Chapter 15: Chemical Equilibrium

Q1:-

Sol:- $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at T = 298^0C Keq = 5.7×10^{-9}

We know,

$$Keq = \frac{[NO_2]^2}{[N_2O_4]} = 5.7\times10^{-9}$$

$$[NO_2]^2 = 5.7\times10^{-9}[N_2O_4]$$

This equation directly implies that concentration of NO_2 is about 10^{-4} times than that of N_2O_4. So concentration of NO_2 at equilibrium will be low & Conc-^{n} of N_2O_4 will be higher.

Note:- If

Keq-$^b >> 1 \Rightarrow$ Products are of higher concentration

Keq-$^b << 1 \Rightarrow$ Reactants are of higher concentration

This is the case in above problem

Caution:- Never apply the above rule for $Kp > 1$ or < 1. It can be other way round for Kp or Kc little larger or smaller than 1.

Q2:-

Sol:- $A(g) \rightleftharpoons B(g)$, Keg-^{b} = 1.1

For this keq-^{b} (just greater than 1), we have to actually see by calculations.

$$Keq,^b = 1.1 = \frac{[B]}{[A]} \Rightarrow [B] = 1.1[A].$$

∴ Concentration of B is greater than that of [A].

Q3:-

Sol:- $2NO_2(g) \rightleftharpoons N_2O_4(g)$, keq-^{b} = 1

$$Keq\text{-}^b = \frac{[N_2O_4]}{[NO_2]^2} = 1$$

It volume is halfed, concentration in mole / ,it because deouble

$$Keq\text{-}^b \text{ New} = \frac{[N_2O_4]_{new}}{[NO_2]_{new}^2} = \frac{[N_2O_4]/2}{\{[NO_2]/2\}^2} = 2$$

If reaction is not adjusted according to le-chaterler principle.

However we know that like equilibrium will shift in the direction in which no. of moles decreases by decrease the volume in such a way that equilibrium constant will remain same.

Note:- Equilibrium constant will change only by changing temperature.

Q4:-

Sol:- $I_2(g) \rightleftharpoons 2I(g)$

In forward reac-^{n}, bond in I_2 molecule dissociated so, forward reaction will be endothermic.

If Temp. is increased, reaction will try to decrease it & to decrease the temperature, it will consume heat & so moves in endothermic dir-^{n} . i.e., after increasing temp we have more

$I_2(g)$ dissociated to I(g). So equilibrium constant will increase

Q5:-

Sol:- $NOBr(g) \rightleftharpoons NO(g) + \frac{1}{2}Br_2(g)$, kp = 0.15 atm at 90^0C

Initial 0.5 atm 0.4 atm 0.2 atm

$$Q = \frac{P_{NO} \times P_{Br_2}^{1/2}}{P_{NOBr}} = \frac{0.4 \times (0.2)^{1/2}}{0.5} = \frac{4}{5}(0.2)^{1/2} = 0.357 atm > K_p$$

So, Q has to decrease & hence product will decrease. In other words, NO & Br_2 will consume & NOBr will produce.

Q6:-

Sol:- $\frac{1}{2}N_2 + \frac{3}{2}H_2 \rightleftharpoons NH_3$; At $P_{total} = 20$ atm

A/q, at eq^{-b} x 3x y ; $T = 427^0C = 700$ K

Also $\frac{y}{x+3x+y} \times 100 = 16$ => $\frac{y}{4x+y} = \frac{16}{100}$

$100y = 64x + 16y \Rightarrow 84y = 64x$

$$y = \frac{64}{84}x = \frac{16}{21}x$$

$$PNH_3 = \frac{x}{\frac{100}{21}x} \times 20 \times P\,total = \frac{\frac{16}{21}x}{4x + \frac{16}{21}x} \times 20 = \frac{16}{100} \times 20 = 3.2\,atm$$

$$PN_2 = \frac{x}{\frac{100}{21}x} \times 20 = \frac{21}{100} \times 20 = 4.2\,atm$$

$$PH_2 = \frac{3x}{\frac{100}{21}x} \times 20 = \frac{63}{100} \times 20 = 12.6\ atm$$

$$Kp = \frac{PNH_3}{Ph_2^{3/2} . PN_2^{1/2}} = \frac{3.2}{(4.2)^{1/2}(12.6)^{3/1}} = 3.49 \times 10^{-2}\ atm^{-1}$$

$$Kp = Kc\ (RT)^{\Delta n}$$

$$3.49 \times 10^{-2} = Kc\ (0.0821 \times 700)^{-1}$$

$$Kp = 3.49 \times 10^{-2} \times 8.21 \times 7 = 2\ lit / mole.$$

Q7:-

Ans:- $A_2 + B_2 \rightleftharpoons 2AB$, $Keq^{-b} = K$

$\frac{1}{2}A_2 + \frac{1}{2}B_2 \rightleftharpoons AB$, $keq^{-b}\ (K)^{1/2}$

$AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$; $keq^{-b''} = \frac{1}{(K)^{1/2}} = (K)^{-1/2}$ => $\left(keq^{-b''} \neq \frac{1}{K}\right)$ So False

Q8:- $PCl_5(g) \longleftrightarrow PCl_3(g) + Cl_2(g)$

Initial $\frac{3}{100}M$ $\left(+\frac{1}{100}\frac{\text{moles}}{\text{lit}}\text{ of } N_2\right)$

at eq-^{b} $(0.03 - 0.03\alpha)$ (0.03α) (0.03α) at T = 500 K

$\therefore$ Total $\frac{\text{moles}}{\text{lit}}$ at eq $-^b$ $= 0.03 - 0.03\alpha + 0.03\alpha + 0.03\alpha + 0.01$

$= 0.04 + 0.03\alpha$

$\therefore$ Total moles = 4 + 3x

$\therefore P_{PCl_3} = \frac{3\alpha}{4+3\alpha} \times 2.05\,\text{atm}$

$Pcl_2(g) = \frac{3\alpha}{4+3\alpha} \times 2.05\,\text{atm}$

$P_{PCl_5}(g) = \frac{3-3\alpha}{4+3\alpha} \times 2.05\,\text{atm}$

From PV = nRT

$2.05 \times 100 = (4+32) \times 0.0821 \times 500$

$\alpha = 0.33$

$$Kp = \frac{Ppcl_3.Pcl_2}{Ppcl_5} = \frac{\frac{0.99}{4.99} \times 2.05 \times \frac{0.99}{4.99} \times 2.05}{\frac{2.01}{4.91} \times 2.05} = 0.205 \text{ atm.}$$

Q9:-

Sol: $2HI(g) \longleftrightarrow H_2(g) + I_2(g)$

Initally. $\frac{20}{128}$ M

At eq-^{b} $\frac{20}{128} - 2\alpha$ M αM αM

Given, 20 gm of HI given at T = 600 K and 1 lit press. At const temperature. & pressure, volume % = no. of moles %

$$Keq-^b = \frac{[H_2][I_2]}{[HI]^2} = \frac{\alpha^2}{\left(\frac{20}{128} - 2\alpha\right)^2} = 0.0559$$

$$\Rightarrow \frac{\alpha}{\frac{20}{128} - 2\alpha} = \sqrt{0.0559}$$

$$\frac{\alpha}{\frac{20}{128} - 2\alpha} = 0.236 \quad \Rightarrow \alpha = \frac{0.037}{1.472} = 0.025$$

$$\text{Volume \% of } H_2 = \frac{\alpha}{\frac{20}{128}} \times 100 = \frac{0.025}{20} \times 128 \times 100 = \frac{2.5 \times 128}{20} = 16\%$$

$$\text{Volume \% of } I_2 = \frac{\alpha}{20/128} \times 100 = 16\%$$

$$\text{Volume \% of HI} = 100 - (16+16) = 68\%$$

Q10:-

Sol:- $H_2 + I_2 \rightleftharpoons 2HI$

	H_2	I_2	$2HI$	
Initially	25 ml	18 ml		T= 456^0C
at eq-^{b}	25-x	18 – x	2x	

A/q, $2x = 30.8$, $x = 15.4$ ml

At const temp & press, volume α no. of moles

$$K_C = \frac{nHI^2}{nH_2.nI_2} = \frac{(30.8)^2}{9.6\times2.6} = 38$$ (Since $\Delta n = 0$ we can use no. of moles in Kc also).

