SOLVED EXAMPLES

Ex. 1 $H_2(g) + I_2(g) \rightleftharpoons 2HI\,(g)$

When 92 g of I_2 and 1g of H_2 are heated at equilibrium at 450°C, the equilibrium mixture contained 1.9 g of I_2. How many moles of I_2 and HI are present at equilibrium.

(A) 0.0075 & 0.147 moles **(B)** 0.0050 & 0.147 moles

(C) 0.0075 & 0.7094 moles **(D)** 0.0052 & 0.347 moles

Sol. **(C)**

$$\text{moles of } I_2 \text{ taken} = \frac{92}{254} = 0.3622$$

$$\text{moles of } H_2 \text{ taken} = \frac{1}{2} = 0.5$$

$$\text{moles of } I_2 \text{ remaining} = \frac{1.9}{254} = 0.0075$$

moles of I_2 used $= 0.3622 - 0.0075 = 0.3547$

moles of H_2 used $= 0.3547$

moles of H_2 remaining $= 0.5 - 0.3547 = 0.1453$

moles of HI formed $= 0.3547 \times 2 = 0.7094$

At equilibrium

moles of $I_2 = 0.0075$ moles

moles of HI $= 0.7094$ moles

Ex. 2 The volume of a closed reaction vessel in which the equilibrium :

$2SO_2\,(g) + O_2(g) \rightleftharpoons 2SO_3\,(g)$ sets is halved, Now -

(A) the rates of forward and backward reactions will remain the same.

(B) the equilibrium will not shift.

(C) the equilibrium will shift to the left.

(D) the rate of forward reaction will become double that of reverse reaction and the equilibrium will shift to the right.

Sol. **(D)**

In the reaction

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

In this reaction three moles (or volumes) of reactants are converted into two moles (or volumes) of products i.e. there is a decrease in volume and so if the volume of the reaction vessel is halved the equilibrium will be shifted to the right i.e. more product will be formed and the rate of forward reaction will increase i.e. double that of reverse reaction.

Ex. 3 The equilibrium constant of the reaction $A_2\,(g) + B_2(g) \rightleftharpoons 2AB\,(g)$ at 100°C is 50. If one litre flask containing one mole of A_2 is connected to a 3 litre flask containing two moles of B_2 the number of moles of AB formed at 373 K will be

(A) 1.886 **(B)** 2.317 **(C)** 0.943 **(D)** 18.86

Sol. **(A)**

The equilibrium is represented as :

$$A_2\,(g) + B_2(g) \rightleftharpoons 2AB\,(g)$$

Initial concentration	1	2	0
Moles at equilibrium	1–x	2–x	2x

Total volume = 1 + 3 = 4 litres

$$[A_2] = \frac{1-x}{4}\,,\,[B_2] = \frac{2-x}{4} \text{ and } [AB] = \frac{2x}{4}$$

$$K = \frac{[AB]^2}{[A_2][B_2]} = \frac{\left(\frac{2x}{4}\right)^2}{\left(\frac{1-x}{4}\right)\left(\frac{2-x}{4}\right)} = 50$$

On solving we get $23x^2 - 75\,x + 50 = 0$

$\therefore$ x = 2.31 or 0.943, since x can't be more than 1

so, x = 0.943

$\therefore$ moles of AB formed = 2 × 0.943 = 1.886

Ex. 4 $A_2(g)$ and $B_2(g)$ at initial partial pressure of 98.4 and 41.3 torr, respectively were allowed to react at 400 K. At equilibrium the total pressure was 110.5 torr. Calculate the value of K_P for the following reaction at 400 K.

$$2A_2(g) + B_2(g) \rightleftharpoons 2\,A_2B\,(g)$$

(A) 124 **(B)** 134 **(C)** 154 **(D)** 174

Sol. **(B)**

The given reaction is,

	$2A_2(g)$ +	$B_2(g)$ ⇌	$2A_2B\,(g)$
Initial pressure (torr)	98.4	41.3	0
At equilibrium	98.4–x	$41.3-\frac{x}{2}$	x

Total pressure at equilibrium = 110.5 torr.

$$(98.4 - x) + (41.3 - \frac{x}{2}) + x = 110.5$$

$\therefore$ x = 58.4 torr (760 torr = 1 atm)

$P_{(A_2B)} = 58.4 \text{ torr} = 7.68 \times 10^{-2}$ atm

$P_{(A_2)} = 98.4 - 58.4 = 40 \text{ torr} = 5.26 \times 10^{-2}$ atm

$$P_{(B_2)} = 41.3 - \frac{58.4}{2} = 12.1 \text{ torr} = 1.59 \times 10^{-2} \text{ atm}$$

$$K_P = \frac{P^2_{A_2B}}{P^2_{A_2} \times P_{B_2}} = \frac{(7.68 \times 10^{-2})^2}{(5.26 \times 10^{-2})(1.59 \times 10^{-2})} = 134$$

Ex. 5 When 1.0 mole of N_2 and 3.0 moles of H_2 was heated in a vessel at 873 K and a pressure of 3.55 atm. 30% of N_2 is converted into NH_3 at equilibrium. Find the value of K_P for the reaction.

(A) $3.1 \times 10^{-2}\,\text{atm}^{-2}$ **(B)** $4.1 \times 10^{-2}\,\text{atm}^{-2}$ **(C)** $5.1 \times 10^{-2}\,\text{atm}^{-2}$ **(D)** $6.1 \times 10^{-2}\,\text{atm}^{-2}$

Sol. **(C)**

$N_2(g)$	+ $3H_2(g)$	$\rightleftharpoons$ $2NH_3(g)$	
1 mole	3 moles	0	Initial moles
1–0.3 = 0.7 moles	3.0 – 0.9 = 2.1 moles	0.6 moles	at equilibrium

Total no. of moles at equilibrium = 3.4

$$K_P = \frac{\left(\frac{0.6}{3.4} \times 3.55\right)^2}{\left(\frac{0.7}{3.4} \times 3.55\right)\left(\frac{2.1}{3.4} \times 3.55\right)^3} = 5.1 \times 10^{-2}\,\text{atm}^{-2}$$

Ex. 6 $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

If the partial pressure of SO_2, O_2 and SO_3 are 0.559, 0.101 and 0.331 atm respectively. What would be the partial pressure of O_2 gas, to get equal moles of SO_2 and SO_3.

(A) 0.188 atm **(B)** 0.288 atm **(C)** 0.388 atm **(D)** 0.488 atm

Sol. **(B)**

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

$$K_P = \frac{[P_{SO_3}]^2}{[P_{SO_2}]^2[P_{O_2}]} = \frac{(0.331)^2}{(0.559)^2(0.101)} = 3.47$$

If SO_2 and SO_3 have same number of moles, their partial pressure will be equal and

$$P_{SO_3} = P_{SO_2} \quad \therefore \quad P_{O_2} = \frac{1}{3.47} = 0.288\,\text{atm}$$

Ex. 7 K_P for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at 400°C is 3.28×10^{-4}. Calculate K_c.

(A) 0.3 $\text{mole}^{-2}\,\text{litre}^2$ **(B)** 0.4 $\text{mole}^{-2}\,\text{litre}^2$ **(C)** 1.0 $\text{mole}^{-2}\,\text{litre}^2$ **(D)** 0.6 $\text{mole}^{-2}\,\text{litre}^2$

Sol. **(C)**

$N_2 + 3H_2 \rightleftharpoons 2NH_3$

$\Delta n = -2$ and $K_P = K_C(RT)^{\Delta n}$

$3.28 \times 10^{-4} = K_c(0.0821 \times 673)^{-2}$

and $K_c = 1.0\,\text{mole}^{-2}\,\text{litre}^2$.

Ex. 8 A mixture of H_2 and I_2 in molecular proportion of 2 : 3 was heated at 444°C till the reaction

$H_2 + I_2 \rightleftharpoons 2HI$ reached equilibrium state. Calculate the percentage of iodine converted into HI.

(K_C at 444°C is 0.02)

(A) 3.38 % **(B)** 4.38% **(C)** 5.38% **(D)** 6.38%

Sol. **(C)**

	H_2	+	I_2	$\rightleftharpoons$	$2HI$
Initial moles	2		3		0
Equi.conc.	$\frac{2-x}{v}$		$\frac{3-x}{v}$		$\frac{2x}{v}$

$$K_C = \frac{4x^2}{(2-x)(3-x)} = 0.02$$

$199x^2 + 5x - 6 = 0$

$x = 0.1615$

Out of 3 moles, 0.1615 moles I_2 is converted into HI.

$\therefore$ Percentage of I_2 converted to HI $= \frac{0.1615 \times 100}{3} = 5.38\%$

Ex. 9 The equilibrium composition for the reaction is :

PCl_3	+	Cl_2	$\rightleftharpoons$	PCl_5
0.20		0.05		0.40 moles/litre

If 0.25 moles of Cl_2 is added at same temperature. Find equilibrium concentration of PCl_5 ($K_C = 20$)

(A) 0.48 moles/litre **(B)** 0.38 moles/litre **(C)** 0.56 moles/litre **(D)** 1.20 moles/litre

Sol. **(A)**

PCl_3	+	Cl_2	$\rightleftharpoons$	PCl_5
0.20		0.05		0.40 moles/litre

If 0.25 moles of Cl_2 is added then at equilibrium [Let V = 1L]

$0.20 - x$ $0.30 - x$ $0.40 + x$

$$20 = \frac{0.40 + x}{(0.20 - x)(0.30 - x)} \quad \text{or} \quad x = 0.08$$

$[PCl_5] = 0.4 + 0.08 = 0.48$ moles/litre

Ex. 10 0.96 g of HI were heated to attain equilibrium $2HI \rightleftharpoons H_2 + I_2$. The reaction mixture on titration requires 15.7 mL of N/20 hypo. Calculate % dissociation of HI.

(A) 18.9% **(B)** 19.9% **(C)** 10.46% **(D)** 21.9%

Sol. **(C)**

	$2HI$	$\rightleftharpoons$	H_2	+	I_2
Initial moles	$\frac{0.96}{128}$ $= 7.5 \times 10^{-3}$		0		0
Moles at equilibrium	$(7.5 \times 10^{-3} - x)$		x/2		x/2

Now Meq. of I_2 formed at equilibrium = Meq. of hypo used

$$\frac{W}{E} \times 1000 = 15.7 \times \frac{1}{20} \quad \text{or} \quad \frac{W}{E} \text{ of } I_2 = 0.785 \times 10^{-3}$$

$\therefore$ Moles of I_2 formed at equilibrium $= \frac{0.785 \times 10^{-3}}{2} = 0.3925 \times 10^{-3}$

or $\frac{x}{2} = 0.3925 \times 10^{-3}$ or $x = 0.785 \times 10^{-3}$

$$\therefore \text{ degree of dissociation of HI} = \frac{\text{moles dissociated}}{\text{initial moles}} = \frac{x}{7.5 \times 10^{-3}}$$

$$\alpha = \frac{0.785 \times 10^{-3}}{7.5 \times 10^{-3}} = 0.1046 = 10.46\%$$

Ex. 11 In an experiment at 500 K, the concentration of different species are $[NH_3] = 0.105$ mol dm^{-3}, $[N_2] = 1.10$ mol dm^{-3} and $[H_2] = 1.50$ mol dm^{-3} then find the followings :-

(A) values of K_C and K_P for the reaction

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(B) value of K_c for the reaction -

$$2NH_3 \rightleftharpoons N_2 + 3H_2$$

Sol. **(A)** For the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$

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

$[NH_3] = 0.105 \text{ mol dm}^{-3}$, $[N_2] = 1.10 \text{ mol dm}^{-3}$ and

$[H_2] = 1.50 \text{ mol dm}^{-3}$

$$K_C = \frac{(0.105 \text{ mol dm}^{-3})^2}{(1.10 \text{ mol dm}^{-3}) \times (1.50 \text{ mol dm}^{-3})^3} = 2.97 \times 10^{-3} \text{ mol}^{-2}\text{dm}^6$$

Now $K_P = K_C \times (RT)^{\Delta n}$ $\Delta n = -2$,

$R = 0.082 \text{ atm dm}^3 \text{K}^{-1} \text{mol}^{-1}$, $T = 500$ K

$\therefore$ $K_P = (2.97 \times 10^{-3} \text{ mol}^{-3} \text{ dm}^6) \times [(0.082 \text{ atm dm}^3 \text{K}^{-1} \text{mol}^{-1}) \times (500 \text{ K})]^{-2}$

$= 1.76 \times 10^{-6} \text{ atm}^{-2}$

(B) The equilibrium constant K_C for the reverse reaction is related to the equilibrium constant K_C for the forward reaction as :

$$K'_C = \frac{1}{K_c} = \frac{1}{2.97 \times 10^{-3} \text{ mol}^{-2}\text{dm}^6} = 3.37 \times 10^{-2} \text{ mol}^2 \text{dm}^{-6}$$

Ex. 12 The equilibrium constant K, for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 1.64×10^{-4} atm^{-2} at 300°C. What will be the equilibrium constant at 400°C, if heat of reaction in this temperature range is – 105185.8 Joules.

(A) 0.64×10^{-5} atm^{-2} **(B)** 6.4×10^{-3} atm^{-2} **(C)** 0.64×10^{-3} atm^{-2} **(D)** 0.64×10^{-1} atm^{-2}

Sol. **(A)**

$K_{p_1} = 1.64 \times 10^{-4}$ atm^{-2}, $K_{p_2} = ?$

$T_1 = 300 + 273 = 573$ K

$T_2 = 400 + 273 = 673$ K

$\Delta H = -105185.8$ Joules

$R = 8.314$ J/K/mole

Applying equation

$$\log K_{p_2} - \log K_{p_1} = \frac{\Delta H}{2.303\,R}\left(\frac{T_2 - T_1}{T_1T_2}\right)$$

$$\log K_{p_2} - \log 1.64 \times 10^{-4} = -\frac{105185.8}{2.303 \times 8.314}\left(\frac{673 - 573}{673 \times 573}\right)$$

$$\text{or } K_{p_2} = 0.64 \times 10^{-5}\ \text{atm}^{-2}$$

Ex. 13 The equlibrium pressure of $NH_4CN\ (s) \rightleftharpoons NH_3(g) + HCN\ (g)$ is 0.298 atm. Calculate K_P. If NH_4CN (s) is allowed to decompose in presence of NH_3 at 0.50 atm then calculate partial pressure of HCN at equilibrium.

Sol. $$NH_4CN\ (s) \rightleftharpoons NH_3(g) + HCN\ (g)$$

	NH_4CN (s)	NH_3(g)	HCN (g)
Pressure at equilibrium	–	P	P

$\therefore$ Total pressure at equilibrium = 2P = 0.298 atm

$\therefore$ P = 0.149 atm

$\therefore K_P = P_{NH_3} \times P_{HCN} = 0.149 \times 0.149 = 0.0222\ \text{atm}^2$

If dissociation is made in presence of NH_3 at 0.5 atm

$$NH_4CN\ (s) \rightleftharpoons NH_3(g) + HCN\ (g)$$

	NH_4CN (s)	NH_3(g)	HCN (g)
Initial pressure	–	0.50	0
Pressure at equli.	–	(0.50+P')	P'

Also $K_P = P'\,(0.50 + P')$

or $0.0222 = P'\,(0.50 + P')$

$\therefore P' = 0.1656$ atm

Ex. 14 Ice melts slowly at higher altitude, why ?

Sol. According to Le Chatelier principle, the melting of ice is favoured at high pressure because the forward reaction ice $\longrightarrow$ water shows a decrease in volume. At higher altitude atmospheric pressure being low and thus ice melts slowly.

Ex. 15 Both metals Mg and Fe can reduce copper from a solution having Cu^{+2} ion according to equilibria.

$$Mg\ (s) + Cu^{+2} \rightleftharpoons Mg^{+2} + Cu\ (s)\ ;\ K_1 = 5 \times 10^{90}$$

$$Fe\ (s) + Cu^{+2} \rightleftharpoons Fe^{+2} + Cu\ (s)\ ;\ K_2 = 2 \times 10^{26}$$

Which metal will remove cupric ion from the solution to a greater extent.

Sol. Since $K_1 > K_2$, the product in the first reaction is much more favoured than in the second one. Mg thus removes more Cu^{+2} from solution than Fe does.

Ex. 16. A vessel at 1000 K contains CO_2 with a pressure of 0.6 atm. some of the CO_2 is converted into CO on addition of graphite. Calculate the value of K, if total pressure at equilibrium is 0.9 atm.

Sol. $$CO_2\ (g) + C\ (s) \rightleftharpoons 2\,CO\ (g)$$

	CO_2 (g)	C (s)	2 CO (g)
Initial pressure	0.6 atm	–	0
Equilibrium pressure	(0.6–x)atm		2x atm

From question, (0.6 – x) + 2x = 0.9 hence, x = 0.3 atm.

$$\text{Now, } K_P = \frac{P_{CO}^2}{P_{CO_2}} = \frac{(2x)^2}{(0.6 - x)} = 1.2\ \text{atm.}$$

Ex. 17 The value of K_C for the reaction,

$N_2 + 2O_2 \rightleftharpoons 2NO_2$ at a certain temperature is 900. Calculate the value of equilibrium constant for

(i) $2NO_2 \rightleftharpoons N_2 + 2O_2$

(ii) $\frac{1}{2} N_2 + O_2 \rightleftharpoons NO_2$

Sol. Equilibrium constant (K_C) for the reaction

$N_2 + 2O_2 \rightleftharpoons 2NO_2$ is

$$K_C = \frac{[NO_2]^2}{[N_2][O_2]^2} = 900$$

(i) For the reaction $2NO_2 \rightleftharpoons N_2 + 2O_2$, $K'_C = \frac{[N_2][O_2]^2}{[NO_2]^2} = \frac{1}{K_c}$

$$K'_C = \frac{1}{900} = 0.0011 \text{ mole litre}^{-1}$$

(ii) For the reaction $\frac{1}{2} N_2 + O_2 \rightleftharpoons NO_2$

$$K''_C = \frac{[NO_2]}{[N_2]^{1/2}[O_2]} = \sqrt{K_C}$$

$$K''_C = \sqrt{900} = 30 \text{ lit}^{1/2} \text{ mol}^{-1/2}$$

Ex. 18 When S in the form of S_8 is heated 800 K, the initial pressure of 1 atmosphere falls by 30 % at equilibrium. This is because of conversion of some S_8 to S_2. Calculate the K_P for reaction.

Sol.

	$S_8(g)$	$\rightleftharpoons 4S_2(g)$
Initial pressure	1 atm	0
Equilibrium pressure	(1–0.30) = 0.70 atm	4× 0.30 = 1.2 atm

$$\text{Now, } K_P = \frac{P_{S_2}^4}{P_{S_8}} = \frac{(1.2)^4}{0.70} = 2.9622 \text{ atm}^3$$

Ex. 19 The equilibrium constant K_C for $Y(g) \rightleftharpoons Z(g)$ is 1.1. Which gas has molar concentration greater than 1.

Sol. For $Y(g) \rightleftharpoons Z(g)$

$$K_C = \frac{[Z]}{[Y]} = 1.1$$

if Z = 1 ;	[Y] = 0.91
Case I	0.9 < [Y] < 1 only Z = 1
Case II	[Y] > 1 both [Y] and [Z] > 1

Ex. 20 The value of K_p is 1×10^{-3} atm^{-1} at 25°C for the reaction, $2NO + Cl_2 \rightleftharpoons 2NOCl$. A flask contains NO at 0.02 atm and 25°C. Calculate the moles of Cl_2 that must be added if 1% of NO is to be converted to NOCl at equilibrium. The volume of the flask is such that 0.2 moles of the gas produce 1 atm pressure at 25°C (Ignore the probable association of NO to N_2O_2).

Sol. Let, initial pressure of added Cl_2 is p atm.

	$2NO$	+	Cl_2	$\rightleftharpoons$	$2NOCl$
Initial	0.02atm		p atm		0
At equilibrium	$\left(0.02 - \dfrac{0.02}{100}\right)$		$\left(p - \dfrac{0.01}{100}\right)$		$\dfrac{0.02}{100}$
	$= 2 \times 10^{-4}(100 - 1)$ $= 198 \times 10^{-4}$ atm		$= p - 10^{-4}$ atm		$= 2 \times 10^{-4}$atm

$$K_p = \frac{P^2_{NOCl}}{P^2_{NO} \times P_{Cl_2}}$$

$$\Rightarrow 10^{-3} = \frac{(2 \times 10^{-4})^2}{(198 \times 10^{-4})^2 \times (p - 10^{-4})}$$

$$\Rightarrow p - 10^{-4} = \frac{4}{(198)^2 \times 10^{-3}} = 0.102$$

$\therefore$ $p = 0.102 + 0.0001 = 0.1021$ atm

Volume of the vessel can be calculated as follows,

PV = nRT

$$\text{or } V = \frac{nRT}{P} = \frac{0.2 \times 0.082 \times 298}{1} L = 4.887 \, L$$

Again applying, (PV = nRT) we can calculate the number of moles of Cl_2

$$n_{Cl_2} = \frac{PV}{RT} = \frac{0.1021 \times 4.887}{0.082 \times 298} = 0.0204 \text{ mol.}$$

Ex. 21 **(i)** Consider the heterogeneous equilibrium

$CaCO_3 (s) \rightleftharpoons CaO (s) + CO_2 (s)$ $K_p = 4 \times 10^{-2}$ atm ....**(i)**

$C (s) + CO_2 (g) \rightleftharpoons 2CO (g)$ $K_p' = 4.0$ atm .... **(ii)**

Calculate the partial pressure of CO (g) when $CaCO_3$ and C are mixed and allowed to attain equilibrium at the temperature for which the above two equilibria have been studied.

(ii) Calculate the pressure of CO_2 gas at 700 K in the heterogeneous equilibrium reaction.

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

If ΔG° for this reaction is 120.2 kJ/mol.

