 1.5$ L, $T = 500$ K

Using the Gas equation, $PV = nRT$, we have :

$$n_T = \frac{PV}{RT} = \frac{8.2\times1.5}{0.0821\times500} = 0.3$$

$\Rightarrow \quad 0.30 = 0.05 + y \quad \Rightarrow \quad y = 0.25$ moles

$\Rightarrow$ moles of H_2 at equilibrium $= y - 0.2$

$$= 0.25 - 0.2 = 0.05$$

Now find K_c as follows :

$$K_c = \frac{[CH_3OH]}{[CO][H_2]^2} = \frac{\frac{0.10}{1.5}}{\frac{0.15}{1.5}\left(\frac{0.05}{1.5}\right)^2} = 600$$

Now find K_p using the relation :

$$K_p = K_c(RT)^{\Delta n_g}$$

$$\Delta n_g = 1 - 3 = -2$$

$\Rightarrow \quad K_p = 600\,(0.0821\times500)^{-2} = 0.356$

(ii) When no reaction takes place, then the total pressure is simply due to H_2 and CO present initially.

$$n_T = n_{(CO)} + n_{H_2} = 0.25 + 0.25 = 0.5$$

$\Rightarrow \quad P = \frac{nRT}{V} = \frac{0.5\times0.0821\times500}{1.5} = 13.68$ atm

Example - 3 *Ammonia under a pressure of 15 atm. at 27°C is heated to 327°C is a closed vessel in the presence of catalyst. Under these conditions, NH_3 partially decomposes to H_2 and N_2. The vessel is such that the volume remains effectively constant, whereas the pressure increases to 50 atm. Calculate the % age of NH_3 actually decomposed.*

SOLUTION :

Ammonia decomposes to N_2 and H_2 as follows :

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

$$\underset{\substack{\text{at }27^\circ C\\(15\text{ atm.})}}{NH_3} \longrightarrow \underset{\substack{\text{at }327^\circ C\\(P = ?)}}{NH_3} \qquad \text{V remains constant}$$

First, let us find initial pressure of NH_3 at 327°C.

$\Rightarrow \quad P \propto T$ (V is constant)

$$\Rightarrow \quad \frac{P_1}{T_1} = \frac{P_2}{T_2} \quad \Rightarrow \quad P_2 = \frac{P_1T_2}{T_1} = \frac{15\times600}{300} = 30 \text{ atm}$$

Partial pressure	NH_3	H_2	N_2
Initial	30	0	0
At equilibrium	$30 - x$	$3x/2$	$x/2$

Now final equilibrium pressure = 50 atm

$$\Rightarrow \quad 50 = 30 - x + \frac{3}{2}x + \frac{x}{2} \quad \Rightarrow \quad x = 20 \text{ atm}$$

$$\Rightarrow \quad \%\ NH_3 \text{ decomposed} = \frac{20}{30}\times100 = 66.7\,\%$$

Alternative method :

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

Let α be the degree of dissociation

Moles	NH_3	H_2	N_2
Initial	a	0	0
At equilibrium	$a - a\alpha$	$3a\alpha/2$	$a\alpha/2$

$\Rightarrow$ Total mole $= a + a\alpha$

$$\frac{\text{initial moles}}{\text{final moles}} = \frac{\text{initial pressure}}{\text{final pressure}}$$

$$\frac{a}{a + a\alpha} = \frac{30}{50} \qquad \Rightarrow \quad \alpha = \frac{20}{30}$$

$$\Rightarrow \quad \%\text{ dissociation} = \frac{20}{30}\times100 = 66.7\%$$

Example - 4 *Solid Ammonium carbamate dissociates as : $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$. In a closed vessel solid ammonium carbamate is in equilibrium with its dissociation products. At equilibrium ammonia is added such that the partial pressure of NH_3 at new equilibrium now equals the original total pressure. Calculate the ratio of total pressure at new equilibrium to that of original total pressure. Also find the partial pressure of ammonia gas added.*

SOLUTION :

$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

Let P = original equilibrium pressure,

From the mole ratio of NH_3 and CO_2 at equilibrium, we have ;

$$p_{NH_3} = \frac{2}{3}P \quad \text{and} \quad p_{CO_2} = \frac{P}{3}$$

$$\Rightarrow \quad K_P = \left(p_{NH_3}\right)^2 . p_{CO_2} = \left(\frac{2}{3}P\right)^2 \left(\frac{P}{3}\right) = \frac{4}{27}P^3$$