$2HI \rightleftharpoons H_2 + I_2$; Keq-$^n = \frac{1}{38} = 0.0263$ at T = 456

$2HI$	H_2	I_2
1	0	0
$1-\alpha$	$\alpha/2$	$\alpha/2$

$$\text{Keq-}^b = \frac{(\alpha/2)(\alpha/2)}{1-\alpha} = \frac{\alpha^2}{4(1-\alpha)}$$

$$0.0263 = \frac{\alpha^2}{4(1-\alpha)}$$

$$\alpha^2 + 0.105\alpha - 0.105 = 0$$

$$\alpha = \frac{-0.105+\sqrt{(0.105)^2+4\times0.1105}}{2} = \frac{-0.105+0.653}{2} = 0.2746$$

$\therefore$ Percentage dissociation = $0.2746\times100 = 27.46\%$

Q11:- $2HI \rightleftharpoons H_2 + I_2$ (Give percentage dissociation = 21.98%)

	$2HI$	H_2	I_2
Initially	1	0	0
at eq-^{b}	1-0.2198	$\frac{0.2198}{2}$	$\frac{0.2198}{2}$

$$\text{Keq-}^b = \frac{\left(\frac{0.2198}{1}\right)\left(\frac{0.2198}{2}\right)}{(1-0.2198)^2} = 0.0198$$

$\therefore$ Keq-^{b} for $H_2 + I_2 \rightleftharpoons 2HI(g) = \frac{1}{0.0198} = 50.398$

the data (1^{st}) given as follows

	$H_2(g)$	$I_2(g)$	$2HI(g)$
Initial	8.10	2.94	0
At eq-^{n}	8.10-x	2.94-x	2x

Given: $2x = 5.65$ => $X = 2.825$

$$Keq\text{-}^{b} = \frac{[HI]^2}{[H_2][I_2]} = \frac{(5-65)^2}{(8.10-2.825)(2.94-2.725)} = = 52.63$$

(Note:- even volume can be used in place of [ ], because $\Delta n = 0$)

Since Keq-^{b} from 1st data is different from Keq-^{b} for 2nd date. So 1st data is not according to law of mass action.

2nd data

$$H_2 + I_2 \longleftrightarrow 2HI$$

Initially: 8.07 3.27

At eq-^{b}: 8.07 – x 9.27 –x 2x

Given 2x = 13.46 $\Rightarrow x = 6.73$

Doesn't match again so the data given are not satisfied by law of mass action.

3rd data

$$H_2 + I_2 \longleftrightarrow 2HI$$

Initially 7.89 33.10 0

At eq-^{b} 7.89–x 33.10–x 2x

A/q, 2x = 15.41 $\Rightarrow$x= 7.705

$$Keq-^{b} = \frac{(15.41)^2}{(7.89-7.705)(33.10-7.705)} = 50.545$$

Matches with keq-^{b} of the reaction, so this is according to the law of mass action.

Q12:

Sol:- $2HI \longleftrightarrow H_2 + I_2$

Also, $I_2 + 2Na_2S_2O_3 \longrightarrow Na_2S_4O_6 + 2NaI$

Mole of I_2 $\equiv$ 2 mole of $Na_2S_2O_3$

2 mole of I_2 = 1 mole of $Na_2S_2O_3$

1 mole of I_2 = $\frac{1}{2}$(mole of $Na_2S_2O_3$)

$$2HI(g) \longleftrightarrow H_2(g) + I_2(g)$$

Initially: 0.28 gm 0 0 (3rd data should be taken, because for eq-^{n} to achie

$\frac{0.38}{128}$ mole 0 0 sufficient time is required)

At eq-^{b}: $\frac{0.28}{128} - 2\alpha$ α α

$\therefore$ Moles of I_2 produced = $\alpha = \frac{1}{2}$(moles of hypo sol–^{n})

$$\alpha = \frac{1}{2} \times 0.015 \times \frac{28.68}{1000} = 0.215 \times 10^{-3}$$

$\therefore$ eq-^{b} moles of HI = 1.757×10^{-3}

eq-^{b} moles of H_2 = 0.215×10^{-3}

- -- -- --- --- $I_2 = 0.215 \times 10^{-3}$

$$\therefore Kc = \frac{[H_2][I_2]}{[HI]_2} = \frac{(0.215\times10^{-3})^{2}}{(1.757\times10^{-3})^{2}} = 0.01496 = 1.496\times10^{-2}$$

[Since $\Delta n = 0$, we can take no. of mole in place of morality also]

Q13:-

Sol:- $PCl_5(g) \longleftrightarrow PCl_3(g) + Cl_2(g)$

Given amount : 5 g

Moles ; $\frac{5}{208.5}$ moles

Molarity : $\frac{5}{208.5\times1.9} = 0.01262$ M

At eq-^{b} : $0.01262 - 0.01262\alpha$ 0.01262α 0.1262α

α = degree of dissociation

Total no. of $\frac{\text{moles}}{\text{lit}} = 0.01262 - 0.01262\alpha + 0.01262\alpha + 0.01262\alpha$

$= 0.01262\,(1+\alpha)$

From PV = nRT => $P = \frac{n}{V}RT = MRT$

(M = Molarity of the solution)

$1 = 0.01262\,(1+\alpha)\times 0.0821\times 523$

$1 = 0.542\,(1+\alpha)$ => $\alpha = 0.845$

$\therefore$ % dissociation $= \alpha\times100 = 84.5\%$

$$\therefore Kc = \frac{0.01262\alpha\times0.012662\alpha}{0.01262(1-\alpha)} = \frac{0.01262\alpha2}{1-\alpha} = \frac{0.01262\times0.845^2}{0.155} = 0.0582$$

$Kp = Kc(RT)^{\Delta n}$

$= 0.0582(0.821\times523)^{+1}(\Delta n = 2-1) = 1)$

$= 2.53$

Q14:-

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

Initially: 15 atm 0 0 (at T = 300 K)

31 atm 0 0 (at T = 620 K) $[P_{T2} = P_{T1}\frac{T_2}{T_1}]$

At Eqb: $31 - 2p$ p 3p

A/q, Total pressure = 31 – 2P + P + 3P = 31 + 2P = 50

$\therefore$ 2P = 19 atm

% degree of dissociation $= \frac{19}{31}\times100 = 61.31\%$

Q15:-

Ans:- $A + 2B \longleftrightarrow 2C + D$

Initially X 1.5 X (A/q : conc-^{n} of B = 1.5 conc-^{n} of A)

At eq-^{b} x– y 1.5x – 2y 2y y

A/q, $x - y = y \Rightarrow y = x/2$

$$\therefore K_{eq^{-b}} = \frac{(2y)^2.y}{(x-y)(1.5x-2y)^2} = \frac{\left(2.x/2\right)^2.x/2}{\left(x-\frac{x}{2}\right)\left(1.5x-2\frac{x}{2}\right)^2} = \frac{x^{3/2}}{\frac{x}{2}.\frac{x^2}{4}} = 8/4 = 4$$ **Ans**

Q16:-

Ans:- $SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3$

Initially: 2 1 0

At eq^{-b} $2-x$ $1-x/2$ x

Total moles $= 2 - x + 1 - x/2 + x = 3 - x/2$

A/q, $\frac{x}{3-x/2}\times 100 = 87$ (volume ratio = molar ratio)

$$\frac{2x}{6-x} = 0.87 \Rightarrow 2x = 5.22 - 0.87\,x \Rightarrow x = \frac{5.22}{2.87} = 1.82$$

Now total pressure becomes = (2.99/3)atm

$$\therefore \text{Press of } SO_2 = \frac{2-x}{3-x/2}\times\frac{2.09}{3} = \frac{0.18}{3-0.91}\times\frac{2.09}{3} = 0.086\text{ atm}\times\frac{2.09}{3}$$

$$\text{Press of } O_2 = \frac{1-x/2}{3-x/2}\times\frac{2.09}{3}\frac{1-0.91}{3-0.91}\times\frac{1.09}{3} = \frac{0.09}{2.09}\times\frac{2.09}{3} = 0.0431\text{ atm}\times\frac{2.09}{3}$$

$$P_{SO_3} = \frac{x}{3-x/2}\times\frac{2.09}{3} = \frac{1.82}{2.09}\times\frac{2.09}{3} = 0.871\text{atm}\times\frac{2.09}{3}$$

$$\therefore K_p = \frac{P_{SO_3}}{P_{SO_2}.P_{O_2}^{1/2}} = \frac{0.871\times\frac{2.09}{3}}{\frac{2.09}{3}\times 0.86\times(0.0431)^{1/2}\times\left(\frac{2.09}{3}\right)^{1/2}}$$

$$= \frac{0.871}{0.086\times 0.2076\times(0.676)^{1/2}} = \frac{0.871}{0.01785\times 0.834} = 58.60$$ **Ans**

Q17:-

Ans:- $2Fe^{3+}(aqs) + Hg_2^{2+}(aqs) \rightleftharpoons 2Fe^{2+}(aqs) + 2Hg^{2+}(aqs)$

$K_c = 9.14\times 10^{-6}$ at 25^0C

Initial $conc^{-n}$

$[Fe^{3+}]_0 = 0.5$ M & $[Hg_2^{2+}]_0 = 0.5$ M

$[Fe^{2+}]_0 = 0.03$ M & $[Hg^{2+}]_0 = 0.03$ M

$$Q=\frac{[Fe^{2+}]^2[Hg^{2+}]^2}{[Fe^{3+}]^2[Hg_2{}^{2+}]}=\frac{(0.03)^2\times(0.03)^2}{(0.5)^2\times(0.5)}=\frac{9\times10^{-4}\times9\times10^{-4}}{25\times10^{-2}\times15\times10^{-2}}$$

$$=\frac{9\times9\times10^{-5}}{25\times05}=6.486\times10^{-7}<Kc.$$

∴ Reaction will move in forward and direction to reach equilibrium.