Sol. **(i)** For Eq. **(i)**, $K_p = P_{CO_2}$

From Eq. **(ii)**, $K_p' = P^2_{CO} / P_{Co_2}$

$\therefore K_p \times K_p' = (P_{CO})^2 = 4 \times 10^{-2} \times 4 = 16 \times 10^{-2}$ atm^2

$\therefore P_{CO} = \sqrt{16 \times 10^{-2} atm^2} = 0.4$ atm

(ii) $\Delta G^\circ = -2.303\,RT\log K_p$

$$\therefore \log K_p = -\frac{\Delta G^\circ}{2.303 \times R \times T} = -\frac{120.2 \times 10^3\,\text{Jmol}^{-1}}{2.303 \times (8.314\,\text{JK}^{-1}\text{mol}^{-1}) \times (700\,\text{K})}$$

$$\therefore K_p = 1.00 \times 10^{-9}\,\text{atm} = P_{CO_2}$$

Ex. 22 For the dissociation reaction $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

derive the expression for the degree of dissociation in terms of K_p and total pressure P.

Sol.

	$N_2O_4\,(g) \rightleftharpoons$	$2NO_2\,(g)$
Let initial no. of moles	1	0
Moles at equilibrium	$(1-\alpha)$	2α

$$K_p = \frac{(n_{NO_2})^2}{n_{N_2O_4}}\left[\frac{P}{\sum n}\right]^{\Delta n_g}$$

$$= \frac{(2\alpha)^2}{(1-\alpha)}\left[\frac{P}{(1-\alpha+2\alpha)}\right]^{(2-1)}$$

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

$$\Rightarrow \frac{4P}{K_p} = \frac{(1-\alpha^2)}{\alpha^2} = \frac{1}{\alpha^2} - 1$$

$$\frac{1}{\alpha^2} = \left(1 + \frac{4P}{K_p}\right) = \frac{4P + K_p}{K_p} \Rightarrow \alpha^2 = \frac{K_p}{4P + K_p} \Rightarrow \alpha = \sqrt{\frac{K_p}{4P + K_p}}$$

Ex. 23 For the reaction, $[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$, the equilibrium constant, K_c at 27°C is 4.0×10^{-19}. To find the silver ion concentration in a solution which is originally 0.10 M in KCN and 0.03 M in $AgNO_3$.

Sol. $Ag^+ + 2CN^- \rightleftharpoons [Ag(CN)_2]^-$

$$K_c' = \frac{[Ag(CN)_2]^-}{[Ag^+][CN^-]^2} = \frac{1}{K_c} = 2.5 \times 10^{20} \qquad \text{........(i)}$$

Very high value of K_c' show that complex forming equilibrium is spontaneous and almost all the Ag^+ ion would have reacted leaving xM in solution :

	Ag^+	$+ \; 2CN^- \rightleftharpoons$	$[Ag(CN)_2]^-$
initial	0.03M	0.1M	0
At eqm.	xM	$(0.1 - 0.03 \times 2x)$M	0.03 M

$$K_c' = 2.5 \times 10^{20} = \frac{0.03}{x(0.1 - 0.03 \times 2x)^2}$$

$$\therefore x = [Ag^+] = 7.5 \times 10^{-18}\,\text{M}$$

Ex. 24 In an experiment, 5 moles of HI were enclosed in a 10 litre container. At 817 K equilibrium constant for the gaseous reaction, $2HI\,(g) \rightleftharpoons H_2\,(g) + I_2\,(g)$, is 0.025. Calculate the equilibrium concentrations of HI, H_2 and I_2. What is the fraction of HI that decomposes?

Sol. Let, 2n be the number of moles of HI which is decomposed, the number of moles of H_2 and I_2 produced will be n mole each. Then molar concentrations of various species at equilibrium are

$$[HI] = \frac{(5-2n)}{10}\text{ mol/L},\quad [H_2] = \frac{n}{10}\text{ mol/L, and }\quad [I_2] = \frac{n}{10}\text{ mol/L}$$

$$\text{Also, } K_c = \frac{[H_2][I_2]}{[HI]^2} = \frac{\frac{n}{10}\times\frac{n}{10}}{\left(\frac{5-2n}{10}\right)^2}$$

$$0.025 = \frac{n^2}{(5-2n)^2}$$

Solving for n, we get n = 0.6

$$\therefore\ [HI] = \frac{5-2\times0.6}{10} = \frac{3.8}{10} = 0.38\text{ mol/L}$$

$$[H_2] = \frac{0.6}{10} = 0.06\text{ mol/L}$$

$$[I_2] = \frac{0.6}{10} = 0.06\text{ mol/L}$$

$$\text{Fraction of HI decomposed} = \frac{2\times0.6}{5}$$

$$= 0.24\text{ or }24\%$$

Ex. 25 When 1-pentyne **(A)** is treated with 4 N alcoholic KOH at 175°C, it is converted slowly into an equilibrium mixture of 1.3% 1-pentyne **(A)**, 95.2% 2-pentyne **(B)** and 3.5% of 1,2-pentadiene **(C)**. The equilibrium was maintained at 175°C. Calculate ΔG° for the following equilibria.

$$B \rightleftharpoons A \qquad \Delta G_1^\circ = ?$$

$$B \rightleftharpoons C \qquad \Delta G_2^\circ = ?$$

From the calculated value of ΔG_1° and ΔG_2° indicate the order of stability of **(A)**, **(B)** and **(C)**. Write a reasonable reaction mechanism showing all intermediates leading to **(A)**, **(B)** and **(C)**.

Sol. $\text{Pentyne} \xrightleftharpoons{KOH} \text{2-Pentyne} + \text{1,2-Pentadiene}$

(A) **(B)** **(C)**

At eqm.% 1.3 95.5 3.5

$$K_c = \frac{[B][C]}{[A]} = \frac{95.2\times3.5}{1.3} = 256.31 \qquad \text{..........(i)}$$

From eqm. $B \rightleftharpoons A$

$$K_1 = \frac{[A]}{[B]}$$

From Eqs. (i) and (ii), $K_1 = \frac{[C]}{K_c} = \frac{3.5}{256.31} = 0.013$ ....(ii)

$\Delta G^\circ = -2.303\ RT \log_{10} K_1$

$= -2.303 \times 8.314 \times 448 \log_{10} 0.013$

$= 16178.4$

$= 16.1784\ \text{kJ}$

Stability order for A and B is B > A

Similarly, $B \rightleftharpoons C$

$$K_2 = \frac{[C]}{[B]} = \frac{K_c \times [A]}{[B]^2} = \frac{256.31 \times 3.1}{95.2 \times 95.2} = 0.0876$$

$\therefore \Delta G_2^\circ = -2.303\ RT \log_{10} K_2$

$= -2.303 \times 8.314 \times 448 \log_{10} 0.0876$

$= 9068.06\ \text{J} = 9.068\ \text{kJ}$

Thus, stability order for B and C is B > C

Total order of stability is B > C > A.

Ex. 26 The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm is 3.62 g/L at 288 K and 1.84 g/L at 348 K. Calculate the entropy change during the reaction at 348 K.

Sol. $N_2O_4 \rightleftharpoons 2NO_2$

Case (i)

$$PV = nRT = \frac{w}{m_{mix}} RT$$

$$\Rightarrow m_{mix} = \frac{w}{V} \times \frac{RT}{P} = \frac{dRT}{P} = 3.62 \times 0.082 \times 288 = 85.6$$

Let, a mole of N_2O_4 and (1–a) mole of NO_2 exist at equilibrium

$\therefore a \times 92 + (1 - a) \times 46 = 85.6$

$\therefore a = 0.86$

$\therefore n_{N_2O_4} = 0.86\ \text{mol}, \qquad n_{NO_2} = 0.14\ \text{mol}$

$$K_p = \frac{0.14 \times 0.14}{0.86} \times \left[\frac{1}{1}\right]^1 = 0.0228\ \text{atm at } 288\ \text{K}.$$

Case (ii)

$$m_{mix} = \frac{dRT}{P} = 1.84 \times 0.0821 \times 348 = 52.57$$

Let, a' mol of N_2O_4 and (1 – a') mol of NO_2 exist at equilibrium

$\therefore a' \times 92 + (1 - a') \times 46 = 52.57$

$\therefore a' = 0.14$

$\therefore n_{N_2O_4} = 0.14\ \text{mol}, \qquad n_{NO_2} = 0.86\ \text{mol}$

$$\therefore K_p = \frac{0.86 \times 0.86}{0.14} \left[\frac{1}{1}\right]^1 = 5.283\ \text{atm at } 348\ \text{K}$$

$$\log_{10}\left(\frac{K_{p_2}}{K_{p_1}}\right)=\frac{\Delta H}{2.303R}\left[\frac{T_2-T_1}{T_1T_2}\right]$$

$$\Rightarrow \log_{10}\frac{5.283}{0.0228}=\frac{\Delta H}{2\times 2.303}\left[\frac{348-288}{348\times 288}\right]$$

$\therefore\ \Delta H = 18195.6\text{ cal} = 18.196\text{ Kcal}$

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

$= -2.303\times\ 2\times 348\times \log 5.283$

$= -1158.7\text{ cal.}$

$$\Delta S=\frac{\Delta H-\Delta G}{T}=\frac{18195.6+1158.7}{348}=55.62\text{ cal}$$

Ex. 27 The value of K_p for the reaction, $2H_2O\,(g) + 2Cl_2\,(g) \rightleftharpoons 4HCl\,(g) + O_2\,(g)$ is 0.035 atm at 500°C, when the partial pressures are expressed in atmosphere. Calculate K_c for the reaction,

$$\frac{1}{2}O_2\,(g)+2HCl\,(g) \rightleftharpoons Cl_2\,(g)+H_2O\,(g)$$

Sol. $K_p = K_c\,(RT)^{\Delta n}$

Δn = moles of products – moles of reactants = 5 – 4 = 1

$R = 0.0821\text{ L atm/mol/K}, T = 500 + 273 = 773\text{ K}$

$\therefore\ 0.035 = K_c\,(0.0821\times 773)$

$K_c = 5.515\times 10^{-4}\text{ mol L}^{-1}$

$\therefore\ K_c'$ for the reverse reaction would be $\dfrac{1}{K_c}$

$$\therefore\ K_c'=\frac{1}{5.515\times 10^{-4}}=1813.24\,(\text{mol L}^{-1})^{-1}$$

When a reaction is multiplied by any number n (integer or a fraction) then K_c' or K_p' becomes $(K_c)^n$ or $(K_p)^n$ of the original reaction.

$$\therefore\ K_c \text{ for } \frac{1}{2}O_2\,(g)+2HCl\,(g) \rightleftharpoons Cl_2\,(g)+H_2O\,(g)$$

is $\sqrt{1813.24} = 42.58\,(\text{mol.L}^{-1})^{-½}$

Ex. 28 K_p for the reaction $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$ is 0.66 at 46°C. Calculate the percent dissociation of N_2O_4 at 46°C and a total pressure of 0.5 atm. Also calculate the partial pressure of N_2O_4 and NO_2 at equilibrium.

Sol. This problem can be solved by two methods.

Method 1 : Let, the number of moles of N_2O_4 initially be 1 and α is the degree of dissociation of N_2O_4.

	N_2O_4	$\rightleftharpoons$	$2NO_2$
Initial moles	1		0
Moles at equilibrium	$1-\alpha$		2α

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

$$p_{N_2O_4} = \frac{1-\alpha}{1+\alpha} \times P_T$$

$$p_{NO_2} = \frac{2\alpha}{1+\alpha} \times P_T$$

$$\therefore K_p = \frac{p^2_{NO_2}}{p_{N_2O_4}} = \frac{4\alpha^2 P_T}{(1-\alpha)(1+\alpha)} = \frac{4\alpha^2 \times 0.5}{1-\alpha^2}$$

$\alpha = 0.5$, i.e. 50% dissociation

Hence, partial pressure of $N_2O_4 = 0.167$ atm.

and partial pressure of $NO_2 = 0.333$ atm.

Method 2 : Let, the partial pressure of NO_2 at equilibrium be p atm, then the partial pressure of N_2O_4 at equilibrium will be $(0.5 - p)$ atm.

$$\therefore K_p = \frac{p^2}{(0.5-p)} = 0.66$$

$p^2 + 0.66\,p - 0.33 = 0$

On solving, $p = 0.333$ atm.

$\therefore\ p_{NO_2} = 0.333$ atm and $p_{N_2O_4} = 0.167$ atm.

Ex. 29 0.5 moles of N_2 and 3 moles of PCl_5 are placed in a 100 litre container heated to 227°C. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation of PCl_5 and value of K_p for its dissociation.

Sol. Dissociation of PCl_5 is written as

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Let, x be the no. of moles of PCl_5 decomposed at equilibrium

	$PCl_5(g) \rightleftharpoons$	$PCl_3(g) +$	$Cl_2(g)$
Initial moles	3	0	0
Moles at eqm.	3 – x	x	x

Now, total gaseous moles in the container = n_T

n_T = moles of $(PCl_5 + PCl_3 + Cl_2)$ + moles of N_2

$n_T = 3 - x + x + x + 0.5 = 3.5 + x$

The mixture behaves ideally, hence $PV = n_T RT$

Let us, calculate no. of moles by using gas equation

$$\Rightarrow n_T = \frac{PV}{RT} = \frac{2.05 \times 100}{0.0821 \times 400} \Rightarrow n_T = 5$$

Now, equating the two values of n_T, we have

$3.5 + x = 5 \Rightarrow x = 1.5 \Rightarrow$ degree of dissociation = 1.5/3 = 1/2 = 0.5

$$\text{Now, } K_p = \frac{P_{PCl_3} \times P_{Cl_2}}{P_{PCl_5}}$$

$$P_{PCl_5} = \frac{3-x}{3.5+x}P = \frac{1.5}{5}\times 2.05 \ = 0.615 \text{ atm}$$

$$P_{PCl_3} = \frac{1.5}{5}\times 2.05 = 0.615 \text{ atm}$$

$$P_{Cl_2} = \frac{1.5}{5}\times 2.05 = 0.615 \text{ atm}$$

$$K_p = \frac{P_{PCl_3}\times P_{Cl_2}}{P_{PCl_5}} \text{ atm} \Rightarrow K_p = \frac{0.615\times 0.615}{0.615} = 0.615 \text{ atm}$$

$$K_p = 0.615 \text{ atm}$$

Note : The inert gases like N_2 or noble gases (He, Ne etc.) though do not take part in the reaction, but still they affect the degree of dissociation and equilibrium concentrations for the reactions in which $\Delta n \neq 0$. They add to the total pressure of the equilibrium mixture ($p \propto n$).

Ex. 30 For the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; K = 0.059 atm at 1000 K. 1 g of $CaCO_3$ is placed in a 10 litre container at 1000 K to reach the equilibrium. Calculate the mass of $CaCO_3$ left at equilibrium.

Sol.

$$\begin{array}{lcccc} & CaCO_3(s) & \rightleftharpoons & CaO(s) & + \quad CO_2(g) \\ \text{At equilibrium} & a-x & & x & x \end{array}$$

Here, a = initial moles of $CaCO_3$

$K_p = P_{CO_2} = 0.059$

$$n_{CO_2} = \frac{P_{CO_2}V}{RT} = \frac{0.059\times 10}{0.082\times 1000} = 7.2\times 10^{-3} \text{ moles}$$

Moles of $CaCO_3$ left = 0.01 – 0.0072 = 0.0028

Mass of $CaCO_3$ left = 0.28 g

Ex. 31 Given below are the values of $\Delta H°$ and $\Delta S°$ for the reaction at 27°C,

$$SO_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow SO_3(g)$$

$\Delta H° = 98.32$ kJ/mol $\qquad \Delta S° = -95$ J/mol. Calculate the value of K_p for the reaction.

Sol. $$\log_{10}K_p = \frac{\Delta H°}{2.303RT} + \frac{\Delta S°}{2.303\times R}$$

$$\therefore \log_{10}K_p = \frac{98320}{2.303\times 8.314\times 300} - \frac{95}{2.303\times 8.314} \Rightarrow K_p = 1.44\times 10^{12} \text{ atm}^{-1/2}$$

Ex. 32 In a mixture of N_2 and H_2, initially they are in a mole ratio of 1 : 3 at 30 atm and 300°C, the percentage of ammonia by volume under the equilibrium is 17.8%. Calculate the equilibrium constant (K_p) of the mixture, for the reaction,

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

Sol. Let, the initial moles N_2 and H_2 be 1 and 3 respectively (this assumption is valid as K_p will not depend on the exact number of moles of N_2 and H_2. One can even start with x and 3x)

	$N_2(g)$	$+ 3H_2(g)$	$\rightleftharpoons$	$2NH_3(g)$
Initially	1	3		0
At equilibrium	1–x	3–3x		2x

Since % by volume of a gas is same as % by mole,

$$\therefore \frac{2x}{4-2x} = 0.178$$

$$\therefore x = \frac{4 \times 0.178}{(2 + 2 \times 0.178)} = 0.302$$

$$\therefore \text{Mole fraction of } H_2 \text{ at equilibrium} = \frac{3-3x}{4-2x} = 0.6165$$

Mole fraction of N_2 at equilibrium $= 1 - 0.6165 - 0.178 = 0.2055$

$$\therefore K_p = \frac{(X_{NH_3} \times P_T)^2}{(X_{N_2} \times P_T)(X_{H_2} \times P_T)^3} = \frac{(0.178 \times 30)^2}{(0.2055 \times 30)(0.6165 \times 30)^3}$$

$K_p = 7.31 \times 10^{-4}\ \text{atm}^{-2}$.

Ex. 33 Ammonium hydrogen sulphide dissociated according to the equation,

$NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$. If the observed pressure of the mixture is 2.24 atm at 106°C, what is the equilibrium constant K_p of the reaction ?

Sol. The reaction is $NH_4HS\ (s) \rightleftharpoons NH_3\ (g) + H_2S\ (g)$.

If α is the degree of dissociation of equilibrium,

Total moles of NH_3 and H_2S at equilibrium $= 2\alpha$.

$$\text{Partial pressure} = \frac{\text{Moles of substance}}{\text{Total no. of moles}} \times \text{Total pressure}$$

$$\therefore p_{NH_3} = \frac{\alpha}{2\alpha} \times P = 0.5\,P\ ;\ p_{H_2S} = \frac{\alpha}{2\alpha} \times P = 0.5\,P$$

$K_p = p_{NH_3} \times p_{H_2S} = 0.5\,P \times 0.5\,P = 0.25P^2$

Substituting the value of $P = 2.24$ atm.

$K_p = 0.25 \times 2.24 \times 2.24 = 1.2544\ \text{atm}^2$

Alternatively :

At equilibrium $p_{NH_3} + p_{H_2S} = 2.24$ atm

As $p_{NH_3} = p_{H_2S}$

$$\therefore p_{NH_3} = \frac{2.24}{2} = 1.12\ \text{atm}$$

$\therefore K_p = 1.12 \times 1.12 = 1.2544\ \text{atm}^2$

Exercise # 1 [Single Correct Choice Type Questions]

1. A chemical reaction is at equilibrium when

(A) Reactants are completely transformed into products

(B) The rates of forward and backward reactions are equal

(C) Formation of products is minimised

(D) Equal amounts of reactants and products are present

2. A reversible reaction is one which

(A) Proceeds in one direction **(B)** Proceeds in both directions

(C) Proceeds spontaneously **(D)** All the statements are wrong

3. According to law of mass action rate of a chemical reaction is proportional to

(A) Concentration of reactants **(B)** Molar concentration of reactants

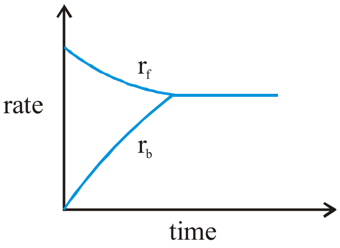
(C) Concentration of products **(D)** Molar concentration of products

4. Molar concentration of 96 g of O_2 contained in a 2 litre vessel is :

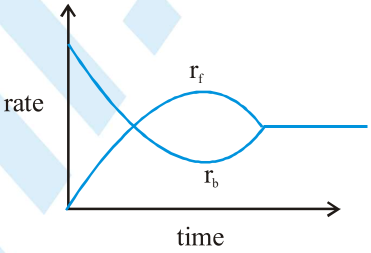
(A) 16 mol/litre **(B)** 1.5 mol/litre **(C)** 4 mol/litre **(D)** 24 mol/litre

5. Rate of reaction curve for equilibrium can be like : [r_f = forward rate , r_b = backward rate]

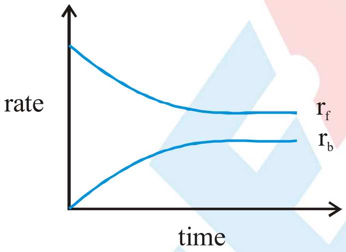
(A)



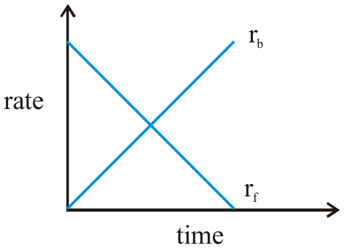
(B)



(C)



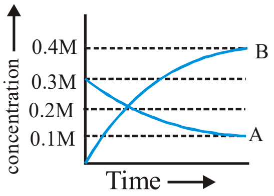
(D)



6. For the reaction 3 A (g) + B (g) $\rightleftharpoons$ 2 C (g) at a given temperature, K_c = 9.0. What must be the volume of the flask, if a mixture of 2.0 mol each of A, B and C exist in equilibrium?

(A) 6 L **(B)** 9 L **(C)** 36 L **(D)** None of these

7. The figure show the change in concentration of species A and B as a fuctional of time . The equilibrium constant K_C for the reaction A(g) $\rightleftharpoons$ 2B (g) is :



(A) $K_c > 1$ **(B)** $K < 1$ **(C)** $K = 1$ **(D)** data insufficient

8. In a reversible reaction $A \underset{k_2}{\overset{k_1}{\rightleftharpoons}} B$, the initial concentration of A and B are a and b in moles per litre, k_1 and k_2 are rate constants for forward & backward reactions respectively and the equilibrium concentrations are $(a-x)$ and $(b+x)$ respectively; express x in terms of k_1, k_2, a and b.

