CHEMICAL EQUILIBRIUM

CONTENTS

JEE(Advanced) Syllabus

Law of mass action; Equilibrium constant, Le Chatelier's principle (effect of concentration, temperature and pressure); Significance of ΔG and ΔG° in chemical equilibrium.

JEE(Main) Syllabus

Meaning of equilibrium, concept of dynamic equilibrium. Equilibria involving physical processes: Solid -liquid, liquid–gas and solid–gas equilibria, Henry's law, general characerics of equilibrium involving physical processes. Equilibria involving chemical processes: Law of chemical equilibrium, equilibrium constants (K_P and K_C) and their significance, significance of ΔG and ΔG° in chemical equilibria, factors affecting equilibrium concentration, pressure, temperature, effect of catalyst; Le-Chatelier's principle.
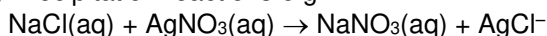
Chemical Equilibrium

Introduction :

Equilibrium is a state in which there are no observable changes as time goes by. When a chemical reaction has reached the equilibrium state, the concentrations of reactants and products remain constant over time and there are no visible changes in the system. However, there is much activity at the molecular level because reactant molecules continue to from product molecules while product molecules react to yield reactant molecules. This dynamic situation is the subject of this chapter. Here we will discuss different types of equilibrium reactions, the meaning of the equilibrium constant and its relationship to the rate constant and factors that can effect a system at equilibrium.

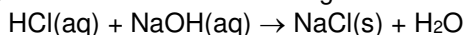## Section (A) : Properties of equilibrium, active mass

Types of chemical reactions

The reaction which proceed in one direction only
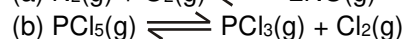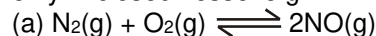(a) Precipitation reactions e.g.
    $NaCl(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl^-$
(b) Neutralization reactions e.g.
    $HCl(aq) + NaOH(aq) \rightarrow NaCl(s) + H_2O$
(c) Reactions in open vessels with one of the gaseous product

Reactions which proceed in both the direction. These are possible only in closed vessel e.g.
(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
(b) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

Types of chemical reactions

	Irreversible reaction		Reversible reaction
1	The reaction which proceeds in one direction (forward direction) only.	1	The reaction which proceed in both the direction under the same set of experimental conditions.
2	Reactants are almost completely converted into products. Products do not react to form reactants again.	2	Reactants form products and products also react to form reactants in backward direction. These are possible in closed vessels .
3	Do not attain equilibrium state.	3	Attain the equilibrium state and never go to completion.
4	Such reactions are represented by single arrow {$\rightarrow$}	4	Represented by double arrow ($\rightleftharpoons$) or ($\rightleftharpoons$)
5	Examples –	5	Examples :–
(a)	Precipitation reactions e.g. $NaCl(aq) + AgNO_3(aq) \rightarrow NaNO_3(aq) + AgCl\downarrow$	(a)	Homogeneous reactions- only one phase is present (i) Gaseous phase– $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ [Birkland eyde process (HNO₃)] $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (Haber's process) (ii) Liquid phase $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$
(b)	Neutralization reactions e.g $HCl(aq) + NaOH(aq) \rightarrow NaCl(aq) + H_2O$		
(c)	$2KClO_3 (s) \xrightarrow{\Delta} 2KCl(s) + 3O_2(g)$	(b)	**Heterogeneous reactions:** More than one phases are present $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ Closed vessel
(d)	**Reactions in open vessel:** Even a reversible reaction will become irreversible if it is carried out in open vessel. Ex. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ Open vessel		

State of Chemical equilibrium :

State of equilibrium means the balance of driving forces i.e. the factors taking the reaction in forward direction and the backword direction are balancing each other.
The equilibrium state represents a compromise between two opposing tendencies.

● Tendency to minimise energy.   ● Molecules try to maximise entropy.

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In a reversible reaction like :

$$\underbrace{R_1 + R_2}_{Reactants} \rightleftharpoons \underbrace{P_1 + P_2}_{Products}$$

Initially only reactants are present. R_1 and R_2 combine to form P_1 and P_2. As soon as P_1 and P_2 are formed, they start the backward reaction. As concentrations of R_1 and R_2 decrease rate of forward reaction decreases and rate of backward reaction increases. Ultimately a stage is reached when both the rates become equal. Such a state is known as "Chemical Equilibrium" or "state of Equilibrium".