	$2Fe^{3+}(aqs)$	+ $Hg_2{}^{2+}(aqs)$	$\longleftrightarrow$ $2Fe^{2+}(aqs)$	+ $2Hg^{2}(aqs)$
Initially	0.5M	0. M	0.03 M	0.03 M
At eq-^{b}	0.5 –x	0.5 - $^x/_2$	0.03 + x	0.03 + x

$$\therefore Kc=\frac{(0.03+x)^2(0.03+x)^2}{(0.5-x)^2\left(0.5-\frac{x}{2}\right)}=\frac{(0.03+x)^4}{(0.5-x)^2\left(0.5-^x/_2\right)}$$

Calculating for x = 0.003 M.

$[Fe^{3+}] = 0.5 - x = 0.5 - 0.003 = 0.497$ M

$[Hg_2{}^{2+}] = 0.5 - {^x/_2} = 0.5-\frac{0.003}{2}=0.499$M

$[Hg^{2+}] = 0.03 + x = 0.033 = 3.3\times10^{-2}$ M

$[Fe^{2+}] = 0.03 + x = 0.033 = 3.3\times10^{-2}$ M

Q18:-

Sol:- $2NO(g)+Br_2(g)\longleftrightarrow 2NOBr(g)$ at T = 1000 K 0.1 mole of B_2 No & BOB_2

$Kc = 1.32\times10^{-2}$

$$\therefore\ Q=\frac{[NOBr]^2}{[NO]^2[Br_2]}=\frac{(0.01)^2}{(0.1)^2\times(0.1)}=\frac{1\times10^{-4}}{1\times10^{-3}}$$

$Q = 10^{-1} > Kc$

∴ Reaction will have in backward direction (reverse dir-^{n})

	$2NO$	+ Br_2	$\longleftrightarrow$ $2NOBr$
Initially:	0.1	0.1	0.1
At eq-^{b} :	0.1+ x	0.1+$^x/_2$	0.01-x

$$Kc=1.32\times10^{-2}=\frac{(0.01-x)^2}{(0.1+x)^2(0.1+^x/_2)}$$

Neglecting x w.r.t. 0.1 we have, $1.32\times10^{-2}=\frac{(0.01-x)^2}{(0.1)^2\times0.1}$

$(0.01-x)^2 = 1.32\times10^{-5}$ => $0.01- X=\sqrt{13.2}\times10^{-3}=3.63\times10^{-3}$

$X = 6.37\times10^{-3}$

Moles of NOBr = 0.01 –x = 3.63 x 10^{-3}

∴ PV = nRT

$P\times1 = 3.63\times10^{-3}\times0.0821\times1000$

$P_{NOBr} = 3.63\times0.0821 = 0.30$ atm **Ans**

Q19:-

Sol:- Press ratio = mole ratio

$$\frac{PN_2}{PO_2} = \frac{79}{21} \text{(at const Volume \& Temp)}$$

	N_2	+ O_2 $\rightleftharpoons$	$2NO$
Initially	79x	21x	0
At eq-^{b}	79x– Px	21x–Px	2Px

Total pressure = 79 x + 21 x – 2px + 2Px = 100x

$$A/q, \frac{PNO}{Ptotal} \times 100 = 1.8$$

$$\frac{2Px}{100x} \times 100 = 1.8 \quad => 2P = 1.8$$

$$\therefore Kp = \frac{(2Px)^2}{(79x - Px)(21x - px)} = \frac{4P^2x^2}{(79 - P)(21 - P)x^2} = \frac{(1.8)^2}{(79 - 0.9)(21 - 0.9)} = 2.1 \times 10^{-3}$$

Ans

Q20:-

Sol:- $CO\ (g) + Cl_2\ (g) \rightleftharpoons COCl_2\ (g)$

	CO (g)	Cl₂ (g)	COCl₂ (g)
Initially:	342 mm	352 mm	0
At eq-^{b} :	342 – P	352-P	P

A.q, at eq-^{b}, To pressure = 440 mm

$$694 - P + 352 - P + P = 440$$

$$694 + P = 440 \quad => P = 694 - 440 = 294 \text{ mm.}$$

$$Kp = \frac{PCOCl_2}{PCO.PCl_2} = \frac{\frac{294}{760}}{\frac{48}{760} \times \frac{58}{760}} = \frac{294 \times 760}{58 \times 48} = 80.\ 26$$

$$COCl_2 \rightleftharpoons CO + Cl_2 \ ; \ Kp^1 = \frac{1}{Kp} = \frac{1}{80.26} = 0.012$$

	$COCl_2$	CO	Cl_2
Initially	1 atm		
At eq-^{b}	1 – P	P	P

$$Kp^1 = \frac{P^2}{1 - P}$$

$$=> 0.012 = \frac{P^2}{1 - P}$$

$$P^2 + 0.012\ P - 012 = 0$$

$$P = \frac{-0.012 + \sqrt{1.44 \times 10^{-4} + 4 \times 0.012}}{2} = 0.1037$$

$$\text{Percentage dissociation} = \frac{P}{1} \times 100 = 10.37\%$$

Ans

Q21:-

Sol:- $\Delta H = \Delta E + \Delta nRT$

$\Delta H - \Delta E = \Delta nRT$

-1190 cal = $\Delta n \times 2 \times 298$ => $\Delta n = \dfrac{-1190}{2 \times 298} = -2$

Also, $Kp = Kc\,(RT)^{\Delta n}$

$$\frac{Kp}{Kc} = (RT)^{\Delta n} = (0.0821 \times 298)^{-2} = 1.67 \times 10^{-3}$$ **Ans**

Q22:-

Sol:- $2H_2O\,(g) + 2Cl_2\,(g) \rightleftharpoons 4HCl\,(g) + O_2(g)$.

$Kp = 0.035$

$Kp = Kc\,(RT)^{\Delta n}$

$0.035 = Kc\,(0.0821 \times 673)^{+1}$ [$\Delta n = (4+1)-(2+2) = 1$]

$Kc = 0.035/\,0.0821 \times 673 = 6.334 \times 10^{-4}$ **Ans**

Q23:-

Sol:- $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3\,COO\,C_2H_5 + H_2O$

Initially	1	1	0	0
At eq-^{b}	1-x	1-x	x	x

Wt. of water formed at eq-^{b} = $x \times 18 = 12$ => $x = \frac{2}{3}$

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

If 2 moles of C_2H_5OH is added then.

$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COO_2H_5 + H_2O$

Initially	$\frac{1}{3}$	$\frac{1}{3}+2$	$\frac{2}{3}$	$\frac{2}{3}$
At new eq-^{b}	$\frac{1}{3}-y$	$\frac{7}{3}-y$	$\frac{2}{3}+y$	$\frac{2}{3}+y$

$$Kc = \frac{\left(\frac{2}{3}+y\right)^2}{\left(\frac{1}{3}-y\right)\left(\frac{7}{3}-y\right)} = 4 \quad \Rightarrow \frac{(2+3y)^2}{(1-3y)(7-3y)} = 4$$

$4 + 9y^2 + 12y = 4\,\{7\text{-}24\,y + 9y^2\}$

$27\,y^2 = 108\,y + 24 = 0$

$9y^2 - 36\,y + 8 = 0$

$$y = \frac{+36 \pm \sqrt{(36)^2 - 4 \times 9 \times 8}}{2 \times 9} = \frac{36 \pm 31.75}{18} = 33.87\,(\text{NOT possible})$$

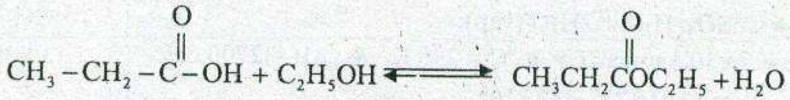
$= 0.236$ possible

because y has to be less than 1/3.