(A) $\dfrac{k_1a-k_2b}{k_1+k_2}$ **(B)** $\dfrac{k_1a-k_2b}{k_1-k_2}$ **(C)** $\dfrac{k_1a-k_2b}{k_1k_2}$ **(D)** $\dfrac{k_1a+k_2b}{k_1+k_2}$

9. The reaction $A(g) + B(g) \rightleftharpoons C(g) + D(g)$ is studied in a one litre vessel at 250°C. The initial concentration of A was 3n and that of B was n. When equilibrium was attained, equilibrium concentration of C was found to the equal to the equilibrium concentration of B. What is the concentration of D at equilibrium?

(A) n/2 **(B)** (3n – 1/2) **(C)** (n – n/3) **(D)** n

10. $K_c = 9$ for the reaction, $A + B \rightleftharpoons C + D$, If A and B are taken in equal amounts, then amount of C in equilibrium is

(A) 1 **(B)** 0.25 **(C)** 0.75 **(D)** None of these

11. Using molar concentration, What is the unit of K_c for the reaction

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

(A) M^{-2} **(B)** M^2 **(C)** M^{-1} **(D)** M

12. What is the unit of K_p for the reaction ?

$$CS_2\,(g) + 4H_2\,(g) \rightleftharpoons CH_4\,(g) + 2H_2S\,(g)$$

(A) atm **(B)** atm^{-2} **(C)** atm^2 **(D)** atm^{-1}

13. N_2 and H_2 are taken in 1 : 3 molar ratio in a closed vessel to attained the following equilibrium

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. Find K_p for reaction at total pressure of 2P if P_{N_2} at equilibrium is $\dfrac{P}{3}$

(A) $\dfrac{1}{3P^2}$ **(B)** $\dfrac{4}{3P^2}$ **(C)** $\dfrac{4P^2}{3}$ **(D)** none

14. The equilibrium constant, K_p for the reaction

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

is 4.0 atm^{-1} at 1000 K. What would be the partial pressure of O_2 if at equilibrium the amount of SO_2 and SO_3 is the same ?

(A) 16.0 atm **(B)** 0.25 atm **(C)** 1 atm **(D)** 0.75 atm

15. For the reaction

$A_2(g) + 2B_2 \rightleftharpoons 2C_2(g)$

the partial pressure of A_2, B_2 at equilibrium are 0.80 atm and 0.40 atm respectively. The pressure of the system is 2.80 atm. The equilibrium constant K_p will be

(A) 20 **(B)** 5.0 **(C)** 0.02 **(D)** 0.2

16. At 527°C, the reaction given below has $K_C = 4$

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

What is the K_p for the reaction ?

(A) $16 \times (800\,R)^2$ **(B)** $\left(\dfrac{800\,R}{4}\right)^{-2}$ **(C)** $4 \times 800\,R$ **(D)** None of these

17. The value of K_p for the reaction, $2H_2O(g) + 2C\bullet_2(g) \rightleftharpoons 4HC\bullet(g) + O_2(g)$ is 0.03 atm at 427° C, when the partial pressure are expressed in atmosphere then the value of K_C for the same reaction is :

(A) 5.23×10^{-4} **(B)** 7.34×10^{-4} **(C)** 3.2×10^{-3} **(D)** 5.43×10^{-5}

18. $\log \frac{K_p}{K_c} + \log RT = 0$ is a relationship for the reaction :

(A) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ **(B)** $2SO_2 + O_2 \rightleftharpoons 2SO_3$

(C) $H_2 + I_2 \rightleftharpoons 2HI$ **(D)** $N_2 + 3H_2 \rightleftharpoons 2NH_3$

19. The equilibrium constant of the reaction $SO_2(g) + ½O_2(g) \rightleftharpoons SO_3(g)$ is 4×10^{-3} atm$^{-1/2}$. The equilibrium constant of the reaction $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ would be :

(A) 250 atm **(B)** 4×10^3 atm **(C)** 0.25×10^4 atm **(D)** 6.25×10^4 atm

20. Equilibrium constant for the reactions,

$2\,NO + O_2 \rightleftharpoons 2\,NO_2$ is K_{C_1} ;

$NO_2 + SO_2 \rightleftharpoons SO_3 + NO$ is K_{C_2} and

$2\,SO_3 \rightleftharpoons 2\,SO_2 + O_2$ is K_{C_3} then correct reaction is :

(A) $K_{C_3} = K_{C_1} \times K_{C_2}$ **(B)** $K_{C_3} \times K_{C_1} \times K^2_{C_2} = 1$

(C) $K_{C_3} \times K_{C_1} \times K_{C_2} = 1$ **(D)** $K_{C_3} \times K^2_{C_1} \times K_{C_2} = 1$

21. At a certain temperature, the following reactions have the equilibrium constant as shown below :

$S(s) + O_2(g) \rightleftharpoons SO_2(g); K_c = 5 \times 10^{52}$

$2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g); K_c = 10^{29}$

What is the equilibrium constant K_c for the reaction at the same temperature ?

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

(A) 2.5×10^{76} **(B)** 4×10^{23} **(C)** 4×10^{-77} **(D)** None of these

22. Sulfide ion in alkaline solution reacts with solid sulfur to form polysulfide ions having formulae S_2^{2-}, S_3^{2-}, S_4^{2-} and so on. The equilibrium constant for the formation of S_2^{2-} is $K_1 = 12$ & for the formation of S_3^{2-} is $K_2 = 132$, both from S and S^{2-}. What is the equilibrium constant for the formation of S_3^{2-} from S_2^{2-} and S?

(A) 11 **(B)** 12 **(C)** 132 **(D)** None of these

23. When alcohol ($C_2H_5OH(\bullet)$) and acetic acid ($CH_3COOH(\bullet)$) are mixed together in equimolar ratio at 27°C , 33% of each is converted into ester. Then the K_C for the equilibrium

$C_2H_5OH(\bullet) + CH_3COOH(\bullet) \rightleftharpoons CH_3COOC_2H_5(\bullet) + H_2O(\bullet)$ is :

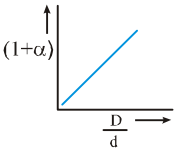
(A) 4 **(B)** 1/4 **(C)** 9 **(D)** 1/9

24. One litre of 2M acetic acid and one litre of 3M ethyl alcohol are mixed to form ester according to the given equation : $CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$.
If each solution is diluted by adding equal volume (1 litre) of water by how many times the initial forward rate is reduced ?

(A) 4 times **(B)** 2 times **(C)** 0.5 times **(D)** 0.25 times

25. In the dissociation of N_2O_4 into NO_2, $(1 + \alpha)$ values with the vapour densities ratio $\left(\frac{D}{d}\right)$ is as given by :

[α-degree of dissociation, D-vapour density before dissociation, d-vapour density after dissociation]

(A)


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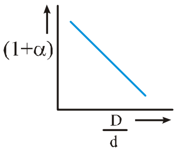
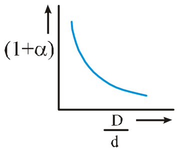


(C)


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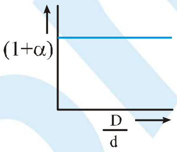
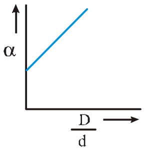
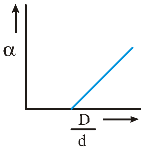
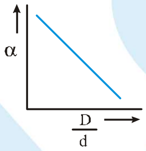
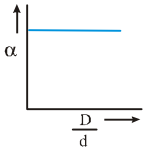


26. In the above question, α varies with $\frac{D}{d}$ according to :

(A)


(B)


(C)


(D)


27. For the reaction $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$, if percentage dissociation of N_2O_4 are 20%, 45%, 65% & 80%, then the sequence of observed vapour densities will be :

(A) $d_{20} > d_{45} > d_{65} > d_{80}$
(B) $d_{80} > d_{65} > d_{45} > d_{20}$
(C) $d_{20} = d_{45} = d_{65} = d_{80}$
(D) $(d_{20} = d_{45}) > (d_{65} = d_{80})$

28. For the dissociation reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the degree of dissociation **(A)** in terms of K_p and total equilibrium pressure P is:

(A) $\alpha = \sqrt{\frac{4p + K_p}{K_p}}$
(B) $\alpha = \sqrt{\frac{K_p}{4p + K_p}}$

(C) $\alpha = \sqrt{\frac{K_p}{4p}}$
(D) None of these

29. The degree of dissociation of SO_3 is α at equilibrium pressure P_0.
K_p for $2SO_3(g) \rightleftharpoons 2SO_2(g) + O_2(g)$ is

(A) $[(P_0\alpha^3)/2(1-\alpha)^3]$
(B) $[(P_0\alpha^3)/(2+\alpha)(1-\alpha)^2]$
(C) $[(P_0\alpha^2)/2(1-\alpha)^2]$
(D) None of these

30. What is the minimum mass of $CaCO_3$(s), below which it decomposes completely, required to establish equilibrium in a 6.50 litre container for the reaction : $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; $K_c = 0.05$ mole/litre

(A) 32.5 g
(B) 24.6 g
(C) 40.9 g
(D) 8.0 gm

31. In the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$, the equilibrium pressure is 12 atm. If 50% of CO_2 reacts then K_p will be

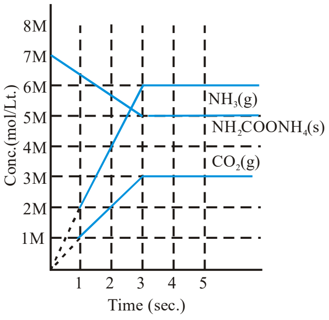
(A) 12 atm
(B) 16 atm
(C) 20 atm
(D) 24 atm

32. Solid ammonium carbamate dissociate to give ammonia and carbon dioxide as follows

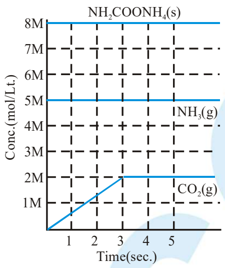
$$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

which of the following graph correctly represents the equilibrium.

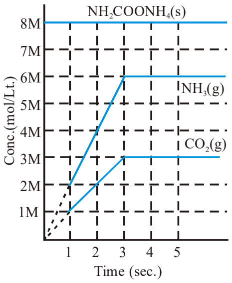
(A)



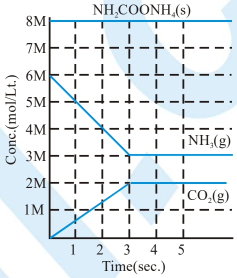
(B)



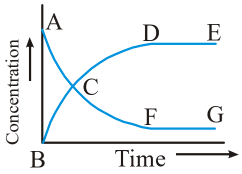
(C)



(D)



33. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $K_c = 4$. This reversible reaction is studied graphically as shown in figure. Select the correct statements out of I, II and III.



I : Reaction quotient has maximum value at point A.

II : Reaction proceeds left to right at a point when

$$[N_2O_4] = [NO_2] = 0.1\text{ M}.$$

III : $K_c = Q$ when point D or F is reached :

(A) I, II **(B)** II, III **(C)** I, III **(D)** I, II, III

34. 2 mole each of SO_3, CO, SO_2 and CO_2 is taken in a one lit. vessel. If K_C for

$$SO_3(g) + CO(g) \rightleftharpoons SO_2(g) + CO_2(g) \text{ is } 1/9 \text{ then}$$

(A) total no. of moles at equilibrium are less than 8

(B) $n(SO_3) + n(CO_2) = 4$

(C) $[n(SO_2)/n(CO)] < 1$

(D) both **(B)** and **(C)**.

35. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$K_c = 66.9$ at 350°C and $K_c = 50.0$ at 448°C. The reaction has

(A) $\Delta H = +$ ve

(B) $\Delta H = -$ ve

(C) $\Delta H =$ zero

(D) ΔH sign can not be determined

36. The correct relationship between standard free energy change in a reaction and the corresponding equilibrium constant K is

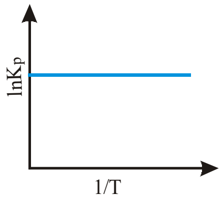
(A) $-\Delta G^o = RT \ln K$ **(B)** $\Delta G = RT \ln K$ **(C)** $-\Delta G = RT \ln K$ **(D)** $\Delta G^o = RT \ln K$

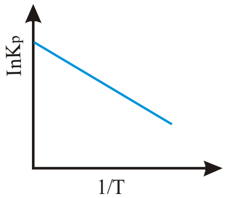
37. The effect of temperature on equilibrium constant is expressed as $(T_2 > T_1)$

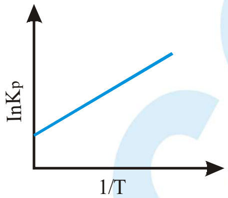
$\log K_2 / K_1 = \dfrac{-\Delta H}{2.303}\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]$. For endothermic reaction false statement is

(A) $\left[\dfrac{1}{T_2} - \dfrac{1}{T_1}\right]$ = positive **(B)** ΔH = positive **(C)** $\log K_2 > \log K_1$ **(D)** $K_2 > K_1$

38. An exothermic reaction is represented by the graph :

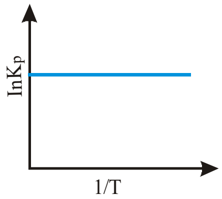
(A)


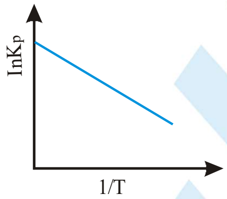
(B)


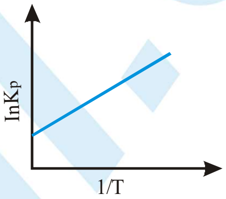
(C)


(D) None of these

39. An endothermic reaction is represented by the graph :

(A)


(B)


(C)


(D) None of these

40. The value of $\Delta G°$ for a reaction in aqueous phase having $K_c = 1$, would be:

(A) –RT **(B)** –1 **(C)** 0 **(D)** +RT

41. For the equilibrium $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$

$K_p = 2.25 \times 10^{-4}$ atm^2 and vapour pressure of water is 22.8 Torr at 298 K.

$CuSO_4.5H_2O(s)$ is efflorescent (i.e., loses water) when relative humidity is :

(A) less than 33.3% **(B)** less than 50 % **(C)** less than 66.6% **(D)** above 66.6%

42. Equilibrium constant for the following equilibrium is given at 0°C.

$Na_2HPO_4 . 12H_2O (s) \rightleftharpoons Na_2HPO_4 . 7H_2O (s) + 5H_2O(g)$ $K_P = 31.25 \times 10^{-13}$

At equilibrium what will be partial pressure of water vapour :

(A) $\dfrac{1}{5} \times 10^{-3}$ atm **(B)** 0.5×10^{-3} atm **(C)** 5×10^{-2} atm **(D)** 5×10^{-3} atm.

43. A liquid is in equilibrium with its vapour at its boiling point. On the average the molecules in the two phases have equal

(A) inter molecular forces **(B)** potential energy **(C)** kinetic energy **(D)** none of these .

44. Densities of diamond and graphite are 3.5 and 2.3 g/mL.

C (diamond) $\rightleftharpoons$ C (graphite) $\Delta_r H = -1.9$ kJ/mole

favourable conditions for formation of diamond are

(A) high pressure and low temperature **(B)** low pressure and high temperature

(C) high pressure and high temperature **(D)** low pressure and low temperature

45. Introduction of inert gas (at the same temperature) will affect the equilibrium if :

(A) volume is constant and $\Delta n_g \neq 0$
(B) pressure is constant and $\Delta n_g \neq 0$
(C) volume is constant and $\Delta n_g = 0$
(D) pressure is constant and $\Delta n_g = 0$

46. For the reaction $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$ at a given temperature the equilibrium amount of $CO_2(g)$ can be increased by :

(A) adding a suitable catalyst
(B) adding an inert gas
(C) decreasing the volume of container
(D) increasing the amount of CO(g)

47. Given the following reaction at equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. Some inert gas at constant pressure is added to the system. Predict which of the following facts will be affected.

(A) More $NH_3(g)$ is produced
(B) Less $NH_3(g)$ is produced
(C) No affect on the equilibrium
(D) K_p of the reaction is decreased

48. The equilibrium, $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed container and an inert gas, helium, is introduced. Which of the following statement(s) is/are correct.

(A) Concentrations of SO_2, Cl_2 and SO_2Cl_2 are changed
(B) No effect on equilibrium
(C) Concentration of SO_2 is reduced
(D) K_p of reaction is increasing

49. An equilibrium mixture in a vessel of capacity 100 litre contain 1 mol N_2, 2 mol O_2 and 3 mol NO. Number of moles of O_2 to be added so that at new equilibrium the conc. of NO is found to be 0.04 mol/lit.:

(A) (101/18)
(B) (101/9)
(C) (202/9)
(D) None of these

50. The reactions $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ and $COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$ are simultaneously in equilibrium at constant volume. A few moles of CO(g) are introduced into the vessel. After some time, the new equilibrium concentration of

(A) PCl_5 will remain unchanged
(B) Cl_2 will be greater
(C) PCl_5 will become less
(D) PCl_5 will become greater

51. The two equilibria, $AB(aq) \rightleftharpoons A^+(aq) + B^-(aq)$ and $AB(aq) + B^-(aq) \rightleftharpoons AB_2^-(aq)$ are simultaneously maintained in a solution with equilibrium constants, K_1 and K_2 respectively. The ratio of concentration of A^+ to AB_2^- in the solution is :

(A) directly proportional to the concentration of B^- (aq.).
(B) inversely proportional to the concentration of B^- (aq.).
(C) directly proportional to the square of the concentration of B^- (aq.).
(D) inversely proportional to the square of the concentration of B^- (aq.).

52. In the preceeding problem, if $[A^+]$ and $[AB_2^-]$ are y and x respectively, under equilibrium produced by adding the substance AB to the solvents, then K_1/K_2 is equal to

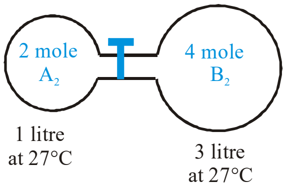
(A) $\frac{y}{x}(y-x)^2$
(B) $\frac{y^2(x+y)}{x}$
(C) $\frac{y^2(x+y)}{x}$
(D) $\frac{y}{x}(x-y)$

[**Note:** Use the information of the preceeding problem]

53. The equilibrium $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ is estabilished in a reaction vessel of 2.5 L capacity. The amounts of N_2 and O_2 taken at the start were respectively 2 moles and 4 moles. Half a mole of nitrogen has been used up at equilibrium. The molar concentration of nitric oxide is :

(A) 0.2
(B) 0.4
(C) 0.6
(D) 0.1

54.



The gas A_2 in the left flask allowed to react with gas B_2 present in right flask as

$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)\,;\ K_c = 4 \text{ at } 27°C.$$

What is the concentration of AB when equilibrium is established?

(A) 1.33 M **(B)** 2.66 M **(C)** 0.66 M **(D)** 0.33 M

55. $X_2(g) + Y_2(g) \rightleftharpoons 2XY(g)$ reaction was studied at a certain temperature. In the beginning 1 mole of X_2 was taken in a one litre flask and 2 moles of Y_2 was taken in another 2 litre flask and both these containers are connected so equilibrium can be established. What is the equilibrium concentration of X_2 and Y_2? Given Equilibrium concentration of $[XY] = 0.6$ moles/litre.

(A) $\left(\frac{1}{3} - 0.3\right), \left(\frac{2}{3} - 0.3\right)$ **(B)** $\left(\frac{1}{3} - 0.6\right), \left(\frac{2}{3} - 0.6\right)$

(C) $(1 - 0.3), (2 - 0.3)$ **(D)** $(1 - 0.6), (2 - 0.6)$

56. The active mass of 64 gm of HI in a two litre flask would be :

(A) 2 **(B)** 1 **(C)** 5 **(D)** 0.25

57. Ratio of active masses of 22 g CO_2, 3g H_2 and 7g N_2 in a gaseous mixture :

(A) 22 : 3 : 7 **(B)** 0.5 : 3 : 7 **(C)** 1 : 3 : 1 **(D)** 1 : 3 : 0.5

58. For the following gases equilibrium, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, K_p is found to be equal to K_c. This is attained when:

(A) 0ºC **(B)** 273 K **(C)** 1 K **(D)** 12.19 K

59. Consider the following reversible gaseous reactions (at 298 K) :

(a) $N_2O_4 \rightleftharpoons 2NO_2$ **(b)** $2SO_2 + O_2 \rightleftharpoons 2SO_3$

(c) $2HI \rightleftharpoons H_2 + I_2$ **(d)** $X + Y \rightleftharpoons 4Z$

Highest and lowest value of $\frac{K_p}{K_c}$ will be shown by the equilibrium

(A) d, b **(B)** a, c **(C)** a, b **(D)** b, c

60. A 10 litre box contains O_3 and O_2 at equilibrium at 2000 K. $K_P = 4 \times 10^{14}$ atm for $2O_3(g) \rightleftharpoons 3O_2(g)$. Assume that $P_{O_2} >> P_{O_3}$ and if total pressure is 8 atm, then partial pressure of O_3 will be :

(A) 8×10^{-5} atm **(B)** 11.3×10^{-7} atm **(C)** 9.71×10^{-6} atm **(D)** 9.71×10^{-2} atm

61. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ in the reversible reaction the moles of PCl_5, PCl_3 and Cl_2 are a, b and c respectively and total pressure is P then value of K_p is :

(A) $\frac{bc}{a}.RT$ **(B)** $\frac{b}{(a+b+c)}.P$ **(C)** $\frac{bc.P}{a(a+b+c)}$ **(D)** $\frac{c}{(a+b+c)}.P$

62. A sample of pure NO_2 gas heated to 1000 K decomposes : $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$. The equilibrium constant K_p is 100 atm. Analysis shows that the partial pressure of O_2 is 0.25 atm. at equilibrium. The partial pressure of NO_2 at equilibrium is:

(A) 0.03 **(B)** 0.25 **(C)** 0.025 **(D)** 0.04

63. Ammonia dissociates into N_2 and H_2 such that degree of dissociation α is very less than 1 and equilibrium pressure is P_0 then the value of α is [if K_p for $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ is $27 \times 10^{-8} P_0^2$] :
(A) 10^{-4} **(B)** 4×10^{-4} **(C)** 0.02 **(D)** can't be calculated.