At equilibrium :

(i) Rate of forward reaction (r_f) = rate of backward reaction (r_b) (dynamic nature)

(ii) All measurable parameters become constant with respect to time.
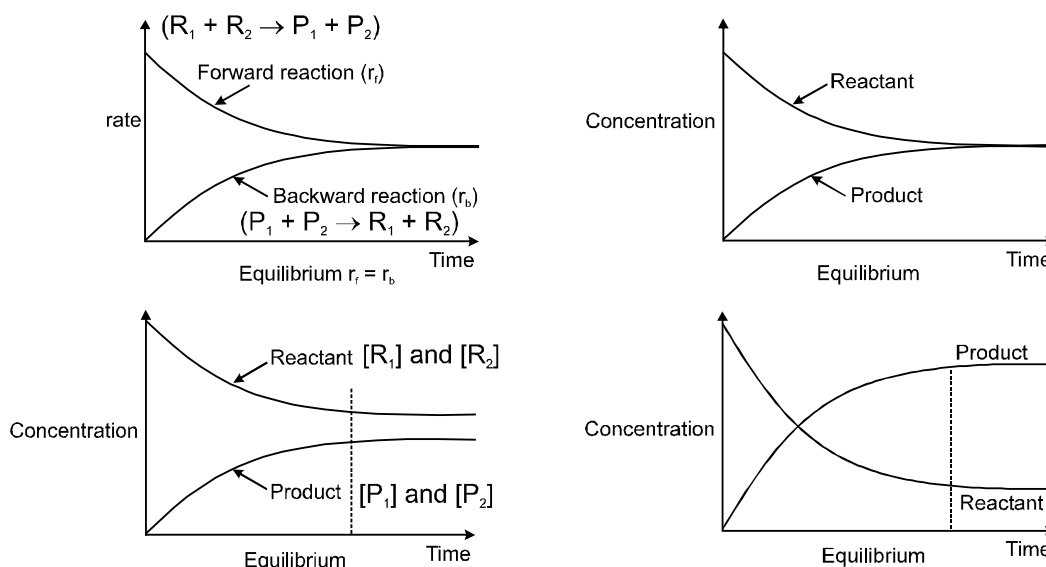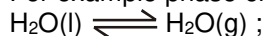

Types of equilibria on the basis of process

Physical Equilibrium

Equilibrium in physical process is called physical equilibrium.

For example phase changes like
$H_2O(l) \rightleftharpoons H_2O(g)$;
Solvation like
$NaCl(s) \xrightleftharpoons[excess]{H_2O} NaCl(aq)$
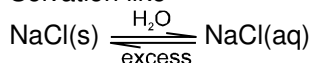
Chemical Equilibrium

Equilibrium in chemical process is called chemical equilibrium.

For example
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
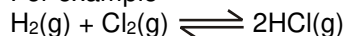
Types of equilibria on basis of physical state

Homogeneous equilibrium
One phase in the system
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$
$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
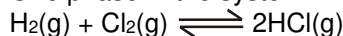
Heterogeneous equilibrium
More than one phase are present in system
$3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$
$2Na_2O_2(s) + 2H_2O(\ell) \rightleftharpoons 4NaOH + O_2(g)$
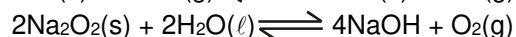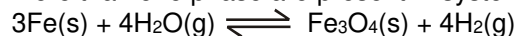
Characteristics of chemical equilibrium :

● The nature and the properties of the equilibrium state are the same regardless of the direction from which it is achieved. It can be achieved in both directions.

● Equilibrium is dynamic in nature.
It means that at microscopic level reaction has not stopped. It appears that no change is occuring but both the opposing reactions are proceeding at the same rate. So there is no net change.Thus equilibrium is not static in nature.

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- A catalyst can alter the rate of approach of equilibrium but does not change the state of equilibrium. By using catalyst, the equilibrium can be achieved in different (more/less) time, but the relative concentrations of reactants and products are same irrespective of the presence or absence of a catalyst.
- Equilibrium can be observed by constancy of some observable properties like colour, pressure, concentration, density, temperature, refractive index etc.which may be suitable in a given reaction.
- At equilibrium, free energy change $\Delta G = 0$
- Equilibrium state can be affected by altering factors like pressure, volume, concentration and temperature etc.(Le chateliers Principle).
- System moves toward an equilibrium state spontaneously even if it is disturbed. It will return to original state.