$\therefore$ Weight of $CH_3COOC_2H_5$ produced = $\left(0.236 \times \frac{2}{3}\right) \times M = 79\,.2g$ **Ans**

Q24:-

Ans:-



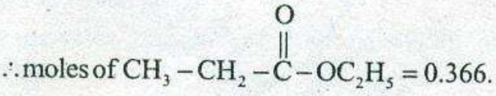
$$CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OH + C_2H_5OH \rightleftharpoons CH_3CH_2\overset{\overset{O}{\|}}{C}OC_2H_5 + H_2O$$

	Propanoic acid	ethyl alcohol	ethyl propanate	
Initially	0.5 mole	0.5 mole	0	0
At eq-^{b}	0.5 –x	0.5 p – x	x	x

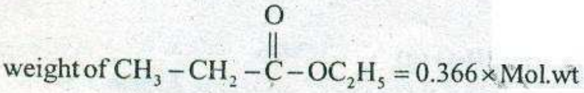
$$Kc = \frac{x^2}{(0.5-x)^2} = 7.36 \quad => \quad \frac{x}{0.5-x} = 2.71$$

$$X = 1.356 - 2.71\ x$$

$$x = \frac{1.356}{3.71} = 0.366$$



$$\therefore \text{moles of } CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 = 0.366.$$



$$\text{weight of } CH_3-CH_2-\overset{\overset{O}{\|}}{C}-OC_2H_5 = 0.366 \times \text{Mol.wt}$$

$$\doteq 37.29\ \text{gm}$$ **Ans**

Q25:-

Ans:- $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3-COOC_2H_5 + H_2O$

Initially	0.1 mole	0.1 mole		
	0.1-x	0.1-x	x	x

$$Kc = \frac{x^2}{(0.1-x)^2} \text{ - - - - - - - - (1)}$$

A/q, $CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$

For complete neutralisation.

mole of CH_3COOH = mole of NaOH

$$= 100 \times 10^{-3} \times 0.85 \times 1$$

$$0.1 - x = 0.085$$

$$X = 0.1 - 0.085 = 0.015$$

Putting the volume, we have

$$Kc = \frac{x^2}{(0.1-x)^2} = \frac{(0.015)^2}{(0.085)^2} = \frac{15^2}{85^2} = 0.31$$ **Ans**

Q26:-

Sol:- $H_2(g) + I_2(s) \rightleftharpoons 2HI\ (g)$, $Kp = 871$ at 25^0C

$$Kp = \frac{PHI^2}{PI_2(3).PH_2(9)} = \frac{PHI^2}{4\times10^{-4}\times PH_2} = 871$$

$$Kp^1 = \frac{PHI^2}{PH_2} = 871\times4\times10^{-4} = 0.3484\,\text{atm}$$

Ans

Q27:-

Sol:- $CuSO_4.\ 3H_2O \rightleftharpoons CuSO_4.\ H_2O + 2H_2O$ (vap)

dissociation pressure = 7×10^{-3} atm at $T = 25^0C = 298$ K & $\Delta H = 2700$ cal

$\therefore$ Kp at 298 K = $(P_{H2O})^2 = (7\times10^{-3})^2 = 49\times10^{6}$.

Let Kp' at $T = 127^0C = 227 + 273 = 400$ K

$$\therefore \log\left(\frac{Kp}{Kp'}\right) = \frac{-\Delta H}{2.303R}\left(\frac{1}{298}-\frac{1}{400}\right) = \frac{-2700}{2.303\times2}\left(\frac{1}{298}-\frac{1}{400}\right)$$

$$= \frac{-1350}{2.303}\left(\frac{102}{400\times298}\right) = -0.5016$$

Taking antilog and putting the value of Kp

$Kp' = 1.55\times10^{-4}$

$\therefore$ $P'\ H_2O = 1.55\times10^{-4}$

$PH_2O = 1.2467\times10^{-2}$ atm **Ans**

Q28:-

Sol:- $CuSO_4\ .5H_2O \rightleftharpoons CuSO_4\ .3H_2O(s) + 2H_2O\ (g)$

Kp = 1.086×10^{-4} atm^2 at 25^0C

Vapour pressure of water at 25^0C = 23.8 mm of Hg

$Kp = PH_2O^2 = 1.086\times10^{-4}$ am^2

$PH_2O = 1.04$ am^2 = 7.92 mm of Hg

$\therefore$ $PCuSO_4.\ 5H_2O$ = 7.92 mm of Hg.

If press of substance > press. of surrounding then water will be released by the substance & is known as efflorescent substance & the phenomena is called efflorescence.

$\therefore$ efflorescence occur if pressure of air is less than 7.92 mm of Hg **Ans**

Similarly a substance $CuSO_4.\ 3H_2O$ will try to absorb water if

Press of surrounding > pressure of substance press. of air (surrounding) > 7.92 mm of Hg

Ans

Q29:-

Ans:- $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ vapour density = 25.67

Initially 1 0

At eq-^{b} 1 – x 2x

$\therefore$ Vapour density = 25.67

$$\text{Mol. wt} = 2\times25.67 = \frac{wt}{moles} = \frac{1\times92}{(1+x)}$$

$$(1+x) = \frac{92}{2\times25.67} = 1.79$$

Degree of dissociation = 0.792 **Ans**

$$\therefore Kp= \frac{PNO_2^{\,2}}{PN_2O_4} = \frac{\left(\frac{2x}{1+x}.1\right)^2}{\left(\frac{1-x}{1+x}\times 1\right)} = \frac{4x^2}{(1+x)(1-x)} = \frac{4x^2}{1-x^2} = \frac{4\times(0.79)^2}{1-(0.79)^2} = \frac{4\times 0.6241}{1-0.6241}$$

$$Kp = \frac{4\times 0.6241}{0.3759} = 6.641$$ **Ans**

Q30:-

Sol:- $2H_2S\ (g) \longleftrightarrow 2H_2\ (g) + S_2\ (g)$, $Kp = 0.0018$, at $T = 1065^0C = 1338$ K

$\Delta H = 42\text{-}4$ kcal $= 42.4\times 10^3$ cal

$T_2 = 1132^0C = 1132 + 273 = 1405$ K

$$\log\left(\frac{Kp_1}{Kp_2}\right) = \frac{-\Delta H}{2.303R} = \left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

Putting the value of each them & taking antilog, we have

$Kp_2 = 0.025$ **Ans**

Q31:-

Sol:- Let pressure of A = 2P & that of B = P

$2A + B \longleftrightarrow A_2B$; $\Delta G = 1200$ cal at $227^0C = 500K$

Initially: 2P P 0

At eq-^{b}: 2P-2x P-x x

$$A/q,\ x = P\times 60\% = P\times\frac{60}{100} = 0.6p$$

Total pressure $= (2p - 2x + p - \cancel{x} + \cancel{x}) = 3P - 2x$

$= 3P - 0.6P\times 2 = 1.8p$ atm

also $\Delta G^0 = -2.303\,RT\,\text{lot kp}$

$1200 = -2.303\times 2\times 500 \log kp$

$$\log Kp = \frac{-6}{2.303\times 5}$$

$$Kp = \text{anti}\log\left(\frac{-6}{2.303\times 5}\right) = \text{anti}\log(-2.520)$$

$= \text{anti}\log(-1 + 0.478) = 0.3$

$$\text{Also } Kp = \frac{PA_2B}{PA^2.PB} = \frac{x}{(2p-2x)^2(P-x)}$$

$$Kp = \frac{0.6P}{4(0.4P)^2\times 0.4P} = \frac{6}{16\times 0.16P^2}$$

$$P^2 = \frac{600}{16^2\times Kp} \Rightarrow P = \sqrt{\frac{600}{16^2 Kp}} = \frac{10}{16}\sqrt{\frac{6}{Kp}}$$

Keeping the value of kp, we have

$$P=\frac{10}{16}\sqrt{\frac{6}{0.3}}=\frac{10}{16}\sqrt{\frac{60}{3}}=\frac{10}{10}\times 2\sqrt{5}$$

$$P=\frac{5}{4}\sqrt{5}=2.79$$

$\therefore$ Total pressure = 1.8 P = 1.8 × 2.79 = 5.03 atm **Ans**

Q32:-

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

$Kp_1 = 0.0266 \text{ at } T_1 = 350^0C = 623K$

$Kp_2 = 0.0129 \text{ at } T_2 = 400^0C = 673K$

Heat of formation of NH_3 will be ΔH of the above reaction.

$$\log\left(\frac{Kp_1}{Kp_2}\right)=\frac{-\Delta H}{2.303R}\left(\frac{1}{623}-\frac{1}{673}\right)$$

$$\log\left(\frac{0.0266}{0.0129}\right)=\frac{-\Delta H}{2.303R}\left(\frac{50}{623\times 673}\right)$$

$\Delta H = -21139.2 \text{ Cal}$ **Ans**

Q33:- $A(g) \rightleftharpoons B(g) + C(g)$: $Kc = 0.45$ at $T = 200^0C = 473$ K

At eq-^{b} $\frac{0.2}{1}M$ $\frac{0.3}{1}M$ $\frac{0.3M}{1}$

(a) If the value of the contains is doubled. i.e, vf = 2 lit then

$$A(g) \rightleftharpoons B(g) + C(g)$$

Initially $\frac{0.2}{2}$ $\frac{0.3}{2}$ $\frac{0.3}{2}$

At eq-^{b} $\frac{0.2}{2}-x$ $\frac{0.3}{2}+x$ $\frac{0.3}{2}+x$

$$Q=\frac{\frac{0.3}{2}\times\frac{0.3}{2}}{\frac{0.2}{2}}=\frac{0.45}{2}<keq-^b$$ $\therefore$ reaction has to move forward

$$keq-^b=\frac{\left(\frac{0.3}{2}+x\right)\left(\frac{0.3}{2}+x\right)}{\left(\frac{0.2}{2}-x\right)}=\frac{(0.15+x)^2}{(0.1-x)}=0.45$$

$$x^2+0.3x+0.0225=0.045-0.45x$$

$$x^2+0.75x-0.0225=0$$

$$x=\frac{-0.75+\sqrt{0.6525}}{2}=\frac{0.807-0.75}{2}$$

$x = 0.0289$

$\therefore$ [A] = 0.1- 0.0289 = 0.071 M.