64. At 727°C and 1.23 atm of total equilibrium pressure, SO_3 is partially dissociated into SO_2 and O_2 according to $SO_3(g) \rightleftharpoons SO_2(g) + 1/2O_2(g)$. The density of equilibrium mixture is 0.9 gm/litre. The degree of dissociation is:
(A) 1/3 **(B)** 2/3 **(C)** 1/4 **(D)** 1/5.

65. If for $2A_2B(g) \rightleftharpoons 2A_2(g) + B_2(g)$, K_p = TOTAL PRESSURE (at equilibrium) and starting the dissociation from 4 mol of A_2B then :
(A) degree of dissociation of A_2B will be (2/3).
(B) total no. of moles at equilibrium will be (14/3).
(C) at equilibrium the no. of moles of A_2B are not equal to the no. of moles of B_2.
(D) at equilibrium the no. of moles of A_2B are equal to the no. of moles of A_2.

66. The formation constant of $[Ni(NH_3)_6]^{2+}$ is 6×10^8 at 25⁰C. If 50 ml of 2.0 M NH_3 is added to 50 ml of 0.20 M solution of Ni^{2+}, the concentration of Ni^{2+} ion will be nearly equal to :
(A) 3×10^{-10} mole litre^{-1} **(B)** 2×10^{-10} mole litre^{-1}
(C) 2×10^{-9} mole litre^{-1} **(D)** 4×10^{-8} mole litre^{-1}

67. At a temperature T, a compound $AB_4(g)$ dissociates as $2AB_4(g) \rightleftharpoons A_2(g) + 4B_2(g)$ with a degree of dissociation x, which is small compared with unity. The expression of K_p in terms of x and total pressure P is ;
(A) $8P^3x^5$ **(B)** $256P^3x^5$ **(C)** $4Px^2$ **(D)** None of these

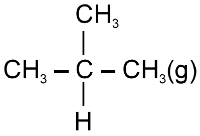
68. The degree of dissociation of PCl_5 (aq) obeying the equilibrium, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, is approximately related to the presure at equilibrium by (given $\alpha << 1$) :
(A) $\alpha \propto P$ **(B)** $\alpha \propto \frac{1}{\sqrt{P}}$ **(C)** $\alpha \propto \frac{1}{P^2}$ **(D)** $\alpha \propto \frac{1}{P^4}$

69. A 10L container at 300K contains CO_2 gas at pressure of 0.2 atm and an excess solid CaO (neglect the volume of solid CaO). The volume of container is now decreased by moving the movable piston fitted in the container. What will be the maximum volume of container when pressure of CO_2 attains its maximum value given that

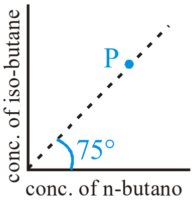
$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \quad K_p = 0.800 \text{ atm}$$

(A) 5 L **(B)** 2.5 L **(C)** 1 L **(D)** The information is insufficient.

70. A reaction mixture containing H_2, N_2 and NH_3 has partial pressure 2 atm, 1 atm and 3 atm respectively at 725 K. If the value of K_P for the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 4.28×10^{-5} atm^{-2} at 725 K, in which direction the net reaction will go :
(A) Forward **(B)** Backward
(C) No net reaction **(D)** Direction of reaction cannot be predicted



71. For the equilibrium $CH_3-CH_2-CH_2-CH_3(g) \rightleftharpoons CH_3-\underset{\underset{H}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3(g)$ equilibrium constant is found to be 1.732 at 298 K. Now if in a vessel at 298 K, a mixture of these two gases be taken as represented by the point P in the figure, predict what will happen
(A) Immediately, above equilibrium will be setup
(B) Above reaction will go in the forward direction till it attains equilibrium
(C) Above reaction will go in the backward direction till it attains equilibrium
(D) Nothing can be said



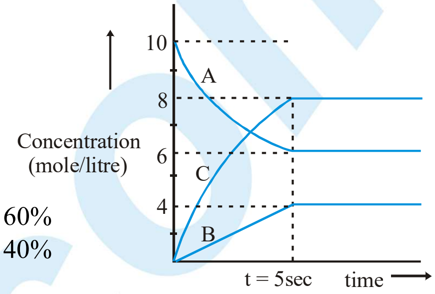
72. Ammonia gas at 15 atm is introduced in a rigid vessel at 300 K. At equilibrium the total pressure of the vessel is found to be 40.11 atm at 300ºC. The degree of dissociation of NH_3 will be:

(A) 0.6 **(B)** 0.4 **(C)** Unpredictable **(D)** None of these

73. Attainment of the equilibrium

$$A(g) \rightleftharpoons 2C(g) + B(g)$$

gave the following graph.



Find the correct option.
(% dissociation = fraction dissociated × 100)

(A) At t = 5 sec equilibrium has been reached and $K_c = 128$ (mol/litre)^2
(B) At t = 5 sec equilibrium has been reached and % dissociation of A is 60%
(C) At t = 5 sec equilibrium has been reached and % dissociation of A is 40%
(D) None of these

74. Addition of water to which of the following equilibria causes it to shift in the backward direction?

(A) $CH_3NH_2\,(aq) + H_2O\,(●) \rightleftharpoons CH_3NH_3^{\oplus}(aq) + OH^-(aq)$
(B) $AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq)$
(C) $HCN\,(aq) + H_2O\,(●) \rightleftharpoons H_3O^+\,(aq) + CN^-\,(aq)$
(D) $[Cr(dien)_2]^{3+}\,(aq) + 3H_2O\,(●) + 3Cl^-\,(aq) \rightleftharpoons [Cr\,(H_2O)_3Cl_3]\,(aq) + 2\,dien\,(aq)$

75. The equilibrium constant for the reaction $Br_2 \rightleftharpoons 2Br$ at 500 K and 700 K are 1×10^{-10} and 1×10^{-5} respectively. The reaction is :

(A) Endothermic **(B)** Exothermic **(C)** Fast **(D)** Slow

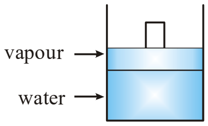
76. The value of k_p for the reaction at 27^0C

$$Br_2(●) + Cl_2(g) \rightleftharpoons 2BrCl(g)$$

is '1 atm'. At equilibrium in a closed container partial pressure of BrCl gas is 0.1 atm and at this temperature the vapour pressure of Br_2(●) is also 0.1 atm. Then what will be minimum moles of Br_2(●) to be added to 1 mole of Cl_2, initially, to get above equilibrium situation :

(A) $\frac{10}{6}$ moles **(B)** $\frac{5}{6}$ moles **(C)** $\frac{15}{6}$ moles **(D)** 2 moles

77. Some quantity of water is contained in a container as shown in figure. As neon is added to this system at constant pressure, the amount of liquid water in the vessel



(A) increases **(B)** decreases
(C) remains same **(D)** changes unpredictably

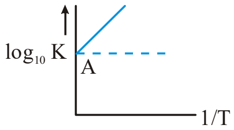
78. When a bottle of cold drink is opened, the gas comes out with a fizz due to :

(A) Decrease in temperature
(B) Increase in pressure
(C) Decrease in pressure suddenly which results in decrease of solubility of CO_2 gas in water
(D) None

79. For an equilibrium $H_2O(s) \rightleftharpoons H_2O(●)$ which of the following statements is true.

(A) The pressure changes do not affect the equilibrium
(B) More of ice melts if pressure on the system is increased
(C) More of liquid freezes if pressure on the system is increased
(D) The pressure changes may increase or decrease the degree of advancement of the reaction depending upon the temperature of the system

80. Variation of $\log_{10} K$ with $\frac{1}{T}$ is shown by the following graph in which straight line is at 45°, hence $\Delta H°$ is :



(A) + 4.606 cal **(B)** – 4.606 cal **(C)** 2 cal **(D)** – 2 cal

81. The equilibrium constant for, $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ is 0.0118 at 1300 K while the heat of dissociation is 597.4 kJ. The standard equilibrium constant of the reaction at 1200 K is :

(A) 1.180×10^{-4}
(B) 11.80
(C) 118.0
(D) cannot be calculated from given data.

82. In the system, $LaCl_3(s) + H_2O(g) + \text{heat} \rightleftharpoons LaClO(s) + 2HCl(g)$, equilibrium is established. More water vapour is added to restablish the equlibrium. The pressure of water vapour is doubled. The factor by which pressure of HCl is changed is:

(A) 2 **(B)** $\sqrt{2}$ **(C)** $\sqrt{3}$ **(D)** $\sqrt{5}$

83. **Statement-1 :** $A(s) \rightleftharpoons B(g) + C(g) \; ; Kp_1$

$X(s) \rightleftharpoons B(g) + Y(g) \; ; Kp_2 = 3Kp_1$

Total pressure of B over the mixture of solid A and X is greater than pressure of B either over excess solid A or over excess solid X But less then their directly sumup value when excess of solid A and excess of solid B kept in different container.

Statement-2 : In presence of each other, degree of dissociation of both solids decreases.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1
(C) Statement-1 is True, Statement-2 is False
(D) Statement-1 is False, Statement-2 is True

84. Two solid A and B are present in two different container having same volume and same temperature following equilibrium are established :

In container (1) $A(s) \rightleftharpoons D(g) + C(g)$ $P_T = 40$ atm at equilibrium

In container (2) $B(s) \rightleftharpoons E(g) + F(g)$ $P_T = 60$ atm at equilibrium

If excess of A and B are added to a third container having double the volume and at same temperature then, the total pressure of this container at equilibrium is :

(A) 50 atm **(B)** 100 atm **(C)** 200 atm **(D)** 70 atm

85. Solid A and B are taken in a closed container at a certain temperature. These two solids decompose and following equilibria are established simultaneously

$A(s) \rightleftharpoons X(g) + Y(g)$ $K_{P_1} = 250 \text{ atm}^2$

$B(s) \rightleftharpoons Y(g) + Z(g)$ $K_{P_2} = ?$

If the total pressure developed over the solid mixture is 50 atm. Then the value of K_P for the 2nd reaction.

(A) 375 **(B)** 625 **(C)** 225 **(D)** 250

86. In the Haber process for the industrial manufacturing of ammonia involving the reaction,

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ at 200 atm pressure in the presence of a catalyst, a temperature of about 500ºC is used. This is considered as optimum temperature for the process because

(A) yield is maximum at this temperature

(B) catalyst is active only at this temperature

(C) energy needed for the reaction is easily obtained at this temperature

(D) rate of the catalytic reaction is fast enough while the yield is also appreciable for this exothermic reaction at this temperature.

87. Two solid compounds X and Y dissociates at a certain temperature as follows

$$X(s) \rightleftharpoons A(g) + 2B(g)\ ;\ K_{p1} = 9 \times 10^{-3}\ atm^3$$

$$Y(s) \rightleftharpoons 2B(g) + C(g)\ ;\ K_{p2} = 4.5 \times 10^{-3}\ atm^3$$

The total pressure of gases over a mixture of X and Y is :

(A) 4.5 atm **(B)** 0.45 atm **(C)** 0.6 atm **(D)** None of these

88. The equilibrium concentration of $[B]_{eq}$ for the reversible reaction $A \rightleftharpoons B$ can be evaluated by the expression:

(A) $K_C[A]_e^{-1}$ **(B)** $\frac{k_f}{k_b}[A]_e^{-1}$ **(C)** $k_f k_b^{-1}[A]_e$ **(D)** $k_f k_b [A]^{-1}$

89. In a chemical equilibrium, the rate constant for the backward reaction is 7.5×10^{-4} and the equilibrium constant is 1.5 the rate constant for the forward reaction is :

(A) 2×10^{-3} **(B)** 5×10^{-4} **(C)** 1.12×10^{-3} **(D)** 9.0×10^{-4}

90. Which of the following is correct for the equilibrium of the reaction

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$$

(A) $p_{H_2} \propto p_{H_2O}$ **(B)** $p_{H_2} \propto \sqrt{p_{H_2O}}$ **(C)** $p_{H_2} \propto p^2_{H_2O}$ **(D)** $p_{H_2} \propto \frac{p^2_{H_2O}}{p_{CO}}$

91. Which of the following is not favourable for SO_3 formation

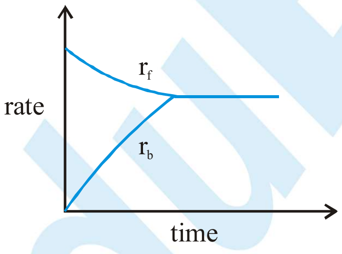
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g);\quad \Delta H = -45.0\ kcal$$

(A) High pressure **(B)** High temperature

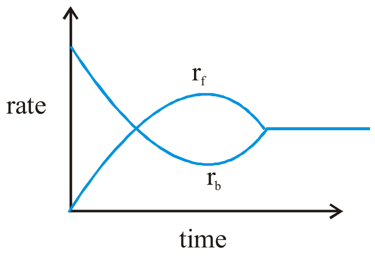
(C) Decreasing SO_3 concentration **(D)** Increasing reactant concentration

92. Rate of reaction curve for equilibrium can be like : $[r_f$ = forward rate , r_b = backward rate$]$

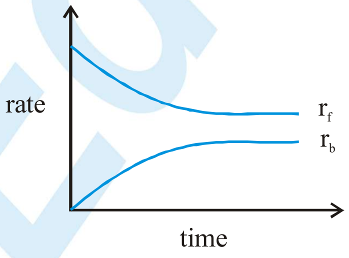
(A)



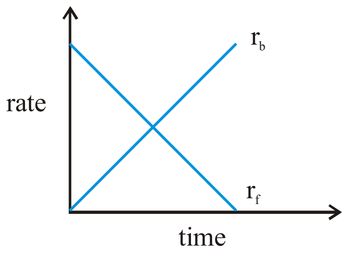
(B)



(C)



(D)



93. For a reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the value of K_C does not depends upon :

(a) Initial concentration of the reactants **(b)** Pressure **(c)** Temperature **(d)** catalyst

(A) Only c **(B)** a,b,c **(C)** a,b,d **(D)** a,b,c,d

94. At 1000 K, the value of K_p for the reaction :

$A(g) + 2B(g) \rightleftharpoons 3C(g) + D(g)$ is 0.05 atmosphere. The value of K_C in terms of R would be :

(A) 20000 R **(B)** 0.02 R **(C)** 5×10^{-5} R **(D)** $5 \times 10^{-5} \times R^{-1}$

95. The equilibrium constant (K_p) for the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is 16. If the volume of the container is reduced to one half its original volume, the value of K_p for the reaction at the same temperature will be :

(A) 32 **(B)** 64 **(C)** 16 **(D)** 4

96. The equilibrium constant for the reaction : $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at 2000 K is 4×10^4 In presence of a catalyst the equilibrium is established ten times faster at the same temperature. What is the value of equilibrium constant in presence of catalyst : -

(A) 40×10^{-4} **(B)** 4×10^{-4} **(C)** 4×10^4 **(D)** None

Exercise # 2 Part # I [Multiple Correct Choice Type Questions]

1. (i) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g),$ K_1

(ii) $\left(\frac{1}{2}\right)N_2(g) + \left(\frac{1}{2}\right)O_2(g) \rightleftharpoons NO(g);$ K_2

(iii) $2NO(g) \rightleftharpoons N_2(g) + O_2(g);$ K_3

(iv) $NO(g) \rightleftharpoons \left(\frac{1}{2}\right)N_2(g) + \left(\frac{1}{2}\right)O_2(g);$ K_4

Correct relation between K_1, K_2, K_3 and K_4 is/are :

(A) $K_1 \times K_3 = 1$ **(B)** $\sqrt{K_1} \times K_4 = 1$ **(C)** $\sqrt{K_3} \times K_2 = 1$ **(D)** None

2. For a reversible reaction $aA + bB \rightleftharpoons cC + dD$; the variation of K with temperature is given by

$$\log\frac{K_2}{K_1} = \frac{-\Delta H^\circ}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \text{ then,}$$

(A) $K_2 > K_1$ if $T_2 > T_1$ for an endothermic change
(B) $K_2 < K_1$ if $T_2 > T_1$ for an endothermic change
(C) $K_2 > K_1$ if $T_2 > T_1$ for an exothermic change
(D) $K_2 < K_1$ if $T_2 > T_1$ for an exothermic change

3. If $\log\frac{k_c}{k_p} - \log\frac{1}{RT} = 0$

then above is true for the following equilibrium reaction

(A) $NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$ **(B)** $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

(C) $2NO_2(g) \rightleftharpoons N_2O_4(g)$ **(D)** $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

4. The equation $\alpha = \frac{D-d}{(n-1)d}$ is not correctly matched for :

(A) $A(g) \rightleftharpoons (n/2)B(g) + (n/3)C(g)$ **(B)** $A(g) \rightleftharpoons (n/3)B(g) + (2n/3)C(g)$
(C) $A(g) \rightleftharpoons (n/2)B(g) + (n/4)C(g)$ **(D)** $A(g) \rightleftharpoons (n/2)B(g) + C(g)$

5. Which of the following is correct about the chemical equilibrium ?
(A) $(\Delta G)_{T,P} = 0$
(B) Equilibrium constant is independent of initial concentration of reactants
(C) Catalyst has no effect on equilibrium state
(D) Reaction stops at equilibrium

6. Four vessel each of volume V = 10 L contains
(A) 16 g CH_4 **(B)** 18 g H_2O **(C)** 35.5 g Cl_2 **(D)** 44 g CO_2
Which container will contain same active mass ?

7. For the reaction : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
The forward reaction at constant temperature is favoured by
(A) introducing chlorine gas at constant volume **(B)** introducing an inert gas at constant pressure
(C) increasing the volume of the container **(D)** introducing PCl_5 at constant volume

8. $2CaSO_4(s) \rightleftharpoons 2CaO(s) + 2SO_2(g) + O_2(g), \Delta H > 0$

Above equilibrium is established by taking some amount of $CaSO_4(s)$ in a closed container at 1600 K. Then which of the following may be correct option.

(A) moles of CaO(s) will increase with the increase in temperature

(B) If the volume of the container is doubled at equilibrium then partial pressure of $SO_2(g)$ will change at new equilibrium.

(C) If the volume of the container is halved partial pressure of $O_2(g)$ at new equilibrium will remain same

(D) If two moles of the He gas is added at constant pressure then the moles of CaO(s) will increase.

9. $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$ $K_p = 10^{-10}$ (atm). 10^{-2} moles of $CuSO_4.5H_2O(s)$ is taken in a 2.5L container at 27°C then at equilibrium [Take : $R = \frac{1}{12}$ litre atm mol^{-1} K^{-1}]

(A) Moles of $CuSO_4 . 5H_2O$ left in the container is 9×10^{-3}

(B) Moles of $CuSO_4 . 5H_2O$ left in the container is 9.8×10^{-3}

(C) Moles of $CuSO_4$ left in the container is 10^{-3}

(D) Moles of $CuSO_4$ left in the container is 2×10^{-4}

10. 1 mole each of $H_2(g)$ and $I_2(g)$ are introduced in a 1L evacuated vessel at 523K and equilibrium $H_2(g) + I_2(g) \rightleftharpoons 2HI\,(g)$ is established. The concentration of HI(g) at equilibrium :

(A) Changes on changing pressure.

(B) Changes on changing temperature.

(C) Changes on changing volume of the vessel.

(D) Is same even if only 2 mol of HI (g) were introduced in the vessel in the begining.

(E) Is same even when a platinum gauze is introduced to catalyse the reaction.

11. An industrial fuel, 'water gas', which consists of a mixture of H_2 and CO can be made by passing steam over red-hot carbon. The reaction is

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g), \Delta H = +131 \text{ kJ}$$

The yield of CO and H_2 at equilibrium would be shifted to the product side by :

(A) raising the relative pressure of the steam

(B) adding hot carbon

(C) raising the temperature

(D) reducing the volume of the system

12. If two gases AB_2 and B_2C are mixed the following equilibria are readily established

$$AB_2(g) + B_2C(g) \rightleftharpoons AB_3(g) + BC\,(g)$$

$$BC(g) + B_2C(g) \rightleftharpoons B_3C_2\,(g)$$

It the reaction is started only with AB_2 with B_2C , then which of the following is necessarily true at equilibrium:

(A) $[AB_3]_{eq} = [BC]_{eq}$

(B) $[AB_2]_{eq} = [B_2C]_{eq}$

(C) $[AB_3]_{eq} > [B_3C_2]_{eq}$

(D) $[AB_3]_{eq} > [BC]_{eq}$

13. The dissociation of phosgene, which occurs according to the reaction

$$COCl_2\,(g) \rightleftharpoons CO(g) + Cl_2(g)$$

Is an endothermic process. Which of the following will increase the degree of dissociation of $COCl_2$?

(A) Adding Cl_2 to the system

(B) Adding helium to the system at constant pressure

(C) Decreasing the temperature of the system

(D) Reducing the total pressure

14. For the gas phase reaction, $C_2H_4 + H_2 \rightleftharpoons C_2H_6$ ($\Delta H = -32.7$ kcal), carried out in a closed vessel, the equilibrium moles of C_2H_4 can be increased by :

(A) increasing the temperature

(B) decreasing the pressure

(C) removing some H_2

(D) adding some C_2H_6

15. $N_2 + O_2 \rightleftharpoons 2NO,\ K_1$; $\left(\frac{1}{2}\right)N_2 + \left(\frac{1}{2}\right)O_2 \rightleftharpoons NO,\ K_2$

$2NO \rightleftharpoons N_2 + O_2,\ K_3$; $NO \rightleftharpoons \left(\frac{1}{2}\right)N_2 + \left(\frac{1}{2}\right)O_2,\ K_4$

Correct relation between K_1, K_2, K_3 and K_4 is :

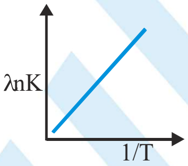
(A) $K_1 \times K_3 = 1$

(B) $\sqrt{K_1} \times K_4 = 1$

(C) $\sqrt{K_3} \times K_2 = 1$

(D) None

16. Variation of equilibrium constant K for the reaction ; $2A(s) + B(g) \rightleftharpoons C(g) + 2D(g)$ is plotted against absolute temperature T in figure as - ℓnK Vs (1/T) :



(ℓnK vs 1/T diagram)

(A) the forward reaction is exothermic

(B) the forward reaction is endothermic

(C) the slope of line is proportional to ΔH

(D) adding 'A' favours forward reaction

(E) removing C favours forward reaction

17. The equilibrium of which of the following reactions will not be disturbed by the addition of an inert gas at constant volume?