Now NH_3 is added such that, $p_{NH_3} = P$

Find the pressure of CO_2.

$$\Rightarrow \quad \frac{4}{27}P^3 = P^2 p_{CO_2} \quad \Rightarrow \quad p_{CO_2} = \frac{4}{27}P$$

Total new pressure = $P_{new} = p_{NH_3} + p_{CO_2}$

$$\Rightarrow \quad P_{New} = P + \frac{4}{27}P = \frac{31}{27}P$$

$$\Rightarrow \quad \text{Ratio} = \frac{P_{New}}{P_{original}} = \frac{\frac{31}{27}P}{P} = \frac{31}{27}$$

Let x be the partial pressure of NH_3 added at original equilibrium.

	$NH_2COONH_4(s) \rightleftharpoons$	$2NH_3(g)$	+	$CO_2(g)$
At eq :		$\frac{2}{3}P$		$\frac{1}{3}P$
When NH_3 is added :		$\frac{2}{3}P + x$		$\frac{1}{3}P$
At new eq :		$\frac{2}{3}P + x - 2y$		$\frac{1}{3}P - y$

$$\Rightarrow \quad \frac{2}{3}P + x - 2y = P_{NH_3} = P \text{ and } \frac{1}{3}P - y = P_{CO_2} = \frac{4}{27}P$$

$$\Rightarrow \quad \text{Solve to get : } \quad x = \frac{19}{27}P$$

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.*

SOLUTION :

(a) $X(s) \rightleftharpoons A(g) + C(g)$

At equilibrium, A and C are in equal proportions, so their pressures will be same.

$$p_A = p_C$$

Also $p_A + p_C = 40 \quad \Rightarrow \quad p_A = p_C = 20 \text{ mm}$

$$\Rightarrow \quad K_P = p_A . p_C = 20^2 = 400 \text{ mm}^2$$

Similarly for $Y(s) \rightleftharpoons B(g) + C(g)$,

$$p_B = p_C = 40 \text{ mm } (p_B + p_C = 80)$$

$$\Rightarrow \quad K_P = p_B . p_C = 40^2 = 1600 \text{ mm}^2$$

(b) Now for a mixture of X and Y, we will have to consider both the equilibrium simultaneously.

$$X(s) \rightleftharpoons A(g) + C(g)$$

and $\quad Y(s) \rightleftharpoons B(g) + C(g)$

Let $p_A = a$ mm, $p_B = b$ mm

Note that the pressure of C due to dissociation of X will also be a mm and similarly the pressure of C due to dissociation of Y will also be b mm.

$$\Rightarrow \quad p_C = (a + b) \text{ mm}$$

K_p (for X) = $p_A . p_C = a(a + b) = 400$ ....(i)

K_p (for Y) = $p_B . p_C = b(a + b) = 1600$ ....(ii)

From (i) and (ii), we get :

$$\frac{a}{b} = \frac{1}{4}$$

as volume and temperature are constant, the mole ratio will be same as the pressure ratio.

(c) The total pressure $= P_T = p_A + p_B + p_C$

$$= a + b + (a + b) = 2\,(a + b)$$

Adding (i) and (ii),

$$a + b = \sqrt{K_{PX} + K_{PY}} = \sqrt{2000} = 20\sqrt{5}\text{ mm}$$

$\Rightarrow$ Total pressure $= 2\,(a + b) = 89.44$ mm

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.*

SOLUTION :

$$P(g) + 2Q(g) \rightleftharpoons R(g)$$

at equilibrium, [P] = 3 M, [Q] = 4 M and let [R] = x M,

$$K_C = \frac{[R]}{[P][Q]^2} = \frac{x}{3 \times 4^2} = \frac{x}{48} \quad \text{....(i)}$$

Now the volume is doubled, hence the concentrations are halved and a new equilibrium will be re-established with same value of K_C. Calculate Q and determine the direction of equilibrium.

$$Q = \frac{[R]}{[P][Q]^2} = \frac{x/2}{(3/2)(4/2)^2} = \frac{x}{12}$$

$\Rightarrow$ $Q > K_C$ Hence the system will predominately move in backward direction so as to achieve new equilibrium state.