$[B] = [C] = 0.15 + 0.0289 = 0.18$ M.

(b) If volume is halfed

$$A(g) \rightleftharpoons B(g) + C(g)$$

Initially: $0.2/\frac{1}{2}$ $\quad \frac{0.3}{1/2}$ $\quad \frac{0.3}{1/2}$

$0.4 \quad 0.6 \quad 0.6$

At eq-^{b} : $0.4+x \quad 0.6\text{-}x \quad 0.6\text{-}x$

$$Q = \frac{(0.6)(0.6)}{0.4} = \frac{3}{2} \times 0.6 0.3 = 0.9 > Kc$$ ∴ Reaction will more back word.

$$Kc = 0.45 = \frac{(0.6-x)^2}{(0.4+x)}$$

$$0.36 + x^2 - 1.2x = 018 + 0.45x$$

$$x^2 - 1.65x + 0.18 = 0$$

$$x = \frac{1.65 \pm \sqrt{(1.65)^2 - 4 \times 0.18}}{2} = \frac{1.65 \pm \sqrt{2.005}}{2} = \frac{1.65 \pm 1.415}{2}$$

Since x can't be greater than 0.6 (because 0.6 x conc-^{n})

∴ +ve sign can be ignored

$$x = \frac{0.235}{2} = 0.117 = 0.12$$

∴ $[A] = 0.4 + x = 0.52$ M

$[B] = [C] = 0.6\text{-}x = 0.6\text{-}0.12 = 0.48$ M **Ans**

Q34:-

Sol:- $CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g)$

At eq-^{b} $\frac{0.48}{2}$M $\quad \frac{0.48}{2}$M $\quad \frac{0.96}{2}$M $\quad \frac{0.96}{2}$M

$$Kc = \frac{\left(\frac{0.96}{2}\right)^2 \times \left(\frac{0.96}{2}\right)^2}{\left(\frac{0.48}{2}\right)\left(\frac{0.48}{2}\right)} = 4$$

(a) Let x moles/lit of H_2 is added to eq-^{b} mixture

$$CO_2(g) + H_2(g) \rightleftharpoons H_2O(g) + CO(g)$$

Initially $0.24 \quad 0.24 + x \quad 0.48 \quad 0.48$

At eq-^{b} $0.24\text{-}y \quad 0.24+x\text{-}y \quad 0.48+y \quad 0.48+y$

A/q, $0.48 + y = 0.6$ M

$Y = 0.12$

$$\therefore Kc = \frac{(0.48+y)(0.48+y)}{(0.24-y)(0.24+x-y)} = \frac{0.6 \times 0.6}{0.12 \times (0.12+x)}$$

$$4=\frac{5\times0.6}{(0.12+x)}=\frac{3}{(0.12+x)}$$

$48 + 4x = 3$

$4x = 3 - 0.48 = 2.52 \Rightarrow x=\frac{2.52}{4}=0.63\,\text{mole/lit}$

$\therefore$ moles added (of H_2) in 2 lit vessel = $0.63\times2 = 1.26$

$\therefore$ weight added = moles × Mol.wt $= 1.26\times2 = 2.52$ g **Ans**

Similarly calculation can be done for b & c also.

Q35:-

Sol:- $F_2 \rightleftharpoons 2F$

Initially 1 0

At eq-^{b} $1-\alpha$ 2α

Total moles = $1-\alpha+2\alpha = 1+\alpha$

$$Pf=\frac{2\alpha}{1+\alpha}P\,total=\frac{2\alpha}{1+\alpha}.4$$

$$Pf_2=\frac{1-\alpha}{1+\alpha}.Ptotal=\frac{1-\alpha}{1+\alpha}.4$$

$$\therefore Kp=\frac{Pf^2}{Pf_2}=\frac{\left(\frac{2\alpha}{1+\alpha}.4\right)^2}{\frac{1-\alpha}{1+\alpha}.4}=\frac{4\alpha^2.16}{(1+\alpha)^2}.\frac{(1+\alpha)}{(1-\alpha).4}$$

$$1.4\times10^{-2}=\frac{16-\alpha^2}{1-\alpha^2}$$

$1.4\times10^{-2}=1.4\times10^{-2}\alpha^2=16\alpha^2$

$1.4\times10^{-2}=(16+0.014)\alpha^2$

$$\alpha^2=\frac{1.4\times10^{-2}}{16.014}=8.74\times10^{-4}$$

$\alpha = 0.029 = 0.03$ **Ans**

Also, Mol. wt at eq-^{b} $=\frac{38}{1+\alpha}=\frac{38}{1.03}=36.91$

$\therefore$ Vapour density $=\frac{\text{Mol.wt}}{2}=18.45$ **Ans**

Q36:-

Sol:- Given: (1) $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$, $K_1 = 0.329$

(2) $2CO(g) + O_2(g) \rightleftharpoons 2CO(g)$, $K_2 = 2.24\times10^{22}$

(1) × 2 + (2)

$2COCl_2(g) + O_2(g) \rightleftharpoons 2CO_2(g) + 2Cl_2(g)$.

$K = K_1^2.K_2$

$= (0.329)^2\times2.24\times10^{22} = 2.43\times10^{21}$ **Ans**

Q37:-

Sol:- For half Cl_2 atom to remain in $COCl_2$ form, only half of moles of $COCl_2$ taken should convert to $Cl_2(g)$.

	$COCl_2(g) \rightleftharpoons$	$CO(g)$ +	$Cl_2(g)$, $K_{1000K} = 0.329$
Initially	x	0	0
At eq-^{b}	$x - x/2$	$x/2$	$x/2$

$$\text{Keq-}^b = 0.329 = \frac{x^2/4}{x/2} = x/2$$

X = 0.658 moles **Ans**

Q38:-

Sol:-	$N_2O_4 \rightleftharpoons$	$2NO_2$	
Initially	1 mole	0	
At eq-^{b}	1-0.25	2×0.25	(25% dissociation)

$$\therefore Kp = \frac{PNO_2^{\,2}}{P_{N_2O_4}} = \frac{\left(\frac{0.5}{1.25}\times 1\right)^2}{\frac{0.75}{1.25}\times 1} = \frac{0.25}{1.25}\times\frac{1}{0.75} = 0.267$$

Let α is the degree of dissociation, then

$$PNO_2 = \frac{2\alpha}{1+\alpha}\times 0.1 \qquad N_2O_4 \rightleftharpoons 2NO_2$$

$$PN_2O_4 = \frac{1-\alpha}{1+\alpha}\times 0.1 \qquad \text{At eq}-^b\ 1-\alpha \qquad 2\alpha$$

$$\text{total moles} = 1+\alpha$$

$$Kp\,_3 = \frac{PNO_2^{\,2}}{PN_2O_4} = \frac{\frac{4\alpha^2}{(1+\alpha)^2}\times(0.1)^2}{\frac{1-\alpha}{1+\alpha}\times 0.1}$$

$$0.267 = \frac{4\alpha^2}{(1-\alpha^2)}\times 0.1 \Rightarrow \frac{\alpha^2}{1-\alpha^2} = 0.667 \Rightarrow \alpha^2 = \frac{0.667}{1.667} = 0.3999 \Rightarrow \alpha = 0.6324$$

$$\therefore \text{ percentage dissociation} = \frac{\alpha}{1}\times 100 = 63.24\%$$

Ans

Q39:-

Sol:- (1) $S + S^{2-} \rightleftharpoons S_2^{\,2-}$, Keq-^{b} 12 (given)

(2) $2S + S^{2-} \rightleftharpoons S_3^{\,2-}$, $\text{Keq}\frac{b}{1} = 130$

(2) –(1) $S + S^{2-} \rightleftharpoons S_3^{\,2-}$, $\text{keq-}^b = \frac{\text{keq}-^{b_2}}{\text{keq}-^{b_1}} = \frac{130}{12} = 10.83$ **Ans**