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

(B) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

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

(D) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$

18. The dissociation of ammonium carbamate may be represented by the equation :

$NH_4CO_2NH_2(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

ΔH^0 for the forward reaction is negative. The equilibrium will shift from right to left if there is

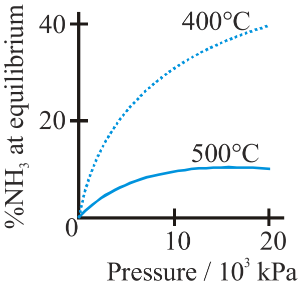
(A) a decrease in pressure

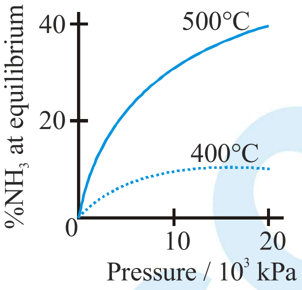
(B) an increase in temperature

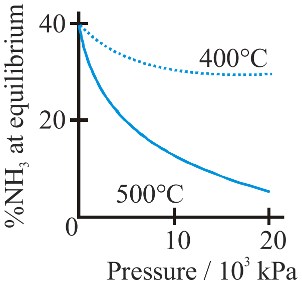
(C) an increase in the concentration of ammonia

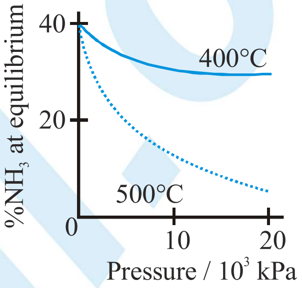
(D) an increase in the concentration of carbon dioxide

19. The percentage of ammonia obtainable, if equilibrium were to be established during the Haber process, is plotted against the operating pressure for two temperatures 400°C and 500°C. Which of the following correctly represents the two graphs ?

(A)


(B)


(C)


(D)


20. In a 0.25 litre tube dissociation of 4 moles of NO is take place. If its degree of dissociation is 10%. The value of K_p for reaction $2NO \rightleftharpoons N_2 + O_2$ is :

(A) $\frac{1}{(18)^2}$ **(B)** $\frac{1}{(8)^2}$ **(C)** $\frac{1}{16}$ **(D)** $\frac{1}{32}$

21. The vapour density of N_2O_4 at a certain temperature is 30. What is the percentage dissociation of N_2O_4 at this temperature ?

(A) 53.3 % **(B)** 106.6% **(C)** 26.7% **(D)** none

22. A sample of mixture of A(g), B(g) and C(g) under equilibrium has a mean molecular weight (observed) is 80.

The equilibrium is A(g) $\rightleftharpoons$ B(g) + C(g)
(mol. wt. = 100) (mol. wt. = 60) (mo. wt. = 40)

Find the degree of dissociation α for A(g).

(A) 0.25 **(B)** 0.5 **(C)** 0.75 **(D)** 0.8

23. In an equilibrium reaction for which $\Delta G° = 0$, the value of equilibrium constant K =

(A) 0 **(B)** 1 **(C)** 2 **(D)** 10

24. A reaction in equilibrium is represent by the following equation –
$2A_{(s)} + 3B_{(g)} \rightleftharpoons 3C_{(g)} + D_{(g)} + O_{2(g)}$ if the pressure on the system is reduced to half of its original value

(A) The amounts of C and D decreases **(B)** The amounts of C and D increases
(C) The amount of B and D decreases **(D)** All the amounts remain constant

25. On cooling of following system at equilibrium $CO_2(s) \rightleftharpoons CO_2(g)$

(A) There is no effect on the equilibrium state **(B)** More gas is formed
(C) More gas solidifies **(D)** None of above

26. $aA + bB \rightleftharpoons cC + dD$

In above reaction low pressure and high temperature, conditions are shift equilibrium in back direction so correct set

(A) $(a + b) > (c + d), \Delta H > 0$ **(B)** $(a + b) < (c + d), \Delta H > 0$

(C) $(a + b) < (c + d), \Delta H < 0$ **(D)** $(a + b) > (c + d), \Delta H < 0$

27. 'a' moles of PCl_5, undergoes, thermal dissociation as : $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, the mole fraction of PCl_3 at equilibrium is 0.25 and the total pressure is 2.0 atmosphere. The partial pressure of Cl_2 at equilibrium is :

(A) 2.5 **(B)** 1.0 **(C)** 0.5 **(D)** None

28. 4.5 moles each of hydrogen and iodine heated in a sealed ten litre vessel. At equilibrium 3 moles of HI were found. The equilibrium constant for $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is :

(A) 1 **(B)** 10 **(C)** 5 **(D)** 0.33

29. 1.50 moles each of hydrogen and iodine were placed in a sealed 10 litre container maintained at 717 K. At equilibrium 1.25 moles each of hydrogen and iodine were left behind. The equilibrium constant, K_c for the reaction. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 717 K is

(A) 0.4 **(B)** 0.16 **(C)** 25 **(D)** 50

30. Consider the reactions

(i) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (ii) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

The addition of an inert gas at constant volume

(A) will increase the dissociation of PCl_5 as well as N_2O_4

(B) will reduce the dissociation of PCl_5 as well as N_2O_4

(C) will increase the dissociation of PCl_5 and step up the formation of NO_2

(D) will not disturb the equilibrium of the reactions

31. A quantity of PCl_5 was heated in a 10 dm^3 vessel at 250°C : $PCl_5\ (g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. At Equilibrium, the vessel contains 0.1 mole of PCl_5 and 0.2 mole of Cl_2. The equilibrium constant of the reaction is :

(A) 0.04 **(B)** 0.025 **(C)** 0.02 **(D)** 0.05

32. 1 mole of N_2 and 2 moles of H_2 are allowed to react in a 1 dm^3 vessel. At equilibrium, 0.8 mole of NH_3 is formed. The concentration of H_2 in the vessel is :

(A) 0.6 mole **(B)** 0.8 mole **(C)** 0.2 mole **(D)** 0.4 mole

33. In a given system, water and ice are in equilibrium. If pressure is applied to the above system then

(A) More of ice is formed **(B)** Amount of ice and water will remain same

(C) More of ice is melted **(D)** Either **(A)** or **(C)**

34. In a 20 litre vessel initially each have 1 – 1 mole CO, H_2O CO_2 is present, then for the equilibrium of

$CO + H_2O \rightleftharpoons CO_2 + H_2$ following is true :

(A) H_2, more then 1 mole **(B)** CO, H_2O, H_2 less then 1 mole

(C) CO_2 & H_2O both more than 1 mole **(D)** All of these

35. For which reaction at 298 K, the value of $\frac{K_p}{K_c}$ is maximum and minimum respectively :

(a) $N_2O_4 \rightleftharpoons 2NO_2$ **(b)** $2SO_2 + O_2 \rightleftharpoons 2SO_3$

(c) $X + Y \rightleftharpoons 4Z$ **(d)** $A + 3B \rightleftharpoons 7C$

(A) d,c **(B)** d,b **(C)** c,b **(D)** d,a

36. For the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, the degree of dissociation varies inversely as the square root of pressure of the system. Supposing at constant temperature. If the volume is increased 16 times the initial volume, the degree of dissociation for this reaction will becomes :

(A) 4 times **(B)** $\frac{1}{4}$ times **(C)** 2 times **(D)** $\frac{1}{2}$ times

37. If K_1, K_2, K_3 are equilibrium constant for formation of AD, AD_2, AD_3 respectively as follows $A + D \rightleftharpoons D$, $AD + D \rightleftharpoons AD_2$, $AD_2 + D \rightleftharpoons AD_3$. Then equilibrium constant 'K' for $A + 3D \rightleftharpoons AD_3$ is related as

(A) $K_1 + K_2 + K_3 = K$ **(B)** $\log K_1 + \log K_2 + \log K_3 = \log K$

(C) $K_1 + K_2 = K_3 + K$ **(D)** $\log K_1 + \log K_2 = \log K_3 + \log K$

38. For the reaction $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ the partial pressure of CO and CO_2 are 2.0 and 4.0 atm. respectively at equilibrium. The K_P for the reaction is :

(A) 0.5 **(B)** 4.0 **(C)** 8.0 **(D)** 1

39. In the following reaction started only with A_8,

$$2A_8(g) \rightleftharpoons 2\,A_3(g) + 3\,A_2(g) + A_4(g)$$

mole fraction of A_2 is found to 0.36 at a total pressure of 100 atm at equilibrium. The mole fraction of $A_8(g)$ at equilibrium is :

(A) 0.28 **(B)** 0.72 **(C)** 0.18 **(D)** None of these

40. 500 ml vessel contains 1.5 M each of A,B, C and D at equilibrium. If 0.5 M each of C and D are taken out, the value of K_C for $A + B \rightleftharpoons C + D$ will be

(A) 1.0 **(B)** 1/9 **(C)** 4/9 **(D)** 8/9

41. The effect of adding krypton (Kr) gas on position of equilibrium, keeping the volume of the system constant is

(A) If $\Delta n = 0$, backward reaction is favoured. **(B)** If, $\Delta n = +$ve, forward reaction is favoured

(C) If $\Delta n = -$ve, forward reaction is favoured **(D)** No effect watever be the value of Δn

42. **S1 :** When a liquid and its vapour are at equilibrium and the pressure is suddenly decreased, cooling occurs.

S2 : If equilibrium constant for the reaction, $A_2 + B_2 \rightleftharpoons 2AB$, is K, then for the backward reaction $AB \rightleftharpoons \frac{1}{2}A_2 + \frac{1}{2}B_2$, the equilibrium constant is $\frac{1}{K}$.

S3 : Catalyst makes a reaction more exothermic.

(A) T F F **(B)** F T F **(C)** T T F **(D)** F T T

43. **S1 :** The rate of an exothermic reaction increases with increasing temperature.

S2 : For the reaction, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, $K_p = P_{CO_2}$.

S3 : A catalyst increases the value of the equilibrium constant for a reaction.

(A) T F F **(B)** F T F **(C)** T T F **(D)** F T T

44. What should be the value of K_C for the reaction $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$. If the amount are $SO_3 = 48g$, $SO_2 = 12.8$ and $O_2 = 9.6$ at equilibrium and the volume of the container is one litre ?

(A) 64 **(B)** 0.30 **(C)** 42 **(D)** 8.5

45. If 0.5 mole H_2 is reacted with 0.5 mole I_2 in a ten-litre container at 444°C and at same temperature value of equilibrium constant K_C is 49, the ratio of [HI] and $[I_2]$ will be :

(A) 7 **(B)** $\frac{1}{7}$ **(C)** $\sqrt{\frac{1}{7}}$ **(D)** 49

46. 1.1 mole of A mixed with 2.2 mole of B and the mixture is kept in a 1 litre at the equilibrium $A + 2B \rightleftharpoons 2C + D$ is reached. At equilibrium 0.2 mole of C is formed then the value of K_C will be :

(A) 0.005 **(B)** 0.001 **(C)** 0.01 **(D)** 0.0001

47. In the reaction, $N_2 + O_2 \rightleftharpoons 2NO$, the moles/litre of N_2, O_2 and NO respectively 0.25, 0.05 and 1.0 at equilibrium, the initial concentration of N_2 and O_2 will respectively be :

(A) 0.75 mol/litre, 0.55 mole/litre **(B)** 0.50 mole/litre, 0.75 mole/litre

(C) 0.25 mole/litre, 0.50 mole/ litre **(D)** 0.25 mole/litre, 1.0 mole/litre

48. **S1 :** In case of endothermic reactions, the equilibrium shifts in backward direaction on increasing the temperature.

S2 : The value of K increases with increases in pressure.

S3 : For the reaction, $H_2 + I_2 \rightleftharpoons 2HI$, the equilibrium constant, K is dimenstionless.

(A) T F F **(B)** F T F **(C)** T T F **(D)** F F T

49. At room temperature, the equilibrium constant for the reaction $P + Q \rightleftharpoons R + S$ was calculated to be 4.32. At 425°C the equilibrium constant became 1.24×10^{-2}. This indicates that the reaction

(A) is exothermic **(B)** is endothermic

(C) is difficult to predict **(D)** no relation between ΔH and K

50. On decomposition of NH_4HS, the following equilibrium is established :

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

If the total pressure is P atm, then the equilibrium constant K_P is equal to

(A) P atm **(B)** P^2 atm^2 **(C)** $P^2 / 4$ atm^2 **(D)** 2P atm

51. The average person can see the red colour imparted by the complex $[Fe(SCN)]^{2+}$ to an aqueous solution if the concentration of the complex is 6×10^{-6} M or greater. What minimum concentration of KSCN would be required to make it possible to detect 1 ppm (part per million) of Fe(III) in a natural water sample? The instability constant for $Fe(SCN)^{2+} \rightleftharpoons Fe^{3+} + SCN^-$ is 7.142×10^{-3}.

(A) 0.0036 M **(B)** 0.0037 M **(C)** 0.0035 M **(D)** None of these

52. For the given reaction at constant pressure ,

	$nA(g)$	$\rightleftharpoons$	$A_n(g)$
Initial moles	1		0
Moles at equilibrium	$1 - \alpha$		α/n

Then the correct relation between initial density (d_i) & final density (d_f) of the system is

(A) $\left[\frac{n-1}{n}\right]\left[\frac{d_f - d_i}{d_f}\right] = \alpha$ **(B)** $\frac{n}{n-1}\,\frac{[d_f - d_i]}{d_f} = \alpha$ **(C)** $\left[\frac{n-1}{n}\right]\left[\frac{d_i - d_f}{d_i}\right] = \alpha$ **(D)** $\frac{1}{(n-1)}\left[\frac{d_i - d_f}{d_i}\right] = \alpha$

53. For the following mechanism, $P + Q \underset{K_B}{\overset{K_A}{\rightleftharpoons}} PQ \underset{K_D}{\overset{K_C}{\rightleftharpoons}} R$ at equilibrium $\frac{[R]}{[P]\ [Q]}$ is :

[k represents rate constant]

(A) $\frac{K_A \cdot K_B}{K_C \cdot K_D}$ **(B)** $\frac{K_A \cdot K_D}{K_B \cdot K_C}$ **(C)** $\frac{K_B \cdot K_D}{K_A \cdot K_C}$ **(D)** $\frac{K_A \cdot K_C}{K_B \cdot K_D}$

54. Select the reaction for which the equilibrium constant is written as $[MX_3]^2 = K_{eq.} [MX_2]^2 [X_2]$

(A) $MX_3 \rightleftharpoons MX_2 + \frac{1}{2} X_2$ **(B)** $2MX_3 \rightleftharpoons 2MX_2 + X_2$

(C) $2MX_2 + X_2 \rightleftharpoons 2MX_3$ **(D)** $MX_2 + \frac{1}{2} X_2 \rightleftharpoons MX_3$.

55. For the reaction, $4\,NH_3(g) + 5\,O_2(g) \rightleftharpoons 4\,NO(g) + 6\,H_2O(\bullet)$, $\Delta H = \text{positive}$.

At equilibrium which factor will not effect the concentration of NH_3 is :

(A) change in pressure **(B)** change in volume **(C)** catalyst **(D)** None of these

56. The reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ is started in a five litre container by taking one mole of PCl_5. If 0.3 mole of PCl_5 is there at equilibrium, concentration of PCl_3 and K_C will respectively be :

(A) $0.14, \dfrac{49}{150}$ **(B)** $0.12, \dfrac{23}{100}$

(C) $0.07, \dfrac{23}{100}$ **(D)** $20, \dfrac{49}{150}$

57. Pure ammonia is placed in a vessel at a temperature where its dissociation constant **(A)** is appreciable. At equilibrium

(A) K_p does not change significantly with pressure.

(B) α does not change with pressure.

(C) concentration of NH_3 does not change with pressure.

(D) concentration of hydrogen is less than that of nitrogen

58. For the following gases equilibrium, $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$

K_p is found to be equal to K_c. This is attained when :

(A) 0ºC **(B)** 273 K **(C)** 1 K **(D)** 12.19 K

59. In a container equili brium $N_2O_4(g) \rightleftharpoons 2NO_2\,(g)$

is attained at 25°C. The total equilibrium pressure in container is 380 torr. If equilibrium constant of above equilibrium is 0.667 atm, then degree of dissociation of N_2O_4 at this temperature will be :

(A) $\dfrac{1}{3}$ **(B)** $\dfrac{1}{2}$ **(C)** $\dfrac{2}{3}$ **(D)** $\dfrac{1}{4}$

Part # II [Assertion & Reason Type Questions]

Each question has 5 choices (A), (B), (C), (D) and (E) out of which only one is correct.

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False.

(D) Statement-1 is False, Statement-2 is True.

(E) Statement-1 and Statement-2 both are False.

1. **Statement-1 :** No term in the concentration of a pure solid or a pure liquid appears in an equilibrium constant expression.

Statement-2 : Each pure solid or pure liquid is in a phase by itself, and has a constant concentration at constant temperature.

2. **Statement-1 :** The reaction quotient , Q has the same form as the equilibrium constant K_{eq}, and is evaluated using any given concentrations of the species involved in the reaction, and not necessarily equilibrium concentrations.

Statement-2 : If the numerical value of Q is not the same as the value of equilibrium constant, a reaction will occur.

3. **Statement-1 :** The dissociation of $CaCO_3$ can be represented as, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. Some solid $CaCO_3$ is placed in an evacuated vessel enclosed by a piston and heated so that a portion of its decomposes. If the piston is moved so that the volume of the vessel is doubled, while the temperature is held constant, the number of moles of CO_2 in the vessel increase.
Statement-2 : The pressure of CO_2 in the vessel will remain the same.

4. **Statement-1 :** A catalyst does not influences the values of equilibrium constant.
Statement-2 : Catalysts influence the rate of both forward and backward reactions equally.

5. **Statement-1 :** For $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. If more Cl_2 is added the equilibrium will shift in backward direction hence equilibrium constant will decrease.
Statement-2 : Addition of inert gas to the equilibrium mixture at constant volume, does not alter the equilibrium.

6. **Statement-I :** The melting point of ice decreases with increase of pressure.
Statement-II : Ice contracts on melting.

7. **Statement-I :** The equilibrium of $A(g) \rightleftharpoons B(g) + C(g)$ is not affected by changing the volume.
Statement-II : K_c for the reaction does not depend on volume of the container.

8. **Statement-I :** For the reaction $A(g) \rightleftharpoons B(g) + C(g)$, $K_p = 1$ atm. If we start with equal moles of all gases at 9 atm of initial pressure, then at equilibrium partial pressure of A increases.
Statement-II : Reaction quotient $Q_p > K_p$ hence equilibrium shifts in backward direction.

9. **Statement-I :** For a reaction at equilibrium, the Gibb's free energy of reaction is minimum at constant temp. and pressure.
Statement-II : The Gibb's free energy of both reactants and products increases and become equal at equilibrium.

10. **Statement-I :** Equilibrium constant for the reverse reaction is the inverse of the equilibrium constant for the reaction in the forward direction.
Statement-II : Equilibrium constant depends upon the way in which the reaction is written.

11. **Statement-I :** For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ if the volume of vessel is reduced to half of its original volume, equilibrium concentration of all gases will be doubled.
Statement-II : According to Le Chatelier's principle, reaction shifts in a direction that tends to minimized the effect of the stress.

12. **Statement-I :** For the reaction at certain temperature

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

there will be no effect by addition of inert gas at constant volume.
Statement-II : Molar concentration of all gases remains constant.

13. **Statement-I :** The catalyst does not alter the equilibrium constant.
Statement-II : For the catalysed reaction and uncatalysed reaction ΔH remains same and equilibrium constant depends on ΔH.

Exercise # 3 Part # I [Matrix Match Type Questions]

1. Match the following :

Column I (Assume only reactant were present initially)	Column II
(A) For the equilibrium $NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$, if pressure is increased at equilibrium	**(p)** Forward shift
(B) For the equilibrium $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ volume is increased at equilibrium	**(q)** No shift in equilibrium
(C) For the equilibrium $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ inert gas is added at constant pressure at equilibrium	**(r)** Backward shift
(D) For the equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ Cl_2 is removed at equilibrium.	**(s)** Final pressure is more than initial pressure

2. Match the following : (Assume only reactants were present initially).

Column I	Column II
(A) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (t = 300°C)	**(p)** $\Delta n_g > 0$
(B) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (t = 50°C)	**(q)** $K_p < K_c$
(C) $C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$	**(r)** K_p not defined
(D) $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$	**(s)** $P_{initial} > P_{eq.}$

3.

Column-I (Reactions)	Column-II (Favourable conditions)
(A) Oxidation of nitrogen $N_2(g) + O_2(g) + 180.5\ kJ \rightleftharpoons 2NO(g)$	**(p)** Addition of inert gas at constant pressure
(B) Dissociation of $N_2O_4(g)$ $N_2O_4(g) + 57.2\ kJ \rightleftharpoons 2NO_2(g)$	**(q)** Decrease in pressure
(C) Oxidation of $NH_3(g)$ $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g) + 905.6\ kJ$	**(r)** Decrease in temperature
(D) Formation of $NO_2(g)$ $NO(g) + O_3(g) \rightleftharpoons NO_2(g) + O_2(g) + 200\ kJ$	**(s)** Increase in temperature

4.

Column-I (Reaction)	Column-II (If α is negligiable w.r.t. 1)
(A) $2X(g) \rightleftharpoons Y(g) + Z(g)$	**(p)** $\alpha = 2 \times \sqrt{K_c}$
(B) $X(g) \rightleftharpoons Y(g) + Z(g)$	**(q)** $\alpha = 3 \times \sqrt{K_c}$
(C) $3X(g) \rightleftharpoons Y(g) + Z(g)$	**(r)** $\alpha = (2K_c)^{1/3}$
(D) $2X(g) \rightleftharpoons Y(g) + 2Z(g)$	**(s)** $\alpha = \sqrt{K_c}$

Part # II [Comprehension Type Questions]

Comprehension # 1

Effect of temperature on the equilibrium process is analysed by using the thermodynamics
From the thermodynamics relation

$\Delta G^o = -2.30\,RT\log k$ .... (1) ΔG^o : Standard free energy change

$\Delta G^o = \Delta H^o - T\Delta S^o$ .... (2) ΔH^o : Standard heat of the reaction.