Solved Examples

Ex-1. (1) Consider the following cases–

(I)
| H_2+I_2 |
| $\rightleftharpoons$ 2HI |
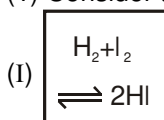
Equilibrium state has been attained

(II) Furnace — Metal Rod — Temperatures becomes constant $T_1 > T_2 > T_3 > T_4$

(III) $H2O(\ell)$ Level of water becomes constant

The nature of flow of energy in case (I) is same as that in–

(A) II   (B) III   (C) II and III   (D) None

Sol. (D) None, because in II and III, the flow of energy or matter is taking place only in one direction. While in equilibrium state, the flow of energy takes place in both directions equally. Thus (I) is a dynamic equilibrium while states in II and III are called steady state (static equilibrium).
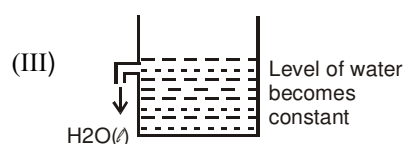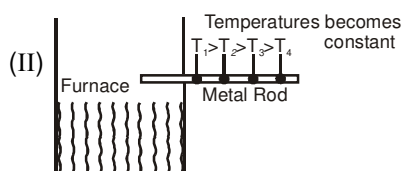
Law of mass action : [By Guldberg and Waage]

Rate at which a substance reacts $\propto$ [Active Mass of the substance]

Active Mass = Molar concentration i.e. Moles/Litres

$$= \frac{\text{Wt of substance (gram)}}{\text{Molar wt.} \times \text{Vol.(Litre)}}$$

It is represented in square brackets i.e. [ ] e.g. [A], [N$_2$] etc.

Note: Active masses are dimensionless quantities but for our purposes we generally take them with dimensions of molarity, partical pressure, etc.

The rate of a chemical reaction at a particular temperature is proportional to the product of active masses of reactants raised to the powers of their stoichiometric coefficients.

Ex. $aA + bB \longrightarrow$ products

Rate of reaction α $[A]^a [B]^b$

Rate = $k [A]^a [B]^b$, where k is the rate constant of the reaction.

Section (B & C) : Homogeneous equilibrium: K_C in gaseous system & K_P in gaseous system

Equilibrium constant (K) :

For a general reaction
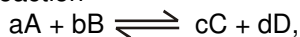
$$aA + bB \rightleftharpoons cC + dD,$$

Forward reaction rate $r_f = k_f [A]^a [B]^b$,

Backward reaction rate $r_b = k_b [C]^c[D]^d$,

At equilibrium $r_f = r_b$

$$k_f [A]^a_{eq} [B]^b_{eq} = k_b [C]^c_{eq} [D]^d_{eq}$$

The concentrations of reactants & products at equilibrium are related by

$$\frac{k_f}{k_b} = K_C = \frac{[C]^c_{eq} [D]^d_{eq}}{[A]^a_{eq} [B]^b_{eq}}$$

○ **K_c** is a constant and is called the **equilibrium constant in terms of concentration.** where all the concentrations are at equilibrium and are expressed in moles/litre.

e.g. $PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2(g)$ $\Rightarrow$ $K_C = \dfrac{[PCl_3]_{eq} \ [Cl_2]_{eq}}{[PCl_5]_{eq}}$

e.g. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ $\Rightarrow$ $K_C = \dfrac{[NH_3]_{eq}^2}{[N_2] \ [H_2]_{eq}^3}$

e.g. $\dfrac{1}{2} H_2(g) + \dfrac{1}{2} I_2(g) \rightleftharpoons HI(g)$ $\Rightarrow$ $K_c = \dfrac{[HI]'_{eq}}{[H_2]_{eq}^{1/2} \ [I_2]_{eq}^{1/2}}$

○ **$K_P \rightarrow$ Equilibrium constant in terms of partial pressure.** It is defined for the equilibrium reaction which contains at least one gaseous component.

e.g. $aA(g) + bB(g) \rightarrow cC(g) + dD(g)$
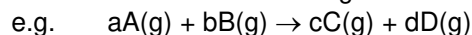
$K_P = \dfrac{[P_C]_{eq}^c \ [P_D]_{eq}^d}{[P_A]_{eq}^a \ [P_B]_{eq}^b}$

Where various pressures are the partial pressures of various gases substances.