Q40:-

Sol:- $PH_3.BCl_3(S) \rightleftharpoons PH_3(g) + BCl_3(g)$

$$\begin{array}{lllll} \text{Initially} & A & 0 & 0 & Kp = 1.57 \\ \text{At eq-}^{b} & A-x & x & x & \end{array}$$

total no. of gaseous moles = 2x

$$\therefore PpH_3 = \frac{x}{2x} \times Ptotal = \frac{P}{2} total$$

$$P_{BCl_3} = \frac{x}{2x} \times Ptotal = \frac{ptotal}{2}$$

$$\therefore Kp = 1.57 = \frac{Ptotal^2}{4}$$

$$Ptotal^2 = 4 \times 1.57$$

$$Ptotal = 2.51 \text{ atm}$$

$$\therefore P_{PH_3} = P_{BCl_3} = \frac{Ptotal}{2} = \frac{2.51}{2} = 1.253 atm$$

Ans

(b) At eq-^{b} $A - x > 0$

$$A > x$$

Also from $PV = nRT$ => $P = \frac{n}{V}RT$

$$1.253 = x. \times 0.0821 \times (273 + 80)$$

$$x = \frac{1.253}{0.0821 \times 353} = 0.043$$

$$\therefore A > 0.043 M \quad \therefore \frac{\text{moles A}}{\text{Volume}} > 0.043$$

moles of PH_3. $BCl_3(s) > 0.043 \times 0.5$

$$\frac{\text{wt of } PH_3BCl_3}{(34 + 11 + 35.5 \times 3)} > 0.0216 \quad => \quad \frac{\text{wt of } PH_3BCl_3}{151.5} > 0.0216$$

$\therefore$ Wt of $PH_3.BCl_3 > 3.27$ g **Ans**

Q41:-

Sol:- $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

$$\begin{array}{lllll} \text{Initially} & \frac{3}{2}M & \frac{4}{2}M & \frac{1}{2}M & \frac{4}{3}M \\ & 1.5\ M & 2\ M & 0.5\ M & 2\ M. \\ \text{At eq-}^{b} & 1.5 - x & 2 - x & 0.5 + x & 2 + x \end{array}$$

A/q, $1.5 - x = \frac{1}{2} = 0.5$ => $X = 1.5 - 0.5 = 1$

$$\text{(a) } \therefore \text{Equilibrium conc}^{n} : \left. \begin{array}{r} [SO_2] = 0.5\ M. \\ [NO_2] = 1.0 M. \\ [NO] = 3M \\ [SO_3] = 1.5\ M \end{array} \right\} \textbf{Ans}$$

(b) $K_c = \dfrac{[SO_3][NO]}{[SO_2][NO_2]} = \dfrac{1.5\times 3}{1\times 0.5} = 9$ **Ans**

Q42:-

Sol:- $CaCO_3(S) \rightleftharpoons CaO\,(s) + CO_2(g)$

20 gm

Initially $\dfrac{20}{100}$ moles = 0.2 moles

A/q, 35% didn't dissociate ∴ 65% dissociat

$$0.2\times\frac{65}{100} = \frac{13}{100} = 0.13 \text{ moles}$$

∴ Moles of CO_2 produced = 0.13 moles

∴ PV = nRT

$$P = \frac{nRT}{V} = \frac{0.13\times 0.0821\times 1073}{10} = 1.145 \text{ atm}$$

∴ $K_p = P_{CO_2}$ = 1.145 atm **Ans**

Q43:-

Sol:- $H_2O + D_2O \rightleftharpoons 2HDO$

Initially conc-^{n} 27.7 27.5 0

At eq-^{b} 27.7-x 27.5-x 2x

Weight of D_2O (given) = 550 g

∴ moles of $D_2O = \dfrac{550}{20} = 55/2$ moles

Volume of $D_2O = \dfrac{\text{weight}}{\text{density}} = \dfrac{5500}{11} = 500$ ml

Weight of H_2O (given) = 498.5 g

moles of $H_2O = \dfrac{498.5}{18}$ moles & Volume of $H_2O = \dfrac{498.5}{18}$ moles

Volume of $H_2O = \dfrac{498.5}{0.997} = 500$ ml

Total volume = $V_2O + VH_2O$ 1000 ml = 1 lit

Initially morality of D_2O = $55/2$ M = 27.5 M

Initially morality of H_2O = 27.7 M

A/q, 47% of H_2O reacts to form HDO.

$$\therefore\ x = 27.7\times\frac{47}{100} = 13.02$$

$$\therefore\ K_c = \frac{(2x)^2}{(27.7-x)(27.5-x)} = \frac{(26.04)^2}{14.68\times 14.66}$$

K_c = 3.17 **Ans**

Q44:-

Sol:- $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; Keq-^{b} $= 6.98\times 10^{24}$

$$\Delta G^0 = -2.303RT\log keq-^b$$
$$= -2.303\times 8.314\times 300\log(6.98\times 10^{24})$$
$$= -142.7\,kJ/mole$$
$$\therefore \Delta G^0 reac-^n = 2\Delta G_f^0 SO_3 - 2\Delta G^0_{fSO_2} - \Delta G^0_{fo_2}$$
$$-147.2 = 2\Delta G_f^0 SO_3 + 600.24 - 0$$
$$2\Delta G_f^0 SO_3 = \frac{-747.44}{2} = -373.72\,kJ/mole$$

Ans

Q45:-

Sol:- For reaction involving gases only

$$\Delta G^0 = -2.303RT\log Kp$$

$\therefore$ Kp can be calculated if ΔG^0 is known.

For reaction happening with solutions

$$\Delta G^0 = -2.303RT\log Kc$$

So Kc can be calculated with this.

Q46:-

Sol:- $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

At eq-^{b}, $PSO_2 = \frac{56.6}{100}\times Ptotal = \frac{56.6}{100}\times 112 = 63.39\,atm$

$$PO_2 = \frac{10.6\times 112}{100} = 11.87\,atm \quad \& \quad PSO_3 = \frac{32.8\times 112}{100} = 36.74\,atm$$

$$\therefore Kp = \frac{PSO_3^2}{PSO_2^2.PO_2} = 0.0283$$ **Ans**

Q47:-

Sol:- $2AB \rightleftharpoons A_2 + B_2$, $\Delta G^0 = 11.8\,kJ$

Initially $\quad 1 \quad 0 \quad 0$

At eq-^{b} $\quad 1-\alpha \quad \alpha/2 \quad \alpha/2$; α = degree of dissociation

$$\Delta G = -2.303RT\log Kp$$
$$11.8\times 10^3 = -2.303\times 8.314\times 230\log Kp.$$
$$-2.679 = \log Kp.$$
$$Kp = \text{anti}\log(0.321)\times 10^{-3}$$
$$= 2.094\times 10^{-3}$$

Let degree of dissociation is α then

$\therefore$ Total moles at eq-^{b} = $1-\alpha + \alpha/2 + \alpha/2 + \alpha/2 = 1.$

$$\therefore \ Kp = \frac{\frac{\cancel{\alpha}/2}{1}\times 1\times \frac{\alpha}{2/1}\times 1}{\left(\frac{1-\alpha}{1}\times 1\right)^2} = \frac{\alpha^2}{4(1-\alpha)^2}$$

$$2.094\times 10^{-3} = \frac{\alpha^2}{4(1-\alpha)^2} \quad => \quad \frac{\alpha^2}{(1-\alpha)^2} = 4\times 2.094\times 10^{-3}$$

$$\frac{\alpha}{1-\alpha} = 0.0915$$

$$\alpha = 0.0915 - 0.915\alpha$$

$$\alpha = \frac{0.0915}{1.0915}.0.0838 \quad \textbf{Ans}$$

Q48:- $H_2(g) + F_2(g) \rightleftharpoons 2HF(g)$, $K = 115$

Initially	$\frac{0.1}{1}$	$\frac{0.05}{1}$	0
At eq-^{b}	0.1-x	0.05-x	2x

$$K = 115 \frac{(2x)^2}{(0.1-x)(0.05-x)} = \frac{4x^2}{0.005-0.15x+x^2}$$

Solving quadratic we have

$X = 0.0485$

$$\left.\begin{aligned} \therefore \ [H_2] &= 0.1 - 0.01485 - 0.05151\ M \\ [F_2] &= 0.5 - 0.0485 - 0.002\ M \\ [HF] &= 2\times 0.0485 = 0.097\ M \end{aligned}\right\} \textbf{Ans}$$

Q49:-

Sol:- $CuO(s) + H_2(g) \rightleftharpoons Cu(s) + H_2O(g)$

Initially		0.2 atm		
At eq-^{b}		0.2 – P	P	p atm

$$\therefore \ Kp = \frac{PH_2O_{(g)}}{PH_2} = \frac{P}{0.2-P} = 1.6\times 10^9$$

$$\therefore \frac{0.2\times 1.6\times 10^{-1}}{(1.6\times 10^9 + 1)} = P \ \Rightarrow \ P \approx 0.2$$

$\therefore PH_2 \approx 0.2 - 0.2 \approx 0$ However will be +ve.