From (1) & (2)

$-2.3\,RT\log k = \Delta H^o - T\Delta S^o$ ΔS^o : Standard entropy change

$$\Rightarrow \quad \log K = -\frac{\Delta H^o}{2.3RT} + \frac{\Delta S^o}{2.3R} \qquad \text{.......... (3)}$$

Clearly if a plot of log k vs 1/T is made then it is a straight line having slope $= \dfrac{-\Delta H^o}{2.3R}$

and Y intercept $= \dfrac{\Delta S^\circ}{2.3R}$

If at temp. T_1 equilibrium constant be k_1 and at temperature T_2 equilibrium constant be k_2 then :
The above equation reduces to:

$$\Rightarrow \quad \log K_1 = -\frac{\Delta H^o}{2.3RT_1} + \frac{\Delta S^o}{2.3R} \qquad \text{.......... (4)}$$

$$\Rightarrow \quad \log K_2 = -\frac{\Delta H^o}{2.3RT_2} + \frac{\Delta S^o}{2.3R} \qquad \text{.......... (5)}$$

Substracting (4) from (5) we get

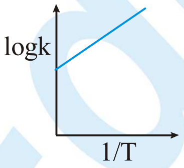
$$\Rightarrow \quad \log\frac{K_2}{K_1} = \frac{\Delta H^o}{2.30R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

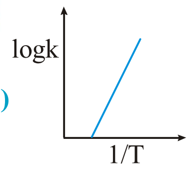
From the above relation we can conclude that the value of equilibrium constant increases with increase in temperature for endothermic reaction but value of equilibrium constant decreases with the increase in temperature for exothermic reaction.

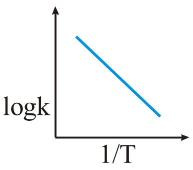
1. If standard heat of dissociation of PCl_5 is 230 cal then slope of the graph of logk vs $\dfrac{1}{T}$ is :

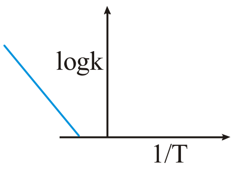
(A) +50 **(B)** – 50 **(C)** 10 **(D)** None

2. For exothermic reaction if $\Delta S_0 < 0$ then the sketch of logk vs $\dfrac{1}{T}$ may be :

(A)


(B)


(C)


(D)


3. If for a particular reversible reaction :

$K_C = 57$ at 355^0C and $K_C = 69$ at 450^0C then :

(A) $\Delta H < 0$ **(B)** $\Delta H > 0$

(C) $\Delta H = 0$ **(D)** ΔH whose sign can't be determined

Comprehension # 2

Le chatelier's principle

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature, the system adjusts itself in such a way as to nulify the effect of that change.

Change of pressure : If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure. To increase the pressure on the system, the volume has to be decreased proportionately. The total number of moles per unit volume will now be more and the equilibirum will shift in the direction in which there is decrease in number of moles i.e., towards the direction in which there can be decrease in pressure .

Effect of pressure on melting point : There are two types of solids :

(A) Solids whose volume decreases on melting, e.g., ice, diamond, carborundum, magnesium nitride and quartz.

$$\text{Solid (higher volume)} \rightleftharpoons \text{Liquid (lower volume)}$$

The process of melting is facilitated at high pressure, thus melting point is lowered.

(B) Solids whose volume increase on melting, e.g., Fe, Cu, Ag, Au, etc.

$$\text{Solid (lower volume)} \rightleftharpoons \text{Liquid (higher volume)}$$

In this case the process of melting become difficult at high pressure; thus melting point becomes high.

(C) **Solubility of substances :** When solid substance are dissolved in water, either heat is evolved (exothermic) or heat is absorbed (endothermic).

$$KCl + aq \rightleftharpoons KCl(aq) - heat$$

In such cases, solubility increase with increase in temperature. Consider the case of KOH; when this is dissolved, heat is evolved.

$$KOH + aq \rightleftharpoons KOH(aq) + heat$$

In such cases, solubility decrease with increase in temperature.

(D) **Solubility of gases in liquids :** When a gas dissolves in liquid, there is decrease in volume. Thus, increase of pressure will favour the dissolution of gas in liquid.

1. A gas 'X' when dissolved in water heat is evolved. Then solublity of 'X' will increase :

(A) Low pressure, high temperature
(B) Low pressure, low temperature
(C) high pressure, high temperature
(D) high pressure, low temperature

2. $Au(s) \rightleftharpoons Au(\bullet)$

Above equilibrium is favoured at :

(A) High pressure low temperature
(B) High pressure high temperature
(C) Low pressure, high temperature
(D) Low pressure, low temperature

3. For the reaction, $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$

If pressure is increased by reducing the volume of the container then :

(A) Total pressure at equilibrium will change.
(B) Concentration of all the component at equilibrium will change.
(C) Concentration of all the component at equilibrium will remain same
(D) Equilibrium will shift in the forward direction

Comprehension # 3

Read the following passage carefully and answer the questions.

$2A_2 \rightleftharpoons A_4$ ... (i) $K_{p_1} = \frac{2}{81}\,\text{atm}^{-1}$

$A_2 + 2C \rightleftharpoons A_2C_2$ ... (ii)

$A_2C_2 \rightleftharpoons 2AC$ ... (iii)

A_2 and C are taken in 3 : 1 mole ratio in a closed container of a certain volume at a fixed temperature and aobve three equilibriums are established simultaneously. K_{p_1} for the first reaction is $\frac{2}{81}$ atm^{-1}. At equiliburm partial pressure of A_4(g) and AC(g) are found to be 1/2 atm each and the total pressure at equilibirum is found to be $\frac{27}{4}$ atm. Then

1. The partical pressure of A_2C_2 at equilibrium is

(A) 1/2 **(B)** 3/4 **(C)** 1/4 **(D)** 1

2. The mole ratio of gases A_2 and AC at equiliburm is

(A) 9/2 **(B)** 7/2 **(C)** 8 **(D)** 9

3. Equilibrium constant K_p for the reaction $2AC \rightleftharpoons A_2C_2$ is

(A) 3/4 **(B)** 1 **(C)** 4 **(D)** 1/3

Comprehension # 4

Questions are based on the manufacture of Na_2CO_3 by Solvay process :

In the manufacture of Na_2CO_3(s) by Solvay process, $NaHCO_3$(s) is decomposed by heating :

$$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

$$K_p = 0.23 \text{ at } 100°C \quad \Delta H° = \ 136 \text{ kJ}$$

1. If a sample of $NaHCO_3$ (s) is brought to a temperature of 100°C in a closed container total gas pressure at equilibrium is :

(A) 0.96 atm **(B)** 0.23 atm

(C) 0.48 atm **(D)** 0.46 atm

2. A mixture of 1.00 mol each of $NaHCO_3$(s) and Na_2CO_3(s) is introduced into a 2.5 L flask in which $P_{CO_2} = 2.10$ atm and $P_{H_2O} = 0.94$ atm.When equilibrium is established at 100°C, then partial pressure of :

(A) CO_2(g) and H_2O(g) will be greater than their initial pressure

(B) CO_2(g) and H_2O(g) will be less than their initial pressure

(C) CO_2(g) will be larger and that of H_2O(g) will be less than their initial pressure

(D) H_2O(g) will be larger and that of CO_2(g) will be less than their initial pressure

Comprehension # 5

On July, 1, 2000, the combined tunnel and bridge connecting Denmark and Sweden was officially opened. It consists of a tunnel from Copenhagen to an artificial Island and a bridge from the island to Malmo in Sweden. The major construction materials employed are concrete and steel. This problem deals with chemical reactions relating to production and degradation of such materials.

Concrete is produced from a mixture of cement, water, sand and small stones. Cement consists primarily of calcium silicates and calcium aluminates formed by heating and grinding of clay and limestone. In the later steps of cement production may lead to formation of unwanted hemihydrate, $CaSO_4 \cdot \frac{1}{2} H_2O$. Consider the following reaction :

$$CaSO_4 \cdot 2H_2O(s) \longrightarrow CaSO_4 \cdot \frac{1}{2} H_2O(s) + 1\frac{1}{2} H_2O(g)$$

The following thermodynamic data apply at 25°C, standard pressure : 1.00 bar :

Compound	**$H^\circ/(kJ\ mol^{-1})$ (ΔH_f°)**	**$S^\circ/(JK^{-1}\ mol^{-1})$**
$CaSO_4 \cdot 2H_2O(s)$	–2021.0	194.0
$CaSO_4 \cdot \frac{1}{2} H_2O(s)$	–1575.0	130.5
$H_2O(g)$	–241.8	188.6

Gas constant ; $R = 8.314\ J\ mol^{-1}\ K^{-1}$

1. ΔH° for the transformation of 1.00 kg of $CaSO_4 . 2H_2O(s)$ to $CaSO_4 \cdot \frac{1}{2} H_2O(s)$ is :

(A) +446 kJ **(B)** +484 kJ **(C)** –446 kJ **(D)** –484 kJ

2. Equilibrium pressure (in bar) of water vapour in a closed vessel containing $CaSO_4 \cdot 2H_2O(s)$, $CaSO_4(s) \cdot \frac{1}{2} H_2O(s)$ and H_2O (g) at 25°C is :

(A) 7.35×10^{-4} bar **(B)** 2.15×10^{-4} bar **(C)** 8.10×10^{-3} bar **(D)** 7.00×10^{-4} bar

3. Temperature at which the equilibrium water vapour pressure is 1.00 bar.

(A) 107°C **(B)** 380°C **(C)** 215°C **(D)** 240°C

Exercise # 4 [Subjective Type Questions]

1. Give one example of each of the following equilibria :

(i) Solid-Liquid Equilibria (ii) Liquid-Gas Equilibria

2. What is the active mass of 5.6 litres of O_2 at S.T.P. ?

3. Write the expressions for equilibrium constant K_C and K_P for the following reactions :

(i) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

(ii) $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

(iii) $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

(iv) $CH_3COOH(\bullet) + C_2H_5OH(\bullet) \rightleftharpoons CH_3COOC_2H_5(\bullet) + H_2O(\bullet)$

(v) $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)$

(vi) $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$

(vii) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

(viii) $NH_4NO_2(\bullet) \rightleftharpoons N_2(g) + 2H_2O(\bullet)$

4. Briefly explain the important characteristics of chemical equilibrium.

5.. In a reaction $A + B \rightleftharpoons C + D$ the rate constant of forward reaction & backward reaction is k_1 and k_2 then the equilibrium constant (k) for reaction is expressed as :

6. The equilibrium $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$ is established in a container of 4L at a particular temperature. If the number of moles of SO_2, O_2 and SO_3 at equilibrium are 2, 1 and 4 respectively then find the value of equilibrium constant.

7. A mixture of SO_3, SO_2 and O_2 gases is maintained at equilibrium in 10 litre flask at a temperature at which K_C for the reaction,

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ is 100 mol^{-1} litre. At equilibrium.

(a) If no. of mole of SO_3 and SO_2 in flask are same, how many mole of O_2 are present ?

(b) If no. of mole of SO_3 in flask are twice the no. of mole of SO_2, how many mole of O_2 are present ?

8. $A(g) + B(g) \rightleftharpoons C(g) + D(g)$

Above equilibrium is established by taking A & B in a closed container. Initial concentration of A is twice of the initial concentration of B. At equilibrium concentrations of B and C are equal. Then find the equilibrium constant for the reaction, $C(g) + D(g) \rightleftharpoons A(g) + B(g)$.

9. The equilibrium constant of the reaction $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$ at 100° C is 50. If a one litre flask containing one mole of A_2 is connected to a two litre flask containing two moles of B_2, how many moles of AB will be formed at 373 K ?

10. The partial pressures of N_2O_4 and NO_2 at 40°C for the following equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ are 0.1 atm and 0.3 atm respectively. Find K_P for the reaction.

11. 1 mole of N_2 and 3 moles of H_2 are placed in 1L vessel. Find the concentration of NH_3 at equilibrium, if equilibrium pressure is 1 atm and the equilibrium constant at 400K is $\frac{4}{27}$

12. n mole each of $H_2O(g)$, $H_2(g)$ and $O_2(g)$ are mixed at a suitable high temperature to attain the equilibrium $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$. If y mole of $H_2O(g)$ are the dissociated and the total pressure maintained is P, calculate the K_P.

13. 1 mole of a gas 'A' is taken in a vessel of volume 1L. It dissociates according to the reaction $A(g) \rightleftharpoons B(g) + C(g)$ at 27°C. Forward and backward reaction rate constants for the reaction are 1.5×10^{-2} and 3×10^{-2} respectively. Find the concentrations of A, B and C at equilibrium. Also find K_p and K_c with proper units.

14. 0.15 mole of CO taken in a 2.5 litre 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 0.08 mole of methanol is formed.Calculate :
(i) K_p & K_c ;
(ii) the final pressure if the same amount of CO and H_2 as before are used, but with no catalyst so that the reaction takes place on its own.

15. Calculate the expression for K_c and K_p if initially a moles of N_2 and b moles of H_2 is taken for the following reaction.
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ ($\Delta n < 0$) (P, T, V given)

16. The equilibrium constant for the reactions $N_2 + O_2 \rightleftharpoons 2NO$ and $2NO + O_2 \rightleftharpoons 2NO_2$ are K_1 and K_2 respectively, then what will be the equilibrium constant for the reaction $N_2 + 2O_2 \rightleftharpoons 2NO_2$?

17. Calculate the equilibrium constant for the reaction : $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ at 1395 K, if the equilibrium constants at 1395 K for the following are

$2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ $K_1 = 2.1 \times 10^{-13}$
$2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$ $K_2 = 1.4 \times 10^{-12}$.

18. Explain the effect of the following on the equilibrium constant.
(i) Concentrations of the reactants are doubled
(ii) The reaction is reversed
(iii) Catalyst is added to the reaction
(iv) Temperature is increased.

19. In an experiment starting with 1 mole of ethyl alcohol, 1 mole of acetic acid and 1 mole of water at T^0C, the equilibrium mixture on analysis shows that 54.3% of the acid is esterfied. Calculate the equilibrium constant of this reaction.

20. The homogeneous reversible reaction, $C_2H_5OH + CH_3COOH \rightleftharpoons CH_3COOC_2H_5 + H_2O$ is studied at various initial concentrations of the reactants at constant temperature . Calculate ' k ' in each case .

	Moles of acid per litre (initial)	**Moles of alcohol per litre (initial)**	**Moles of ester per litre at equilibrium**
(i)	1	1	0.667
(ii)	1	4	0.93

21. N_2O_4 is 25% dissociated at 37°C and one atmosphere pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atmosphere and 37°C.

22. At temperature T, the compound $AB_2(g)$ dissociates according to the reaction; $2AB_2(g) \rightleftharpoons 2AB(g) + B_2(g)$.With a degree of dissociation *x*, which is small compared with unity.Deduce the expression for *x* in terms of the equilibrium constant, K_p and the total pressure, P.

23. Vapour density of the equilibrium mixture of NO_2 and N_2O_4 is found to be 38.33. For the equilibrium

$$N_2O_4(g) \rightleftharpoons 2NO_2(g).$$

Calculate :
(i) abnormal molecular weight.
(ii) degree of dissociation.
(iii) percentage of NO_2 in the mixture.
(iv) K_P for the reaction if total pressure is 2 atm.

24. When sulphur in the form of $S_8(g)$ is heated at 900 K, the initial partial pressure of $S_8(g)$ which was 1 atm falls by 29% at equilibrium. This is because of conversion of some $S_8(g)$ to $S_2(g)$. Find the K_p for reaction, $S_8\,(g) \rightleftharpoons 4S_2\,(g)$.

25. Solid ammonium carbamate dissociates to give ammonia and carbon dioxide as follows:

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

At equilibrium, ammonia is added such that partial pressures of NH_3 at new equilibrium equals the original total pressure (at previous equilibrium). Calculate the ratio of the total pressures now to the original total pressure.

26. In a container $H_2O(g)$, $CO(g)$ and $H_2(g)$ are present in the molar ratio of 1 : 2 : 3 respectively at temperature of 300 K. Find the pressure in the container at which solid carbon (graphite) will start forming in the container given that:

$$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g) \quad K_p = 3 \text{ atm}$$

27. A mixture of 1.57 mol of N_2, 1.92 mole of H_2 and 8.13 mol of NH_3 is introduced into a 20 L reaction vessel at 500 K. At this temperature, the equilibrium constant, K_c for the reaction

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is 1.7×10^2.

Is the reaction mixture at equilibrium? If not what is the direction of the net reaction?

28. At 460°C, $K_C = 81$ for the reaction, $SO_2(g) + NO_2(g) \rightleftharpoons NO(g) + SO_3(g)$

A mixture of these gases has the following concentrations of the reactants and products :

$[SO_2] = 0.04$ M $\qquad [NO_2] = 0.04$ M

$[NO] = 0.30$ M $\qquad [SO_3] = 0.3$ M

Is the system at equilibrium? If not, in which direction must the reaction proceed to reach equilibrium. What will be the molar concentrations of the four gases at equilibrium?

29. For the reaction, $SO_2\,(g) + 1/2O_2(g) \rightleftharpoons SO_3(g)$

$\Delta H^0_{298} = -98.32$ kJ/mole, $\Delta S^0_{298} = -95.0$ J/mole-K. Find the K_p for this reaction at 298K. (Given that $10^{.27} = 1.86$)

30. From the following data :

(i) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$; $\qquad K_{2000K} = 4.4$

(ii) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$; $\qquad K_{2000K} = 5.31 \times 10^{-10}$

(iii) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$; $\qquad K_{1000K} = 2.24 \times 10^{22}$

State whether the reaction (iii) is exothermic or endothermic?

31. The dissociation pressure of silver oxide at 445°C is 207 atm. Calculate ΔG^0 for the formation of 1 mole $Ag_2O(s)$ from metal and oxygen at this temperature. (log 207 = 2.315)

32. Equilibrium constants are given (in atm) for the following reaction 0°C :

$Na_2HPO_4.12H_2O(s) \rightleftharpoons Na_2HPO_4.7H_2O(s) + 5H_2O(g) \qquad K_p = 2.43 \times 10^{-13}$

The vapour pressure of water at 0°C is 4.56 torr.

At what relative humidities will $Na_2HPO_4.12H_2O(s)$ be efflorescent when exposed to air at 0°C ?

33. For the equilibrium $SrCl_2{\cdot}6H_2O(s) \rightleftharpoons SrCl_2{\cdot}2H_2O(s) + 4H_2O(g)$ the equilibrium constant $K_P = 16 \text{ x } 10^{-12}$ atm^4 at 1^0C. If one litre of air saturated with water vapour at 1^0C is exposed to a large quantity of $SrCl_2{\cdot}\ 2H_2O(s)$, what weight of water vapour will be absorbed? Saturated vapour pressure of water at 1^0C = 7.6 torr.

34. A vessel contain 5 mole of A & 10 mole of B, total pressure of vessel is 18 atm. Calculate the P_B & P_A

35. Using Le Chatelier's principle, predict the effect of
(i) decreasing the temperature and
(ii) increasing the pressure on each of the following equilibria :

(A) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$ (B) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g) + \text{Heat}$

(C) $H_2O(g) + \text{Heat} \rightleftharpoons H_2(g) + \frac{1}{2}O_2(g)$ (D) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g) + \text{Heat}$

36. Hydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction.

$$CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g);$$

(a) Write an expression for K_p for the above reaction.
(b) How will the value of K_p and composition of equilibrium mixture be affected by :
 (i) increasing the pressure
 (ii) increasing the temperature
 (iii) using a catalyst ?

37. Which of the following reactions will get affected by increase of pressure ? Also mention, whether change will cause the reaction to go into the right or left direction ?

(i) $CH_4(g) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S(g)$ (ii) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$

(iii) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$ (iv) $C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$

38. Two solids A and D dissociates into gaseous products as follows

$$A(s) \rightleftharpoons B(g) + C(g);\ K_{P_1} = 300; \qquad D(s) \rightleftharpoons E(g) + C(g)\ \ K_{P_2} = 600$$

at 27°C , then find the total pressure of the solid mixture.

39. In a vessel, two equilibrium are simultaneously established at the same temperature as follows:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad \text{...(1)}$$
$$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g) \qquad \text{...(2)}$$

Initially the vessel contains N_2 and H_2 in the molar ratio of 9 : 13. The equilibrium pressure is $7P_0$, in which pressure due to ammonia is P_0 and due to hydrogen is $2P_0$. Find the values of equilibrium constants (K_p's) for both the reactions

40. The decomposition of solid ammonium carbamate, $(NH_4)(NH_2CO_2)$, to gaseous ammonia and carbon dioxide is an endothermic reaction.

$$(NH_4)(NH_2CO_2)(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$$

(a) When solid $(NH_4)(NH_2CO_2)$ is introduced into an evacuated flask at 25°C, the total pressure of gas at equilibrium is 0.116 atm. What is the value of K_p at 25°C ?

(b) Given that the decomposition reaction is at equilibrium, how would the following changes affect the total quantity of NH_3 in the flask once equilibrium is re-established ?

(i) Adding CO_2 (ii) Adding $(NH_4)(NH_2CO_2)$
(iii) Removing CO_2 (iv) Increasing the total volume
(v) Adding neon (vi) Increasing the temperature.

41. Following equilibrium is established at temperature T.

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

at eq. 1M 2M 2M.

If volume of the vessel is doubled then find the equilibrium concentration of each species.

(Given that : $\sqrt{40}$ = 6.324)

42. At 700 K equilibrium constant for the reaction

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

is 54.8. If 0.5 mol L^{-1} of HI(g) is present at equilibrium at 700K, what are the concentration of H_2(g) and I_2(g) assuming that we initially started with HI(g) and allowed it to reach equilibrium at 700K. (Given that : $\sqrt{54.8}$ =7.4)

43. The equilibrium constant for the reaction :

$$H_3BO_3 + \text{glycerine} \rightleftharpoons (H_3BO_3 + \text{glycerine}) \text{ complex is } 0.90.$$

How much glycerine should be added to one litre of 0.10 M H_3BO_3 solution, so that 60% of the H_3BO_3 is converted to boric acid-glycerine complex ? (Assume volume remains same even after adding glycerine and one mole each of boric acid and glycerine react to give one mole of the complex.)