Let y M be the decrease in concentration of R.

Concentrations	P	Q	R
Initially	1.5	2	$x/2$
At new equilibrium	1.5 + y	2 + 2y	$x/2 - y$

Given : [Q] = 3 M at new equilibrium

$\Rightarrow$ $2 + 2y = 3$ $\Rightarrow$ $y = 0.5$ M

$\Rightarrow$ At new equilibrium, [P] = 1.5 + 0.5 = 2 M;

[Q] = 3 M (*given*) ; [R] = $x/2 - 0.5$ M

$$\Rightarrow \quad Q = \frac{[R]}{[P][Q]^2} = \frac{(x/2 - 0.5)}{(2)(3)^2}$$

Equating this value of K_C with (i)

$$\Rightarrow \quad \frac{(x/2 - 0.5)}{(2)(3)^2} = \frac{x}{48} \quad \Rightarrow \quad x = 4\text{ M}$$

Hence [R] = 4 M and

at new equilibrium [R] = $x/2 - 0.5 = 1.5$ M

$$\text{and } K_C = \frac{x}{48} = \frac{1}{12}$$

Example - 7 *The degree of dissociation of HI at a particular temperature is 0.8. Find the volume of 1.6 M sodium thiosulphate solution required to react completely with the iodine present at equilibrium in acidic condition, when 0.1 mol each of H_2 and I_2 are heated at 440 K in a closed vessel of capacity 2.0 L.*

SOLUTION :

First find the value of K_C for dissociation of HI from its degree of dissociation.

$$2HI\,(g) \rightleftharpoons H_2\,(g) + I_2(g)$$

(degree of dissociation is 0.8)

Concentrations	HI	H_2	I_2
Initially	a	0	0
At new equilibrium	a – aα	aα/2	aα/2

$$K_C = \frac{[H_2][I_2]}{[HI]^2} = \frac{(a\alpha/2)(a\alpha/2)}{(a-a\alpha)^2} = \frac{\alpha^2}{4(1-\alpha)^2}$$

Here $\alpha = 0.8 \Rightarrow K_C = \dfrac{0.8^2}{4(1-0.8)^2} = 4$

Now we have to start with 0.1 mol each of H_2 and I_2 and the following equilibrium will be established.

$$H_2 + I_2 \rightleftharpoons 2HI \text{ with } K_C = 1/4$$

Moles	H_2	I_2	HI
Initially	0.1	0.1	0
At new equilibrium	$0.1-x$	$0.1-x$	$2x$

$$\Rightarrow \quad K_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(2x/V)^2}{\dfrac{(0.1-x)}{V}\dfrac{(0.1-x)}{V}} = \frac{1}{4}$$

$$\Rightarrow \quad x = 0.02$$

Now find the moles of I_2 left un-reacted at equilibrium.

$$n(I_2) = 0.1 - 0.02 = 0.08$$

I_2 reacts with sodium thiosulphate ($Na_2S_2O_3$) as follows :

$$2Na_2S_2O_3 + I_2 \rightleftharpoons Na_2S_4O_6 + 2NaI$$

Applying the mole concept, we have,

2 moles of $Na_2S_2O_3 \equiv 1$ mole of I_2

$\Rightarrow$ 0.08 moles of $I_2 \equiv 2 \times 0.08$

$= 0.16$ moles of $Na_2S_2O_3$

$\Rightarrow$ moles $= MV_L$

(M = molarity, V_L = volume in litres)

$\Rightarrow$ $0.16 = 1.6\,V_L$

$\Rightarrow$ $V_L = 0.1\text{ L} = 100\text{ mL}$

Example - 8 *At 25°C and 1 atm, N_2O_4 dissociates by the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$*

If it is 35% dissociated at given condition, find the volume of above mixture will diffuse if 20 ml of pure O_2 diffuses in 10 minutes at same temperature and pressure.