Section (D) : Relation between K_P and K_C

○ **Relation between K_p & K_C**

$PV = nRT$ or, $P = \dfrac{n}{V} RT$

$P = CRT$ where $C = \dfrac{n}{V}$ = (moles per litre)

$P_C = [C] RT$; $P_D = [D] RT$; $P_A = [A] RT$; $P_B = [B] RT$

$\Rightarrow$ $K_P = \dfrac{[C]^c (RT)^c [D]^d (RT)^d}{[A]^a (RT)^a [B]^b (RT)^b} = \dfrac{[C]^c [D]^d}{[A]^a [B]^b} (RT)^{(c+d) - (a+b)}$

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

Where $\Delta n_g = (c + d) - (a + b)$, calculation of Δn involves only gaseous components.

$\Rightarrow$ Δn_g = sum of the number of moles of gaseous products – sum of the number of moles of gaseous reactants. $\underline{\Delta n_g \text{ can be positive, negative, zero or even fraction.}}$
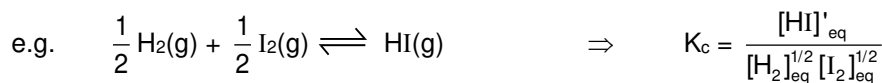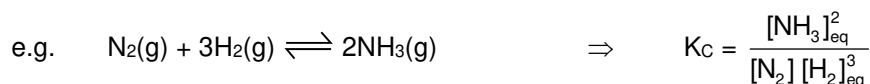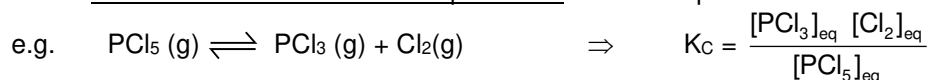
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
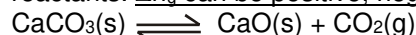
$\Delta n_g = 1$ (because there is only one gas component in the products and no gas component in the reaction)

$\Rightarrow K_p = K_c.(RT)$

Unit of Equilibrium contants :
- Unit of K_p is $(atm)^{\Delta n}$
- Unit of K_c is $(mole/Lit)^{\Delta n} = (conc.)^{\Delta n}$

Note : ○ In fact, equilibrium constant does not carry any unit because it is based upon the activities of reactants and products and activities are unitless quantities. Under ordinary circumstances, where activities are not known, above types of equilibrium constant and their units are employed.

○ **For pure solids and pure liquids, although they have their own active masses but they remain constant during a chemical change (reaction). Therefore, these are taken to be unity for the sake of convenience.**

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

$K_C = [CO_2]$, $K_P = P_{CO_2}$

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Section (E) : Reaction quotient and Its applications

● **Predicting the direction of the reaction**
Reaction Quotient (Q)

At each point in a reaction, we can write a ratio of concentration terms having the same form as the equilibrium constant expression. This ratio is called the reaction quotient denoted by symbol Q.
It helps in predicting the direction of a reaction.

The expression $Q = \dfrac{[C]^c [D]^d}{[A]^a [B]^b}$ <u>at any time during reaction</u> is called reaction quotient. The concentrations

[C], [D], [A], [B] are not necessarily at equilibrium.
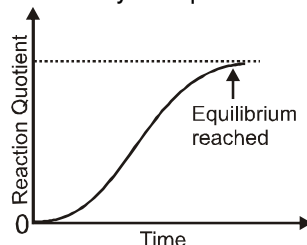
● *The reaction quotient is a variable quantity with time.*
● *It helps in predicting the direction of a reaction.*

❍ if $Q > K_c$ reaction will 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.

eg. $2A(g) + B(g) \rightleftharpoons C(g) + D(g)$

Q_C = Reaction quotient in terms of concentration

$Q_C = \dfrac{[C][D]}{[A]^2[B]}$

$K_C = \dfrac{[C]_{eq}[D]_{eq}}{[A]^2_{eq}[B]_{eq}}$ [Here all the conc. are at equilibrium]

Solved Examples

Ex-2. For the reaction NOBr (g) $\rightleftharpoons$ NO(g) + $\dfrac{1}{2}$ Br₂ (g)

K_P = 0.15 atm at 90°C. If NOBr, NO and Br₂ are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 0.2 atm respectively, will Br₂ be consumed or formed ?