44. For the reaction;CO (g) + 2H_2(g) $\rightleftharpoons$ CH_3OH (g), hydrogen gas is introduced into a five litre flask at 327° C, containing 0.2 mole of CO (g) and a catalyst, until the pressure is 4.92 atm (at eqilibrium). At this point 0.1 mole of CH_3OH(g) is formed. Calculate the equilibrium constants K_p & K_c .

45. At 540 K, 0.10 mol of PCl_5 are heated in a 8.0 L flask. The pressure of the equilibrium mixture is found to be 1.0 bar. Calcualted K_p and K_c for the reaction.

46. Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as:

$$CH_3COOH\,(l) + C_2H_5OH\,(l) \rightleftharpoons CH_3COOC_2H_5\,(l) + H_2O\,(l)$$

(i) Write the concentration ratio (reaction quotient), Q_c, for this reaction (note: water is not in excess and is not a solvent in this reaction)

(ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after sometime. Has equilibrium been reached?

47. Two gases A and B in the molar ratio 1 : 2 were admitted to an empty vessel and allowed to reach equilibrium at 400°C and 8 atm pressure as A + 2B $\rightleftharpoons$ 2C. The mole fraction of C at equilibrium is 0.4. Calculate

(a) K_p for the reaction

(b) The pressure at which mole fraction of A in equilibrium mixture is 0.16.

48. Reaction between N_2 and O_2 takes place as follows:

$$2N_2\,(g) + O_2\,(g) \rightleftharpoons 2N_2O\,(g)$$

If a mixture of 0.482 mol N_2 and 0.933 mol of O_2 is placed in a 10 L reaction vessel and allowed to form N_2O at a temperature for which $K_c = 2.0 \times 10^{-40}$, determine the composition of equilibrium mixture.

(Given that : $\sqrt{43}$ = 6.6)

49. One mole of $Cl_2(g)$ and 3 moles of $PCl_5(g)$ are placed in a 100 litre vessel heated to 227ºC. The equilibrium pressure is 2.05 atm. Assuming ideal behaviour, calculate the degree of dissociation of $PCl_5(g)$ and K_p for the reaction, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$.

50. 8.34 g of PCl_5 (molecular weight 208.5) were completely vaporized at 227ºC where it decomposed and the equilibrium gas mixture occupied 2.05 litre at one atmospheric pressure. Calculate the degree of dissociation of PCl_5 and equilibrium constant K_p of following reactions at this temperature. ($R = 0.082$ L atm mol^{-1} K^{-1})

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

51. The degree of dissociation is 0.39 at 500 K & 1.0 atm for the gasoues reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$. Assuming ideal behaviour of all gases. Calculate the density of equilibrium mixture at 500 K & 1.0 atm pressure.

52. For the equilibrium : $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

the standard enthalpy and entropy changes at 300 K and 1200 K for the forward reaction are as follows:

$\Delta H^o_{300\,K} = -41.16$ kJ mol^{-1} $\Delta S^o_{300\,K} = -0.0424$ kJ mol^{-1}

$\Delta H^o_{1200\,K} = -32.93$ kJ mol^{-1} $\Delta S^o_{1200\,K} = -0.0296$ kJ mol^{-1}

In which direction will the reaction be spontaneous

(a) At 300 K(b) At 1200 K,

(any time of reaction $P_{CO} = P_{CO2} = P_{H2} = P_{H_2O} = 1$ atm)

Also calculate K_p for the reaction at each temperature. (Given that : $10^{-.11} = 0.77$)

53. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

This reaction is carried out at 298 K and 20 bar. 5 mole each of N_2O_4 and NO_2 are taken initially.

Given : $\Delta G^\circ_{N_2O_4} = 100$ kJ mol^{-1} ; $\Delta G^\circ_{NO_2} = 50$ kJ mol^{-1}

(i) Find ΔG for for reaction at 298 K under given condition.

(ii) Find the direction in which the reaction proceeds to achieve equilibrium.

54. Consider the reaction, $2Cl_2(g) + 2H_2O(g) \rightleftharpoons 4HCl(g) + O_2(g)$ $\Delta H^o = +113$ kJ

The four gases, Cl_2, H_2O, HCl and O_2, are mixed and the reaction is allowed to come to equilibrium. State and explain the effect (increase, decrease, no change) of the operation in the left column (below) on the equilibrium value of the quantity in the right column. Each operation is to be considered separately. Temperature and volume are constant unless stated otherwise.

(a) Increasing the volume of the container	Number of moles of H_2O
(b) Adding O_2	Number of moles of H_2O
(c) Adding O_2	Number of moles of HCl
(d) Decreasing the volume of the container	Number of moles of Cl_2
(e) Decreasing the volume of the container	Partial pressure of Cl_2
(f) Decreasing the volume of the container	K_C
(g) Raising the temperature	K_C
(h) Raising the temperature	Concentration of HCl
(i) Adding He	Number of moles of HCl
(j) Adding catalyst	Number of moles of HCl

55. Consider the following equilibrium process:

$$N_2F_4(g) \rightleftharpoons 2NF_2(g) \qquad \Delta H^\circ = 38.5\ kJ$$

Predict the changes in the equilibrium if (a) the reacting mixture is heated at constant volume; (b) NF_2 gas is removed from the reacting mixture at constant temperature and volume ; (c) the pressure on the reacting mixture is decreased at constant temperature; and (d) an inert gas, such as helium, is added to the reacting mixture at constant volume and temperature.

56. The density of an equilibrium mixture of N_2O_4 and NO_2 at 1 atm and 346 K is 1.8 g/L. Calculate K_C for the reaction,

$$N_2O_4\ (g) \rightleftharpoons 2NO_2(g).$$

57. K_p is 9 atm² for the reaction : $LiCl.3NH_3\ (s) \rightleftharpoons LiCl.NH_3(s) + 2NH_3(g)$ at 40°C. How many moles of ammonia must be added at this temperature to a 5 litre flask containing 0.1 mole of $LiCl.\ NH_3$ in order to completely convert the solid to $LiCl.3NH_3$?

58. At certain temperature, the equilibrium constant (K_c) is 16 for the reaction

$$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$$

If we take one mole each of all the four gases in 1 L container, what be concentration of NO and NO_2 at equilibrium ?

59. Consider the equilibrium

$$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g) \quad ; \quad K_p = 0.125\ atm^{-3}.$$

If equal number of moles of CO and $Ni(CO)_4$ (ideal gases) are mixed in a small container fitted with a piston, find the maximum total pressure (in atm) to which this mixture must be brought in order to just precipitate out metallic Ni ?

60. Two solid compounds A and B dissociate into gaseous products at 20°C as

(i) $A(s) \rightleftharpoons A'(g) + H_2S(g)$ (ii) $B(s) \rightleftharpoons B'(g) + H_2S(g)$

At 20°C pressure over excess solid A is 50 mm and that over excess solid B is 68 mm find :

(a) The dissociation constant of A and B

(b) Relative no. of moles of A′ and B′ in the vapour phase over a mixture of solid A and B.

(c) Show that the total pressure of the gas over the solid mixture would be 84.4 mm

61. When NO & NO_2 are mixed, the following equilibria readily obtained;

$$2NO_2 \rightleftharpoons N_2O_4 \qquad K_p = 6.8\ atm^{-1}$$

$$NO + NO_2 \rightleftharpoons N_2O_3 \qquad K_p = ?$$

In an experiment when NO & NO_2 are mixed in the ratio of 1 : 2, the total final pressure was 5.05 atm & the partial pressure of N_2O_4 was 1.7 atm. Calculate

(a) the equilibrium partial pressure of NO. (b) K_p for $NO + NO_2 \rightleftharpoons N_2O_3$

62. At 700 K, CO_2 and H_2 react to form CO and H_2O. For this purpose K_C is 0.11. If a mixture of 0.45 mole of CO_2 and 0.45 mole of H_2 is heated to 700 K.

(a) Find out the amount of each gas at equilibrium.

(b) When equilibrium has been reached, another 0.34 mole of CO_2 and 0.34 mole of H_2 are added to the reaction mixture. Find the composition of mixture at new equilibrium. (Given that : $\sqrt{.11} = .33$)

63. A container contains three gases. A, B and C in equilibrium $A(g) \rightleftharpoons 2B(g) + C\ (g)$

At equilibrium the concentration of A was 3 M, and of B was 4M. On doubling the volume of container, the new equilibrium concentration of B was 3M. Calculate K_C and initial equilibrium concentration of C.

Exercise # 5

Part # I [Previous Year Questions] [AIEEE/JEE-MAIN]

1. What is the equilibrium constant expression for the reaction $P_4(s) + 5O_2(g) \rightleftharpoons P_4O_{10}(s)$? **[AIEEE 2004]**

(1) $K_C = [P_4O_{10}]/[P_4][O_2]^5$ **(2)** $K_C = 1/[O_2]^5$

(3) $K_C = [O_2]^5$ **(4)** $K_C = [P_4O_{10}]/5[P_4][O_2]$

2. For the reaction, $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$ then K_p/K_c is equal to : **[AIEEE 2004]**

(1) 1/RT **(2)** 1.0 **(3)** $\sqrt{RT}$ **(4)** RT

3. The equilibrium constant for the reaction, $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction, $NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is

(1) 2.5×10^2 **(2)** 0.02 **(3)** 4×10^{-4} **(4)** 50 **[AIEEE 2004]**

4. For the reaction, $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$, ($K_C = 1.8 \times 10^{-6}$ at 184°C)
(R = 0.0831 kJ/(mol.K))

When K_p and K_c are compared at 184°C it is found that **[AIEEE 2005]**

(1) Whether K_p is greater than, less than or equal to K_c depends upon the total gas pressure

(2) $K_p = K_c$

(3) K_p is less than K_c

(4) K_p is greater than K_c

5. The exothermic formation of ClF_3 is represented by the equation : **[AIEEE 2005]**

$$Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g)\ ;\ \Delta_r H = -329\ J$$

which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3.

(1) Adding F_2 **(2)** Increasing the volume of container

(3) Removing Cl_2 **(4)** Increasing the temperature

6. An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature at 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm? The equilibrium constant for NH_4HS decomposition at this temperature is : **[AIEEE 2005]**

(1) 0.11 **(2)** 0.17 **(3)** 0.18 **(4)** 0.30

7. Phosphorus pentachloride dissociates as follows in a closed reaction vessel.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$

If total pressure at equilibrium of the reaction mixture is P and degree of dissociation of PCl_5 is x, the partial pressure of PCl_3 will be : **[AIEEE 2006]**

(1) $\left(\frac{x}{x+1}\right)P$ **(2)** $\left(\frac{2x}{1-x}\right)P$ **(3)** $\left(\frac{x}{x+1}\right)P$ **(4)** $\left(\frac{x}{1-x}\right)P$

8. The equilibrium constant for the reaction, $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g)$

is $K_C = 4.9 \times 10^{-2}$. The value of K_C for the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ will be **[AIEEE 2006]**

(1) 416 **(2)** 2.40×10^{-3} **(3)** 9.8×10^{-2} **(4)** 4.9×10^{-2}

9. For the following three reactions a, b and c, equilibrium constants are given:

(A) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$; K_1

(B) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$; K_2

(C) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g)$; K_3

Which of the following relations is correct ? **[AIEEE 2008]**

(1) $K_2K_3 = K_1$ **(2)** $K_3 = K_1K_2$ **(3)** $K_3K_2^3 = K_1^2$ **(4)** $K_1\sqrt{K_2} = K_3$

10. The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressures at these equilibria is **[AIEEE 2008]**

(1) 1 : 1 **(2)** 1 : 3 **(3)** 1 : 9 **(4)** 1 : 36

11. If 10^{-4} dm³ of water is introduced into a 1.0 dm³ flask at 300 K, how many moles of water are in the vapour phase when equilibrium is established ? **[AIEEE 2010]**

(Given : Vapour pressure of H_2O at 300 K is 3170 Pa ; R = 8.314 J K^{-1} mol^{-1})

(1) 5.56×10^{-3} mol **(2)** 1.53×10^{-2} mol **(3)** 4.46×10^{-2} mol **(4)** 1.27×10^{-3} mol

12. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is : **[AIEEE 2011]**

(1) 1.8 atm **(2)** 3 atm **(3)** 0.3 atm **(4)** 0.18

13. The equilibrium constant (K_c) for the reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_c for the reaction $NO(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is : **[AIEEE 2012]**

(1) 0.02 **(2)** 2.5×10^2 **(3)** 4×10^{-4} **(4)** 50.0

14. For the reaction, $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$, if $K_p = K_C(RT)^x$ where the symbols have usual meaning then the value of x is : (assuming ideality) **[JEE MAIN 2014]**

(1) $\frac{1}{2}$ **(2)** 1 **(3)** – 1 **(4)** $-\frac{1}{2}$

15. The standard Gibbs energy change at 300K for the reaction $2A \rightleftharpoons B + C$ is 2494.2J. At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}$, [B] = 2 and $[C] = \frac{1}{2}$. The reaction proceeds in the : **[JEE MAIN 2015]**

[R = 8.314 J/K/mol, e = 2.718]

(1) forward direction because $Q < K_C$ **(2)** reverse direction because $Q < K_C$

(3) forward direction because $Q > K_C$ **(4)** reverse direction because $Q > K_C$

16. The equilibrium constant at 298 K for a reaction $A + B \rightleftharpoons C + D$ is 100. If the initial concentration of all the four species were 1M each, then equilibrium concentration of D (in mol L^{-1}) will be: **[JEE MAIN 2016]**

(1) 0.818 **(2)** 1.818 **(3)** 1.182 **(4)** 0.182

17. Given **[JEE MAIN 2017]**

$C_{(graphite)} + O_2(g) \rightarrow CO_2(g)$:

$\Delta_r H° = -393.5 \text{ kJ mol}^{-1}$

$H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(\bullet)$;

$\Delta_r H° = -285.8 \text{ kJ mol}^{-1}$

$CO_2(g) + 2H_2O(\bullet) \rightarrow CH_4(g) + 2O_2(g)$;

$\Delta_r H° = +890.3 \text{ kJ mol}^{-1}$

Based on the above thermochemical equations, the value of $\Delta_r H°$ at 298 K for the reaction

$C_{(graphite)} + 2H_2(g) \rightarrow CH_4(g)$ will be :

(1) $+74.8 \text{ kJ mol}^{-1}$ **(2)** $+144.0 \text{ kJ mol}^{-1}$ **(3)** $-74.8 \text{ kJ mol}^{-1}$ **(4)** $-144.0 \text{ kJ mol}^{-1}$

Part # II [Previous Year Questions][IIT-JEE ADVANCED]

1. $N_2 + 3H_2 \rightleftharpoons 2\,NH_3$ $K = 4 \times 10^6$ at 298
$K = 41$ at 400 K

Which statements is correct? **[JEE 2006]**

(A) If N_2 is added at equilibrium condition, the equilibrium will shift to the forward direction because according to IInd law of thermodynamics the entropy must increases in the direction of spontaneous reaction.

(B) The condition for equilibrium is $2\Delta G_{NH_3} = 3\Delta G_{H_2} + \Delta G_{N_2}$ where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure.

(C) Addition of catalyst does not change K_p but changes ΔH.

(D) At 400 K addition of catalyst will increase forward reaction by 2 times while reverse reaction rate will be changed by 1.7 times.

2. The value of $\log_{10}K$ for a reaction $A \rightleftharpoons B$ is :

(Given : $\Delta_r H^\circ_{298K} = -54.07$ kJ mol^{-1}, $\Delta_r S^\circ_{298K} = 10$ JK^{-1} mol^{-1} and $R = 8.314$ JK^{-1} mol^{-1}; $2.303 \times 8.314 \times 298 = 5705$)

[JEE 2007]

(A) 5 **(B)** 10 **(C)** 95 **(D)** 100

3. **Statement-1 :** For every chemical reaction at equilibrium, standard Gibbs energy of reaction is zero.

Statement-2 : At constant temperature and pressure, chemical reactions are spontaneous in the direction of decreasing Gibbs energy. **[JEE 2008]**

(A) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False.

(D) Statement-1 is False, Statement-2 is True.

(E) Statement-1 and Statement-2 both are False.

4 According to the Arrhenius equation, **[JEE 2016]**

(A) a high activation energy usually implies a fast reaction.

(B) rate constant increases with increase in temperature. This is due to a greater number of collisions whose energy exceeds the activation energy.

(C) higher the magnitude of activation energy, stronger in the temperature dependence of the rate constant.

(D) the pre-exponential factor is a measure of the rate at which collisions occur, irrespective of their energy.

PARAGRAPH (5-6)

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes palce according to the following equation :

[JEE 2016]

$$X_2(g)\ ƒ\ \ 2X(g)$$

The standard reaction Gibbs energy, $\Delta_f G^\circ$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus, $\beta_{equilibrium}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally.

(Given : $R = 0.083$ L bar K^{-1} mol^{-1})

5. The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{\text{equilibrium}}$, is

(A) $\dfrac{8\beta^2_{\text{equilibrium}}}{2-\beta_{\text{equilibrium}}}$ **(B)** $\dfrac{8\beta^2_{\text{equilibrium}}}{4-\beta^2_{\text{equilibrium}}}$

(C) $\dfrac{4\beta^2_{\text{equilibrium}}}{2-\beta_{\text{equilibrium}}}$ **(D)** $\dfrac{4\beta^2_{\text{equilibrium}}}{4-\beta^2_{\text{equilibrium}}}$

6. The INCORRECT statement among the following, for this reaction, is

(A) Decrease in the total pressure will result in formation of more moles of gaseous X

(B) At the start of the reaction, dissociation of gaseous X_2 takes place spontaneously

(C) $\beta_{\text{equilibrium}} = 0.7$

(D) $K_C < 1$

MOCK TEST

SECTION - I : STRAIGHT OBJECTIVE TYPE

1. Solid ammonium carbamate dissociates to give ammonia and carbon dioxide as follows.

$NH_2COONH_4(s)$ ƒ $2NH_3(g) + CO_2(g)$

At equilibrium, ammonia is added such that partial pressures of NH_3 now equals the original totoal pressure. Calculate the ratio of the total pressure now to the original total pressure.

(A) $\frac{31}{27}$ **(B)** $\frac{60}{40}$ **(C)** $\frac{31}{9}$ **(D)** $\frac{62}{27}$

2. In the Haber process for the industrial manufacture of ammonia involving the reaction, $N_2 + 3H_2$ ƒ $2NH_3$ at 200 atm pressure in the presence of a catalyst, a temperature of about 500°C is used. This is considered as optimum temperature for the process because

(A) yield is maximum at this temperature

(B) catalyst is active only at this temperature

(C) energy needed for the reaction is easily obtained at this temperature

(D) rate of the catalytic reaction is fast enough while the yield is also appreciable for this exothermic reaction at this temperature.

3. For the equilibrium of the reaction, $HgO(s)$ ƒ $Hg(g) + \frac{1}{2}O_2(g)$, k_p for the reaction at total pressure of P is :

(A) $K_p = \frac{2}{3^{3/2}}p^{3/2}$ **(B)** $K_p = \frac{2}{3^{1/2}}p^{1/2}$ **(C)** $K_p = \frac{1}{3^{2/3}}p^{3/2}$ **(D)** $K_p = \frac{1}{3^{2/3}}p$

4. The average person can see the red colour imparted by the complex $[Fe(SCN)]^{2+}$ to an aqueous solution if the concentration of the complex is 6×10^{-6} M or greater. What minimum concentration of KSCN would be required to make it possible to detect 1 ppm (part per million) of Fe(III) in a natural water sample? The instability constant for

$Fe(SCN)^{2+}$ ƒ $Fe^{3+} + SCN^-$ is 7.142×10^{-3}.

(A) 0.0036 M **(B)** 0.0037 M **(C)** 0.0035 M **(D)** None of these

5. $\frac{1}{2}N_2(g) + O_2(g)$ ƒ $NO_2(g)$ ...K_1

$2NO_2(g)$ ƒ $N_2O_4(g)$ ...K_2

Given that above reactions have equilibrium constants K_1 and K_2 respectively. What would be the expression for the equilibrium constant K for the following reaction in terms of K_1 and K_2?

(A) $K_1 K_2$ **(B)** $\frac{1}{K_1(K_2)^2}$ **(C)** $\frac{1}{K_2(K_1)^2}$ **(D)** $\frac{1}{K_1K_2}$

6. The value of K_p for the reaction at 27°C

Br_2(●) $+ Cl_2(g)$ ƒ $2BrCl(g)$

is ‘1 atm’. At equilibrium in a closed container partial pressure of BrCl gas ia 0.1 atm and at this temperature the vapour pressure of Br_2(●) is also 0.1 atm. Then what will be minimum moles of Br_2(●) to be added to 1 mole of Cl_2, to get above equilibrium situation :

(A) $\frac{10}{6}$ moles **(B)** $\frac{5}{6}$ moles **(C)** $\frac{15}{6}$ moles **(D)** 2 moles

7. The two equilibria, $AB(aq) \rightleftharpoons A^+(aq) + B^-(aq)$ and $AB(aq) + B^-(aq) \rightleftharpoons AB_2^-(aq)$ are simultaneously maintained in a solution with equilibrium constants, K_1 and K_2 respectively. If $[A^+]$ and $[AB_2^-]$ are y and x respectively, under equilibrium produced by adding the substance AB to the solvents, then K_1 / K_2 is equal to

(A) $\frac{y}{x}(y-x)^2$ **(B)** $\frac{y^2(x+y)}{x}$ **(C)** $\frac{y^2(x+y)}{x}$ **(D)** $\frac{y}{x}(x-y)$

[**Note** : Use the information of the preceding problem]

8. 5 mol $PCl_5(g)$ and one mole N_2 gas is placed in a closed vessel. At equilibrium $PCl_5(g)$ decomposes 20% and total pressure in to the container is found to be 1 atm. the k_p for equilibrium $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(A) $\frac{1}{24}$ atm **(B)** $\frac{1}{4}$ atm **(C)** $\frac{1}{16}$ atm **(D)** $\frac{1}{28}$ atm

9. Degree of association can be defined as the number of moles of a particular substance associated per mole of the substance taken.