Q50:-

Sol:- $C(S) + CO_2(g) \rightleftharpoons 2CO(g)$. $Kp = 1.5$

At eq-^{b}	P_1	P_2 (say)

$$Kp = \frac{P_2^{\,2}}{P^1} = 1.5 \quad => P_2^2 = 1.5\ P_1$$

Also $P_1 + P_2 = 1$

$P_2 = 1 - P_1$

$P_2^2 = 1 + P_1^2 - 2P_1 = 1.5\ P_1$

$1 + P_1^2 - 3.5\,P_1 = 0$

$P_1 = 0.314$ atm, $\Rightarrow PCO_2 = 0.314$ atm **Ans**

$P_2 = 0.686$ atm $\Rightarrow PCO = 0.686$ atm **Ans**

Q51:-

Sol:- $NH_4Cl\,(s) \rightleftharpoons NH_3(g) + HCl\,(g)$, $\Delta H = 176$ kJ/ mole

(a) Temp. is decreased, eq-^{b} will move in exothermic direction. (i.e. formation of NH_3 increases).

(b) NH_3 is added, eq-^{b} will consume the added NH_3, however some more amount of NH_3 than before will remain present - & so mass of NH_3 increases from before.

(c) HCl is added, eq^b will shift leftward, and so amount of NH_3 consumed & so decreases.

(c) No effect of addition of solid NH_4Cl or removing.

(e) volume decreases, no of gases molecule try to decrease this happens by shifting eq-^{b} in backward dir^n, So wt of NH_3 decreases.

Q52:-

Sol:- $Cl_2(g) \rightleftharpoons 2Cl(g)$

Initially 1 0

At eq-b $1-\alpha$ 2α

Total moles = $1+\alpha$

If Cl_2 molecule is 1% dissociated.

$$A/q,\ \alpha = \frac{1}{100} = 0.01$$

$$\therefore Kp = \frac{\left(\frac{2\alpha}{1+\alpha}.1\right)^2}{\frac{1-\alpha}{1+\alpha}.1} = \frac{4\,\alpha^2}{1-\alpha^2} = \frac{4\times10^{-4}}{1-0.01} = 4.09\times10^{-4} \quad \textbf{Ans}$$

$$\therefore Kp = Kc(RT)^{\Delta n} = Kc(RT)^1$$

$$Kc = \frac{KP}{RT} = \frac{4.04\times10^{-4}}{0.0821\times975} = 5.09\times10^{-6} \quad \textbf{Ans}$$

Q53:-

Sol:- $\Delta G^0 = -2.303\,RT\log K$

$$\Delta H^0 - T\Delta S^0 = -2.303\,RT\log K$$

$$2.303\log K = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} \quad \textbf{proved}$$

Q54:-

Sol:- $A + B \rightleftharpoons C + D$, $\Delta G^0 = 460\,cal$

2 2 2 2

At eq-^{b} 2-x 2-x 2+x 2+x

$$\Delta G^0 = -2.303\times R\times300\log K$$

$$\frac{460}{2.3\times2\times300} = \log\ K$$

$$\log K = -\frac{1}{3} = -0.33$$

$$K = 0.467 = \frac{(2+x)^2}{(2-x)^2}$$

$$\frac{[C]}{[A]} = \left(\frac{2+x}{2-x}\right) = \sqrt{0.467} = 0.68$$ **Ans**

Q55:-

Sol:- $2A(g) + B(g) \rightleftharpoons A_2B(g).$

$\Delta S^0 = 5\,J/K$

$K = 1\times10^{-10}$

$T = 300k$

$$\Delta G^0 = -2.303\times8.314\times300\log K$$

$$= -5744.14\,(-10) \quad = 57441.43\ J/K$$

$$\Delta H^0 - T\Delta S^0 = \Delta G^0 = 57441.43$$

$$\Delta H^0 - 300\times5 = 57441.43$$

$$\Delta H^0 = 57441.43 + 1500 \quad = 58941.43\ J$$

$$\Delta H^0 = \Delta E^0 + \Delta nRT$$

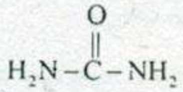
$$\Delta E^0 = 58941.43 - \Delta nRT$$

$$= 58941.43 + 2\times8.314\times300 = 63829.82\ J = 63.83\ KJ$$ **Ans**

Objective Problems:-

Q:1 Ans:- (b):- urea is

$CO(NH_2)_2$



$$H_2N-\overset{\overset{\large O}{\|}}{C}-NH_2$$

$\therefore$ Mol. Wt. $= 16\times2 + 12 + 16 = 60$ g

$\therefore$ no. of moles in 120 g $= \frac{120}{60} = 2$ moles

Volume of solution = 5 lit

$\therefore$ Molarity $= \frac{\text{moles}}{\text{volume}} = \frac{2}{5} = 0.4\,M$ **Ans**

Q2: Ans :- (d) For forward eq-^{b} reaction it is $\frac{[C][D]}{[A][B]}$

For backward eq-^{b} reaction it is $\frac{[A][B]}{[C][D]}$

Q3: Ans:- (b) From unit of Kp, it clear than $\Delta n = 1$

Since Kp has unit $(atm)^{\Delta n}$

here Kp = 0.5 atm given

this directly implies that $\Delta n = 1$, which is only in case of (b) option.

Q4:Ans:- (d) $Kp = Kc\ (RT)^{\Delta n}$

Both are equal if $\Delta n = 0$.

Actually $\Delta n = 0 \Rightarrow Kp = Kc = Kn = 1$-------

Unit of Kc = $\left(\text{mol}/_{\text{lit}}\right)^{\Delta n}$

unit of Kp = $(\text{atm})^{\Delta n}$

Q5:Ans:- (b) $\frac{Kp}{Kc} = (RT)^{-1/2} = \frac{1}{\sqrt{RT}}$

Q6:Ans:- (d) From stoichiometric coefficient, it is clear that x mole of N_2 reacts with 3 x moles of H_2 to produce 2x moles of NH_3

	N_2 +	$3H_2 \rightleftarrows$	$2NH_3$
Initial mole	1	2	3
At eq-^{b}	1-x	2-3x	3+2x

Q7:Ans:-(c)

	$PCl_5 \rightleftarrows$	PCl_3 +	Cl_2
Initially	2M	0	0
At eq-^{b}	2-x	x	x

$$A/q,\ Kc = \frac{x^2}{2-x} = 1$$

$$x^2 + x - 2 = 0$$

$$x = \frac{-1 \pm \sqrt{1+8}}{2} = \frac{3-2}{2} = 1$$

$\therefore$ degree of dissociation = $\frac{1}{2}$

Q8:Ans:- (a)

	$N_2O_4 \rightleftarrows$	$2NO_2$
Initially	1	
At eq-^{b}	1-x	2x (total no. of moles = 1+x)

$\therefore$ Mol. wt at eq-^{b} = $\frac{(1-x)\times 92 + 2x \times 46}{1+x} = \frac{92}{1+x}$

$$2 \times 24.5 = \frac{92}{1+x}$$

$$49 + 49x = 92$$

=> $49\,x = 43 \quad x = \frac{43}{49} = 0.8775$

$\therefore$ Percentage dissociation = $x/_1 \times 100 = 87\%$

Q9:Ans:-(a)

$$SO_2 + \frac{1}{2}O_2 \rightleftharpoons SO_3, K_1$$

$$SO_3 \rightleftharpoons SO_2 + \frac{1}{2}O_2, \frac{1}{K_1}$$

$$2SO_3 \rightleftharpoons 2SO_2 + O_2 = \left(\frac{1}{K_1}\right)^2$$

$$\therefore K_2 = \left(\frac{1}{K_1}\right)^2$$

Q10: Ans :- (d)

$$A \rightleftharpoons D, K_c = 2 \times 4 \times 6 = 48$$

Q11: Ans :-(c)

$K_p = P_{CO_2}$ because $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

Q12: Ans:- (a)

$$C(S) + CO_2(g) \rightleftharpoons 2CO(g)$$

$$K_p = \frac{P_{CO_2}}{P_{CO_2}} = \frac{8^2}{4} = \frac{64}{4} = 16$$

Q13:Ans(a)

$$A + B \rightleftharpoons 3C, \quad K_c = 20. \text{ At } 25^0C$$

Initial mole $\frac{1}{2}$ $\quad 2/2$ $\quad 4/2$

$$Q = \frac{(4)^3}{1 \times 1/2} = \frac{80}{1/2} = 16 < kc$$

$\therefore$ reaction will move in dir-^{n} in which q increases, hence in backward direction. (from left to right)

Q14: Ans:-(a)

$$A + B \rightleftharpoons C + D$$

$$1 \quad 2 \quad 3 \quad 4 \quad Q = \frac{[C][D]}{[A][B]} = \frac{4 \times 3}{2} = 6 < 10$$

$\therefore$ Q has to be increased, SO reaction will be moved from left to right.