Sol. $Q_P = \dfrac{[P_{Br_2}]^{1/2}[P_{NO}]}{[P_{NOBr}]} = \dfrac{[0.2]^{1/2}[0.4]}{[0.50]} = 0.36$

$K_P = 0.15$

∴ $Q_P > K_P$

Hence, reaction will shift in backward direction ∴ Br₂ will be consumed

● **Predicting the extent of the reaction**

$K = \dfrac{[Product]_{eq}}{[Reactant]_{eq}}$
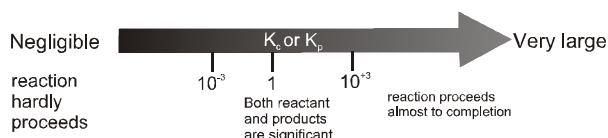
Case-I: If K is large (K > 10³) then product concentration is very very larger than the reactant ([Product] >>[Reactant]) Hence concentration of reactant can be neglected with respect to the product. In this case, the reaction is product favourable and equilibrium will be more in forward direction than in backward direction.

Case-II : If K is very small (K < 10^{-3})

[Product] << [Reactant]

Hence concentration of Product can be neglected as compared to the reactant.

In this case, the reaction is reactant favourable.

Solved Examples

Ex-3. The K$_P$ values for three reactions are 10^{-5}, 20 and 300 then what will be the correct order of the percentage composition of the products.

Sol. Since K$_p$ order is 10^{-5} < 20 < 300 so the percentage composition of products will be greatest for K$_p$ = 300.

Section (F) : Properties of equilibrium Constant

● Equilibrium constant <u>does not depend</u> upon concentration of various reactants, presence of catalyst, direction from which equilibrium is reached

● The equilibrium constant does not give any idea about time taken to attain equilibrium.

● **K depends on the stoichiometry of the reaction.**

❍ If two chemical reactions at equilibrium having equilibrium constants K$_1$ and K$_2$ are added then the resulting equation has equilibrium constant K = K$_1$. K$_2$

$$\text{Equation constant}$$

$$\text{A (g)} \rightleftharpoons \text{B(g)} \qquad K_1$$
$$\text{B (g)} \rightleftharpoons \text{C(g)} \qquad K_2$$

On adding $\qquad$ A(g) $\rightleftharpoons$ C(g) $\qquad\qquad$ K = K$_1$. K$_2$

❍ If the reaction having eq. constant K$_1$ is reversed then resulting equation has eq. constant $\dfrac{1}{K_1}$

$$\text{A(g) + B(g)} \rightleftharpoons \text{C(g) + D(g)}$$

On reversing, $\quad$ C(g) + D(g) $\rightleftharpoons$ A(g) + B(g) $\quad$ K = $\dfrac{1}{K_1}$
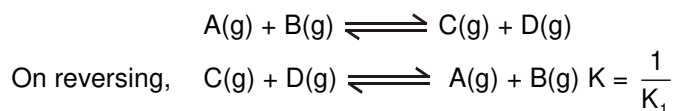
❍ If a chemical reaction having equilibrium constant K$_1$ is multiplied by a factor n then the resulting equation has equilibrium constant K = (K$_1$)^n , n can be fraction

eg. $\qquad\qquad\qquad\qquad$ D$_2$(g) $\rightleftharpoons$ 2A(g) $\qquad\qquad$ K$_1$

Multiplying by $\left(\dfrac{1}{2}\right)$, $\qquad \dfrac{1}{2}$ D$_2$ $\rightleftharpoons$ A $\qquad\qquad$ K = (K$_1$)$^{1/2}$ = $\sqrt{K_1}$
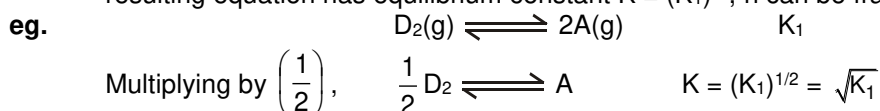
● **Equilibrium constant is dependent only on the temperature.**

It means K$_p$ and K$_c$ will remain constant at constant temperature no matter how much changes are made in pressure, concentration, volume or catalyst.

❍ However if temperature is changed,

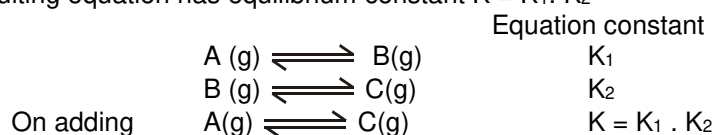$$\log\dfrac{k_2}{k_1} = \dfrac{\Delta H}{2.303\,R}\left[\dfrac{1}{T_1} - \dfrac{1}{T_2}\right] ; \quad \Delta H = \text{Enthalpy of reaction}$$

If T$_2$ > T$_1$ then $\quad$ K$_2$ > K$_1$ provided ΔH = +ve (endothermic reaction)

$\qquad\qquad\qquad\qquad$ K$_2$ < K$_1$ if ΔH = –ve (exothermic reaction)

In the above equation, the unit of R and ΔH/T should be same.