SOLUTION :

For equilibrium system, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$,

Moles	N_2O_4	NO_2
Initial	a	0
At equilibrium	$a - a\alpha$	$2a\alpha$

$\Rightarrow$ Total moles at equilibrium $= a + a\alpha$

$$p_{N_2O_4} = \frac{a-a\alpha}{a+a\alpha}P \quad \text{and} \quad p_{NO_2} = \frac{2a\alpha}{a+a\alpha}P$$

Here $P = 1.0$ atm and $K_P = \dfrac{p^2_{NO_2}}{p_{N_2O_4}} = \dfrac{4\alpha^2 P}{1-\alpha^2}$ $[\alpha = 0.35]$

$$\Rightarrow \quad K_P = \frac{4\times(0.35)^2}{1-(0.35)^2}\times 1 = 0.56\text{ atm}$$

Using $\dfrac{a+a\alpha}{a} = \dfrac{M_{mix,\,i}}{M_{mix,\,f}} \equiv \dfrac{M_{N_2O_4}}{M_{mix,\,f}}$

$$\Rightarrow \quad 1+0.35 = \frac{92}{M_{mix,\,f}}$$

$$\therefore \quad M_{mix,\,f} = \frac{92}{1.35} = 68.15$$

Let V(ml) volume of mixture diffused in.

From Graham's law of diffusion.

$$\frac{r_{O_2}}{r_{mix,\,f}} = \sqrt{\frac{M_{mix,\,f}}{M_{O_2}}}$$

$$\frac{20/10}{V/10} = \sqrt{\frac{68.15}{32}} \Rightarrow V = 13.70\text{ ml}$$

Example - 9 *For the reaction $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$;*

Show that the degree of dissociation of NH_3 is given as $\alpha = \left[1 + \dfrac{3\sqrt{3}}{4}\dfrac{P}{K_P}\right]^{-1/2}$ *where P is the equilibrium pressure and α is the degree of dissociation. If K_P of the above reaction is 82.1 atm at 727°C, determine the value of K_c.*

SOLUTION :

Let α be the degree of dissociation of $NH_3(g)$.

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$

Initial moles	1	0	0
At equilibrium	$1-\alpha$	$\alpha/2$	$3\alpha/2$

Total number of moles at equilibrium = $1 + \alpha$

Now,

$$p_{NH_3} = \frac{1-\alpha}{1+\alpha}P,\ p_{N_2} = \frac{\alpha/2}{1+\alpha}P \quad \text{and} \quad p_{H_2} = \frac{3\alpha/2}{1+\alpha}P$$

$$K_P = \frac{(p_{N_2})^{1/2}(p_{H_2})^{3/2}}{p_{NH_3}}$$

$$\Rightarrow \frac{\left[\frac{\alpha}{2(1+\alpha)}P\right]^{1/2}\left[\frac{3\alpha}{2(1+\alpha)}P\right]^{3/2}}{\frac{1-\alpha}{1+\alpha}\times P} = \left[\frac{3\sqrt{3}P}{4}\right]\left[\frac{\alpha^2}{1-\alpha^2}\right]$$

$$\Rightarrow \frac{1-\alpha^2}{\alpha^2} = \frac{3\sqrt{3}}{4}\frac{P}{K_P}$$

$$\Rightarrow \frac{1}{\alpha^2} = \left[1 + \frac{3\sqrt{3}}{4}\frac{P}{K_P}\right] \text{ or } \alpha = \left[1 + \frac{3\sqrt{3}}{4}\frac{P}{K_P}\right]^{-1/2}$$

Δn_g, change in number of the moles of the given reaction = +1

$$K_P = K_C(RT)^{\Delta n_g} \Rightarrow K_C = K_P(RT)^{-\Delta n_g}$$

$$\Rightarrow K_C = 82.1 \times [0.0821 \times 1000]^{-1} = 1.0 \text{ mol/L}$$

ANSWERS TO IN-CHAPTER EXERCISES

A	**1.** Backward	**2.** Forward	**4.** $K_p = 9 \times 10^{-10}$		**5.** 30	**6.** $\alpha = 0.02$ %	
	7. $\alpha = 0.41$	**8.** C	**9.** D	**10.** B	**11.** B	**12.** C	**13.** A
	14. C	**15.** D	**16.** AB	**17.** ABCD	**18.** A	**19.** D	**20.** D
	21. ABC	**22.** C					
B	**1.** 2.5, 0.4	**2.** 29.07 %	**3.** B	**4.** C	**5.** D	**6.** A	**7.** C
	8. D	**9.** C	**10.** C	**11.** C	**12.** ACD	**13.** A	**14.** B
	15. D	**16.** B					