Q15: Ans;- (b)

$$A + B \rightleftharpoons C + D$$

Initially $\frac{2}{1}$ $\frac{2}{1}$ $\quad \frac{2}{1}$ $\frac{2}{1}$ $\quad K_c = \frac{[C][D]}{[A][B]} = \frac{2 \times 2}{2 \times 2} = 1$

Q16:Ans:-(c)

Since degree of dissociation depend on equilibrium constant not on the initial concentrations.

Q17: Ans :-(d)

Only temp. changes equilibrium constant, other changes just affect equilibrium position.

Q18: Ans:-(a)

$$\begin{array}{llll} & 2HI \rightleftharpoons & H_2 & + \ I_2 \\ \text{Initially} & 1 & 0 & 0 \\ \text{At eq-}^{b} & 1-\frac{1}{3} & \frac{1}{6} & \frac{1}{6} \end{array}$$

$$\therefore Kc\frac{\frac{1}{6}\times\frac{1}{6}}{\left(1-\frac{1}{3}\right)^2}=\frac{\frac{1}{36}}{\frac{4}{9}}=\frac{1}{36}\times\frac{9}{4}$$

Q19:Ans:- (c)

$$\begin{array}{llll} & N_2 + & 3H_2 \rightleftharpoons & 2NH_3 \\ \text{Initially} & \frac{28}{28} & \frac{6}{2} & 0 \\ & 1 & 3 & 0 \\ \text{At eq-}^{b} & 1-x & 3-3x & 2x \end{array}$$

$$(2x)\times 17 = 17$$

$$2x = 1 \Rightarrow x = \frac{1}{2}$$

$$\therefore \text{ Moles of } N_2 = 1-\frac{1}{2}=\frac{1}{2}$$

$$\therefore \text{ Wt of } N_2 = \frac{1}{2}\times \text{Mol.wt} = \frac{1}{2}\times 28 = 14\,\text{gm}$$

$$\text{Wt of } H_2 = 3-\frac{3}{2}=\frac{3}{2}\times\text{Mol.wt}=\frac{3}{2}\times 2 = 3\,\text{gm}$$ **Ans**

Q20:Ans(d)

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

Kp changes only with temperature.

Q21:Ans(d)

$$SO_2+\frac{1}{2}O_2 \rightleftharpoons SO_3 \qquad \Delta H = -ve$$

By Le-chatelier principle, if Temp is decreased, reaction will move in exothermic direction. So SO_3 will be formed. Also as pressure decreases, no of moles increase & since in SO_3 side less no. of moles are present, we have to increase the pressure to reduce the no. of moles i,e, to produce SO_3.

Q22:Ans- (a), (b), (c), (d)

(Same explanation as above)

Q23:- Ans-(a)

Kp doesn't change with pressure & concentration.

Q24:-Ans(d)

Because in all, a, b, c reaction, some of the product precipitated out and or some product are evolved out from the reaction mixture as gases.

Q25 Ans (c)

$$NaNo_3(S) \rightleftharpoons O_2(g) + NaNO_2(s), \Delta H = +ve$$

As temp is increased, reaction will move in forward direction, $NaNO_3$ & $NaNO_2$ are solid, so their addition or removal doesn't effect equilibrium.

Q26:Ans-(All are wrong options)

Addition of inert substance (which doesn't take part in reaction) doesn't change the concentration & it doesn't effect the equilibrium position also

Q27:Ans-(C)

$$N_2O_4 \rightleftharpoons 2NO_2$$

$$\text{Ateq}-^b \frac{0.2}{2}M \qquad \frac{2\times10^{-3}}{2}M$$

$$Kc = \frac{(10^{-3})^2}{10^{-1}} = 1\times10^{-5}$$

Q28:Ans-(a)

$$Br_2 \rightleftharpoons 2Br, \Delta H$$

$T_1 = 500$ k & $T_2 = 700$ K

$K_1 = 1\times10^{-10}$ & $K_2 = 1\times10^{-5}$

$$\log\left(\frac{K_1}{K_2}\right) = \frac{-\Delta H}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \Rightarrow \log\left(\frac{10_{-10}}{10_{-5}}\right) = \frac{-\Delta H}{2.303R}\left(\frac{1}{500}-\frac{1}{700}\right)$$

$$-5 = \frac{-\Delta H}{2.303R}\left(\frac{1}{500}-\frac{1}{700}\right)$$

$$\Delta H = +Ve$$

Q29:Ans-(d)

Q30:Ans-(None) At eq $-^b$, $\Delta G = 0$

$$\Delta G^0 = -2.303RT\log K_p$$

Q31:Ans-(b) Solid $\rightleftharpoons$ liquid

At s press ↑, equilibrium will try to shift left or right which depends on nature of solids & Liquid

Q32:Ans-(b) liquid $\rightleftharpoons$ Vapour

As press ↑ no. of gaseous molecules try to decrease & hence for having more vapour we have to increase the temperature

Q33:Ans- (c)

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2, Kp = \frac{\alpha^2}{(1-\alpha)V}$$

As volume changes, α will affect equilibrium position;

Q34:Ans-(c)

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

Only temp. & amount of CO_2 will affect equilibrium position;

Q35:Ans-(a), (e) & (c)

As inert gas added at court pressure, partial pressure decreases and hence to increase partial pressure no. of moles have to increase which occur in forward dis-^{s}

Q36:Ans-(b)

Where $\Delta G = 0$, $G_{Product} = G_{reactants}$

i,e stability of both reactants & products are same which is a rare case

Q37:Ans-(a)

$\Delta G < 0$ Since $\Delta G < 0 = G_{Product} - G_{reactants} < 0$ $G_{Product} > G_{reactants}$ in (c)

Q38:Ans-(c) $\Delta G > 0$ for $G_{product} - G_{reactants} > 0$

$G_{Product} > G_{reactants}$ in (C)

Q39:Ans-(b) $\Delta G = 0 \Rightarrow$ $\Delta G^0 = -2.303\,RT\log Kp$

in (b) $\log Kp = 0 \Rightarrow Kp = 1$

Q40:Ans-(d)

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_3(g)$

(a) As only $CaCO_3(s)$ is present it will produce CaO & CO_2

(b) CaO & CO_2 such that $PCO_2 > Kp$ reaction will more backward so eg achieved.

(c) $CaCO_3$ & CO_2 such that $Pco_2 > Kp$ will try to move reaction in backward direction, So eqb is achieved.

(d) If both $CaCO_3$ & CaO are present, it doesn't affect anything.

Q41:Ans-(d) Kp will change only by changing temperature, however by changing volume, α - change in such a way that Kp remain same.

Q42:Ans-(c) $Q = \frac{[Product]}{[reactants]}$

At initiar condition, [Product] = O

$\therefore Q = 0$, initially

Q43:Ans-(a) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $K_c = 0.05$ mole/lit

$K_c = [CO_2] = 0.05$ mole / lit

$\therefore \frac{\text{mole of } CO_2}{\text{vol of } CO_2} = 0.05\text{ mole/lit}$

mole of $CO_2 = 0.05 \times 6.5$ mole $= 0.325$ mole

At least > 0.325 moles should be present

Min-^{m} weight of $CaCO_3 \geq 0.325 \times 100 \geq 32.5$ gm

Q44:Ans-(a)

As Temp is increased, reaction constant increases in endothermic reaction

$$\text{by} \quad \log\left(\frac{K_1}{K_2}\right) = \frac{-\Delta H}{2.303R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\text{If } T_2 > T_1 \quad \frac{1}{T_1} - \frac{1}{T_2} > 0$$

$$\therefore \frac{-\Delta H}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)<0$$

$$\log\left(\frac{K_1}{K_2}\right)<0 \quad \Rightarrow \frac{K_1}{K_2}<1 \Rightarrow K_1<K_2$$

So If $T_2 > T_1$ $K_2 > K_1$.

Q45:Ans-(a) $NiO(s) + CO(g) \longleftrightarrow Ni(s) + CO_2(g)$

150 mm of Hg

$$\frac{150}{760} - P$$

total pressure $= \frac{15}{76}$ atm $= 150$ mm of Hg < 760

So there is always tendency to occur reaction forward

Q46:Ans-(c). $\text{Log } K = \frac{-\Delta H}{2.303RT} + C$

$\therefore$ Curve will be (c) with –ve slope