For example : If out of 10 mole of N_2, 3 mol of N_2 combine with H_2 to form NH_3, then degree of association of $N_2 = 0.3$.

Consider the equilibrium situation :

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

Initially N_2 & H_2 were mixed in 1 : 3 molar ratio and after long time the mean molar mass of the mixture was found to be $\frac{23}{3}$ g. The degree of association of N_2 is

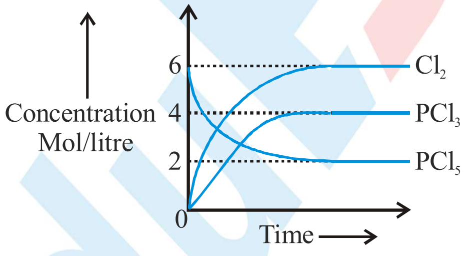
(A) 0.5 **(B)** 0.4 **(C)** 0.9 **(D)** 0.25

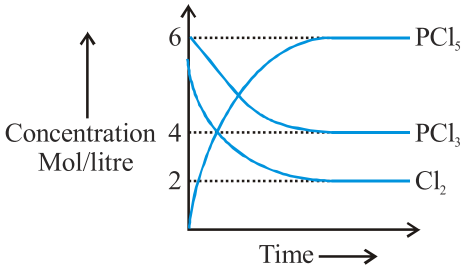
SECTION - II : MULTIPLE CORRECT ANSWER TYPE

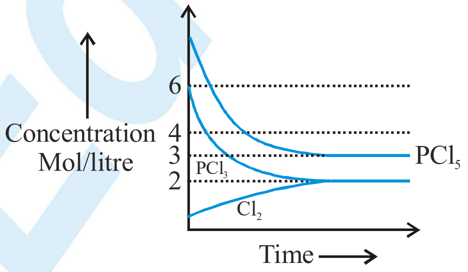
10. For the equilibrium

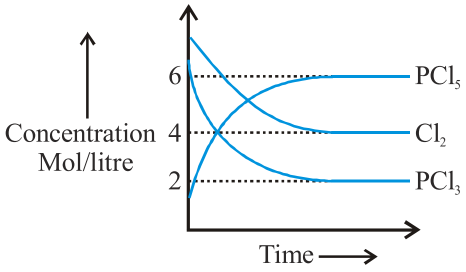
$$PCl_5 \rightleftharpoons PCl_3(g) + Cl_2(g)$$

Which of the following sketch may represent above equilibrium. Assume equilibrium can be achieved from either side and by taking any one or more components initially. (Given K_c for the reaction < 2).

(A)


(B)


(C)


(D)


11. 138 gm of N_2O_4 (g) is placed in 8.2 L container at 300 K. The equilibrium vapour density of mixtue was found to be 30.67. Then (R = 0.82 L atm mol^{-1} K^{-1})

(A) α = degree of dissociation of $N_2O_4 = 0.25$

(B) K_p of $N_2O_4 \rightleftharpoons 2NO_2(g)$ will be 9 atm.

(C) Total pressure at equilibrium = 6.75 atm.

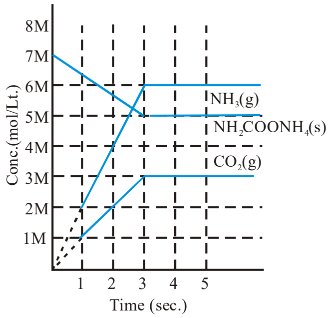
(D) The density of equilibrium mixture will be 16.83 gm/litre.

12. Solid ammonium carbamate dissociate to give ammonia and carbon dioxide as follows

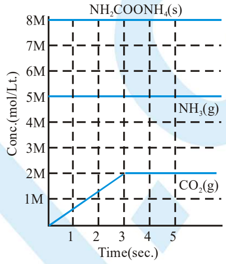
$NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$

which of the following graph incorrectly represents the equilibrium.

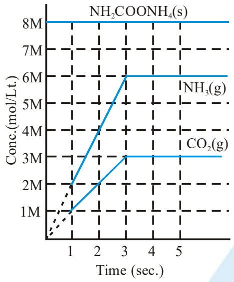
(A)



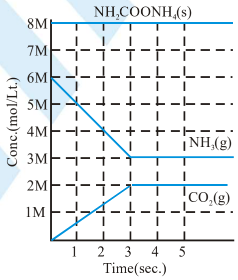
(B)



(C)



(D)



13. $2CaSO_4(g) \rightleftharpoons 2CaO(s) + 2SO_2(g) + O_2(g), \quad \Delta H > 0$

Above equilibrium is established by taking sufficient amount of $CaSO_4(g)$ in a closed container at 1600 K. Then which of the following may be correctoption (Assume that solid $CaSO_4$ is present in the container in each case)

(A) moles of CaO(s) will increase with the increase in temperature

(B) If the volume of the container is doubled at equilibrium then partial pressure of $SO_2(g)$ will change at new equilibrium.

(C) If the volume of the container is halved partial pressure of $O_2(g)$ at new equilibrium will remain same

(D) If two moles of the He gas is added at constant pressure then the moles of CaO(s) will increase.

14. For a reversible reaction $aA + bB \rightleftharpoons cC + dD$; the variation of K with temperature is given by log

$$\frac{K_2}{K_1} = \frac{-\Delta H^\circ}{2.303R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right] \text{ then,}$$

(A) $K_2 > K_1$ if $T_2 > T_1$ for an endothermic change

(B) $K_2 < K_1$ if $T_2 > T_1$ for an endothermic change

(C) $K_2 > K_1$ if $T_2 > T_1$ for an exothermic change

(D) $K_2 < K_1$ if $T_2 > T_1$ for an exothermic change

15. The following reaction attains equilibrium at high temperature.

$$N_2(g) + 2H_2O(g) + \text{heat} \rightleftharpoons 2NO(g) + 2H_2(g)$$

The yield of NO is affected by

(A) increasing the nitrogen concentration

(B) decreasing the hydrogen concentration

(C) compressing the reaction mixture

(D) none of these

SECTION - III : ASSERTION AND REASON TYPE

16. **Statement - 1**: $A(s) \rightleftharpoons B(g) + C(g)\ ;\ Kp_1$

$$X(s) \rightleftharpoons B(g) + Y(g)\ ;\ Kp_2 = 3Kp_1$$

Total pressure of B over the mixture of solid A and X is greater than pressure of B either over excess solid A or over excess solid X But less then their directly sumup value when excess of solid A and excess of solid B kept in different container.

Statement - 2 : In presence of each other, degree of dissociation of both solids decreases.

(A) Statement-1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement-1

(C) Statement-1 is True, Statement-2 is Fasle

(D) Statement-1 is False, Statement-2 is True

17. **Statement-1** : For the equilibrium $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$ then mean molar mass of the equilibrium mixture is always more than 46 and less than 92.

Statement-2 : Addition of $Xenon_{(g)}$, at constant volume to the equilibrium mixtue will result in decrease in the mean molar mass of the mixture.

(A) Statement -1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

18. **Statement-1** : Ice melts at 0°C under normal conditions, it would melt at lower temperature under higher pressure.

Statement - 2 : Formation of ice is an exothermic process.

(A) Statement -1 is True, Statement-2 is True, Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True, Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False

(D) Statement-1 is False, Statement-2 is True

SECTION - IV : COMPREHENSION TYPE

Read the following comprehensions carefully and answer the questions.

Comprehension # 1

Le chatelier's principle

If a system at equilibrium is subjected to a change of any one of the factors such as concentration, pressure or temperature, the system adjusts itself in such a way as to (Nulify) the effect of that change.

Change of pressure : If a system in equilibrium consists of gases, then the concentrations of all the components can be altered by changing the pressure. When the pressure on the system is increased, the volume decreases proportionately. The The total number of mols per unit volume will now be more and the equilibrium will shift in the direction in which there is decrease in number of moles i.e., towards the direction in which there is decrease in volume.

Effect of pressure on melting point : There are two types of solids :

(a) Solids whose volume decreases on melting, e.g. ice, diamond, carborundum, magnesium nitride and quartz.

Solid (higher volume) $\rightleftharpoons$ Liquid (lower volume)

The process of melting is facilitated at high pressure, thus melting point is lowered.

(b) Solids whose volume increase on melting, e.g., Fe, Cu, Ag, Au, etc.

Solid (lower volume) $\rightleftharpoons$ Liquid (higher volume)

In this case the process of melting become difficult at high pressure; thus meltingpoint becomes high.

(c) **Solubility of substances** : When solid substance are dissolved in water, either heat is evolved (exothermic) or heat is absorbed (endothermic).

$KCl + aq \rightleftharpoons KCl(aq) - heat$

In susch cases, solubility increase with increase in temperature. Consider the case of KOH; when this is dissolved, heat is evolved.

$KOH + aq \rightleftharpoons KOH(aq) + heat$

In such cases, solubility decrease with increase in temperature.

(d) **Solubility of gases in liquids** : When a gas dissolves in liquid, there is decrease in volume. Thus, increase of pressure will favour the dissolution of gas in liquid.

Effect of temperature : Le–Chatelier's principle predicts a system at equilibrium will tend to shift in the endothermic direction when temperature is raised, for then energy is absorbed as heat and the rise in temperature is opposed. Conversely, an equilibrium will shift in the exothermic direction if the temperature is lowered, for then that energy is released and the reduction in temperature is opposed.

Van't Hoff equation shows the dependence of equilibrium constant K on temperature as :

$$\frac{d}{dT}\ln K = \frac{\Delta H^\circ}{RT^2} \quad \text{or} \quad \ln K = \text{constant} - \frac{\Delta H^\circ}{R}\cdot\frac{1}{T}$$

19. A gas 'X' when dissolved in water heat is evolved. Then solubility of 'X' will increase

(A) Low pressure, high temperature
(B) Low pressure, low temperature
(C) High pressure, high temperature
(D) High pressure, low temperatue

20. $Au(s) \rightleftharpoons Au(\ell)$

Above equilibrium is favoured at

(A) High pressure low temperature
(B) High pressure high temperature
(C) Low pressure, high temperature
(D) Low pressure, low temperature

21. For the reaction

$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$$

If pressure is increased by reducing the volume of the container then

(A) Total pressure at equilibrium will change
(B) Concentration of all the component at equilibrium will change
(C) Concentration of all the component at equilibrium will remain same
(D) Equilibrium will shift in the forward direction

22. The plot of log K against $\frac{1}{T}$ is a straight line with positive slope (K being the equilibrium constant of a reaction), which of the following is then correct?

(A) The reaction is endothermic in nature
(B) The reaction will be exothermic in nature
(C) The reaction goes to farther extent on raising the temperature
(D) None of these

Comprehension # 2

The rate of chemical reaction at a particular temperature is proportional to the product of the molar concentration of reactants with each concentration term raised to the power equal to the number of molecules of the respective reactant taking part in the reaction. $aA + bB \longrightarrow$ products, rate of reaction $\alpha\ [A]^a [B]^b = k\ [A]^a [B]^b$, where k is the rate constant of the reaction.

Equilibrium constant (k)

For a general reaction $aA + bB \Leftrightarrow cC + dD$, forward rate $r_f = k_f [A]^a [B]^b$, backward rate $r_b = k_b [C]^c [D]^d$, concentrations of reactants & bproducts at equilibrium

are related by $\frac{K_f}{K_b} = K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$ where all the concentrations are expressed in mole/liter.

e.g. $PCl_5 \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$

In the expression of equilibrium constant those components are kept whose concentration changes with time.

If equilibrium is estabilished by taking all the components in the reaction then to predict the direction of reactions we calculate the reaction quotient (Q).

The values of expression $Q = \frac{[C]^c[D]^d}{[A]^a[B]^b}$

at any time during reaction is called reaction quotient
if $Q > K_c$ reaction proceed in backward direction until equilibrium in reached
if $Q < K_c$ reaction will proceed in forward direction until equilibrium is established
if $Q = K_c$ Reaction is at equilibrium

23. $A(g) + B(g) \rightleftharpoons 2C(g)$

Initial concentration of 'A' is twice the initial concentration of 'B'. At equilibrium concentration of 'A' and 'C' are same then equilibrium constant for the reaction is

(A) $\frac{4}{3}$ **(B)** $\frac{4}{9}$ **(C)** $\frac{16}{9}$ **(D)** 4

24. $A(g) + B(g) \rightleftharpoons C(g) + D(g)$

Above homogeneous reaction is carried out in a 2 litre container at a particular temperature by taking 1 mole each of A, B, C and D respectively. If K_C for the reaction is $\frac{1}{4}$ ten equilibrium concentration of C is.

(A) $\frac{1}{3}$M **(B)** $\frac{2}{3}$M **(C)** $\frac{4}{3}$M **(D)** $\frac{1}{2}$M

25. When C_2H_5OH and CH_3COOH are mixed in equivalent proportion equilibrium is reached when 2/3 of acid and alcohol are used. How much ester will be present when 2 moles of acid were to react with 2 moles of alcohol?

(A) 1.33 **(B)** 1 **(C)** 2.33 **(D)** 2

SECTION - V : MATRIX - MATCH TYPE

26. Match List I (equilibrium) with List II (conditio for reaction) and select the correct answer using the option below the lists.

Column I **(equilibrium)**		**Column II** **(condition for reaction)**
(A) $A_2(g) + B_2(g) \xrightleftharpoons{\text{endothermic}} 2AB(g)$	**(p)**	High Temperature
(B) $2AB_2(g) + B_2(g) \xrightleftharpoons{\text{exothermic}} 2AB_3(g)$	**(q)**	Low Temperature
(C) $2AB_2(g) + B_2(g) \xrightleftharpoons{\text{exothermic}} A_2(g) + 3B_2(g)$	**(r)**	High Pressure
	(s)	Low Pressure
	(t)	Independent of Pressure

27. Match the following (multiple)

Left column : Represents an equilibrium situation through a chemical equation and below each equation a stimulus is given which may or may not disturb the equilibrium situation.

Right column : Represents the responses immediately after the disturbance is created.

With
R_1 : Rate of forward reaction
R_2 : Rate of backward reaction
R_3 : Reaction quotient
K : Equilibrium constant

(A) $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$ Pressure is increased	**(p)**	R_1 increases
(B) $\frac{1}{2}N_{2(g)} + \frac{3}{4}H_{2(g)} \rightleftharpoons NH_{3(g)}$	**(q)**	R_b increases
(C) $PCl_{3(g)} + Cl_{2(g)} \rightleftharpoons PCl_{5(g)}$ PCl_5 is added	**(r)**	$R_1 = R_b$
(D) $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$ Inert gas added at court volume	**(s)**	$Q \neq K$

28. Match the following :

Column I		**Column II**
(A) For the equilibrium $NH_4I(s) \rightleftharpoons NH3(g) + HI(g)$, if pressurel is increased at equilibrium	**(p)**	Forward shift
(B) For the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$ at equilibrium volume is increased at equilibrium	**(q)**	No change
(C) For the equilibrium $H_2O(g) + CO(g) \rightleftharpoons H_2(g) + CO_2(g)$ inert gas is added at constant pressure at equilibrium	**(r)**	Backward shift
(D) For the equilibrium $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ Cl_2 is removed at equilibrium	**(s)**	Final pressure is more than initial pressure

SECTION - VI : SUBJECTIVE TYPE

29. At certain temperature, the equilibrium constant for the gaseous reaction of CO with O_2 to produce CO_2 is 5.0×10^3 lit/mole. Calculate [CO] at equilibrium, if 1.0 mol each of CO and O_2 are placed in a 2.0 L vessel and allowed to come to equilibrium .

30. At 827°C, K_p for the reaction between $CO_2(g)$ and excess hot graphites(s) is 10 atm. Calculate the equilibrium concentration of gases at 827°C and total equilibrium pressure equal to 5.6 atm

31. The equilibrium consant for the following reaction, $H_2(g) + Br_2(g) \leftrightarrow 2HBr\ (g)$ is 1.6×10^5 at 1024 K. Find the equilibrium pressure of all gases if 10 bar of HBr is introduced into a sealed container at 1024 K.

or

The equilibrium constant for the following reaction is 1.6×10^5 at 1024 K,

$$H_2(g) + Br_2(g)\ ƒ\ \ 2HBr(g)$$

Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

32. A container of volume V litre contains an equilibrium mixture which consists of 2 mol each of $PC●_5$, $PC●_3$ and $C●_2$ (all gases). The equilibrium pressure is 3 atm. and tempereature is TK. A certain amont of $C●_2(g)$ is now introduced into the container keeping the pressure and temperature constant, until the equilibrium volume becomes 2V litre. Calculate the number of moles of $C●_2$ that were added.

[Fill your answer in the multiple of 10^{-2}, for example if your answer is 2.53 then fill 253 as your answer.]

33. NH_3 is heated initialy at 15 atm from 27°C to 127°C at constant volume. At 127°C equilibrium is established. The new pressue at equilibrium at 127°C becomes 30 atm for the reaction $2NH_3(g)\ ƒ\ \ N_2(g) + 3H_2(g)$. Then find the % of moles of NH_3 actually decomposed.

34. For the equilibrium :

$$LiCl.\,3NH_3\,(s)\ ƒ\ \ LiCl.\,NH_3(s) + 2NH_3\,(g) \qquad [K_p = 9\ atm^3]$$

at 40°C. A 5 litre vessel contains 0.1 mole of $LiCl.NH_3$. How many mole of Nh3 should be added to the flask at this temperature to derive the backward reaction for completion?

35. In a container of constant volume at a particular temparature N_2 and H_2 are mixed in the molar ratio of 9 : 13. The following two equilibria are found to be coexisting inthe container

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

$$N_2\,(g) + 2H_2\,(g)\ ƒ\ \ N_2H_4\,(g)$$

The total equilibrium pressure is found to be 3.5 atm while partial pressure of NH_3 (g) and H_2 (g) are 0.5 atm and 1 atm respectively. Calculate of equilibrium constants of the two reactions given above.

ANSWER KEY

EXERCISE - 1

1. B **2.** B **3.** B **4.** B **5.** A **6.** A **7.** A **8.** A **9.** A **10.** C **11.** B **12.** B **13.** B
14. B **15.** A **16.** A **17.** A **18.** B **19.** D **20.** B **21.** C **22.** A **23.** B **24.** D **25.** A **26.** B
27. A **28.** B **29.** B **30.** A **31.** B **32.** C **33.** B **34.** D **35.** B **36.** A **37.** A **38.** C **39.** B
40. C **41.** B **42.** D **43.** D **44.** C **45.** B **46.** D **47.** B **48.** B **49.** A **50.** C **51.** D **52.** A
53. B **54.** C **55.** A **56.** D **57.** D **58.** D **59.** A **60.** B **61.** C **62.** C **63.** C **64.** B **65.** A
66. D **67.** A **68.** B **69.** B **70.** B **71.** C **72.** B **73.** C **74.** D **75.** A **76.** C **77.** B **78.** C
79. B **80.** B **81.** A **82.** B **83.** A **84.** B **85.** A **86.** D **87.** B **88.** C **89.** C **90.** B **91.** B
92. A **93.** C **94.** D **95.** C **96.** C

EXERCISE - 2 : PART # I

1. A, B, C **2.** A, D **3.** A, B **4.** A, C, D **5.** A, B, C **6.** A, B, D
7. B, C, D **8.** A, C, D **9.** B, D **10.** A, B, C, D, E **11.** A, C **12.** C, D
13. B, D **14.** A, B, C, D **15.** A, B, C **16.** A, C, E **17.** A, B, C, D **18.** B, C, D
19. A **20.** A **21.** A **22.** A **23.** B **24.** B **25.** C **26.** D **27.** C **28.** A **29.** B **30.** D **31.** A
32. B **33.** C **34.** B **35.** B **36.** A **37.** B **38.** D **39.** A **40.** A **41.** D **42.** A **43.** B **44.** B
45. A **46.** B **47.** B **48.** D **49.** A **50.** C **51.** A **52.** B **53.** D **54.** C **55.** C **56.** A **57.** A
58. D **59.** B

PART # II

1. A **2.** B **3.** A **4.** A **5.** D **6.** A **7.** D **8.** A **9.** C **10.** A **11.** B **12.** A **13.** A

EXERCISE - 3 : PART # I

1. A → (r), B → (r), C → (q), D → (p)

2. A → (q,s), B → (p), C → (p), D → (r)

3. A → (s), B → (p, q, s), C → (p, q, r), D → (r)

4. A → (p), B → (s), C → (q), D → (r)

PART # II

Comprehension # 1 : **1.** B **2.** B **3.** B

Comprehension # 2 : **1.** D **2.** C **3.** A, B

Comprehension # 3 : **1.** C **2.** D **3.** B

Comprehension # 4 : **1.** A **2.** B

Comprehension # 5 : **1.** B **2.** C **3.** A

EXERCISE - 5 : PART # I

1. 2	**2.** 1	**3.** 4	**4.** 4	**5.** 1	**6.** 1	**7.** 1	**8.** 1	**9.** 2
10. 4	**11.** 4	**12.** 1	**13.** 4	**14.** 4	**15.** 4	**16.** 2	**17.** 3	

PART # II

1. B	**2.** B	**3.** D	**4.** BCD	**5.** B	**6.** C

MOCK TEST

1. A	**2.** D	**3.** A	**4.** A	**5.** C	**6.** C	**7.** A
8. D	**9.** A	**10.** (B, D)	**11.** (B, C, D)	**12.** (A, B, D)	**13.** (A, C, D)	**14.** (A, D)
15. (A, B, C)	**16.** A	**17.** C	**18.** B	**19.** D	**20.** C	**21.** (A, B)
22. B	**23.** D	**24.** A	**25.** A			

26. A → (p, t) ; B → (q, r) ; C → (q, s)

27. A → (p, q, r) ; B → (p, q, s) ; C → (q, s) ; D → (p, q, r)

28. A → (r, s) ; B → (r) ; C → (q) ; D → (p, s)

29. A → (q, s) ; B → (p) ; C – q, s) ; D → (r)