Section (G) : Homogenuous Equilibrium (liquid system)

The reaction between alcohol and acid to form ester is an example of homogeneous equilibrium in liquid system.

$$\text{CH}_3\text{COOH}(\ell) + \text{C}_2\text{H}_5\text{OH}(\ell) \rightleftharpoons \text{CH}_3\text{COOC}_2\text{H}_5(\ell) + \text{H}_2\text{O}(\ell)$$

$$K_C = \dfrac{[\text{CH}_3\text{COOC}_2\text{H}_5][\text{H}_2\text{O}]}{[\text{CH}_3\text{COOH}][\text{C}_2\text{H}_5\text{OH}]}$$

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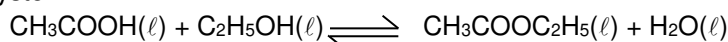
—— *Solved Examples* ——

Ex-4. In an experiment starting with 1 mole of ethyl alcohol, 1 mole of acetic acid and 1 mole of water at T°C, the equilibrium mixture on analysis shows that 54.3% of the acid is esterfied. Calculate the equilibrium constant of this reaction.

Sol. $CH_3COOH(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$

Initial	1	1	0	1
At equilibrium	1 – x	1 – x	x	1 + x
	1 – 0.543	1 – 0.543	0.543	1 + 0.543

$$\left(54.3\% \text{ of 1 mole} = \frac{1 \times 54.3}{100} = 0.543 \text{ mole}\right)$$
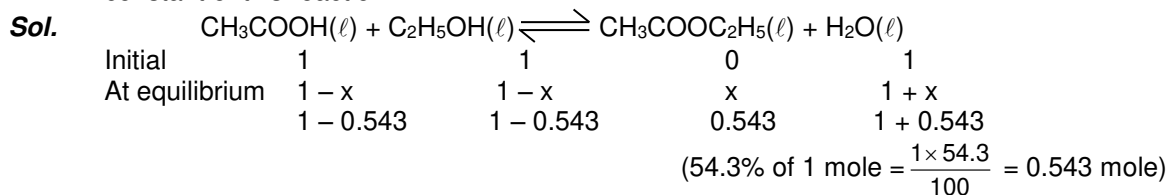
Hence given x = 0.543 mole

Applying law of mass action : $K_C = \dfrac{[ester][water]}{[acid][alcohol]} = \dfrac{0.543 \times 1.543}{0.457 \times 0.457} = 4.0$

○ **EQUATION INVOLVING IONS :**
Equilibrium involving ions always take place in aquous medium. In case of expression of K_C concentration of ion is taken.

Ex. $Ag^+(aq.) + Cl^-(aq.) \rightleftharpoons AgCl(s)$ $K_c = \dfrac{1}{[Ag^+][Cl^-]}$
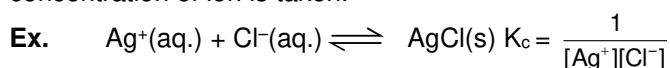
Section (H) : Heterogenuous equilibrium

For pure solid and pure liquid, active mass is taken to be unity i.e. 1 as they remain constant throughout the reaction :

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

$K_P = (P_{CO_2})_{eq}$, $K_C = [CO_2 (g)]_{eq}$

$$[CaCO_3(s)] = \frac{moles}{volume} = \frac{W_{CaCO_3}}{\dfrac{M_{CaCO_3}}{V}} = \frac{density\, CaCO_3}{M_{CaCO_3}} = constant$$

$$K = \frac{[CaO(s)]_{eq}\,[CO_2(g)]_{eq}}{[CaCO_3(s)]_{eq}}$$

$$\frac{K.[CaCO_3(s)]_{eq}}{[CaO(s)]_{eq}} = [CO_2(g)]_{eq}$$

$K_C = [CO_2(g)]_{eq}$

● $H_2O(\ell) \rightleftharpoons H_2O(g)_{eq}$

$K_P = (P_{H_2O(g)})_{eq}$, $K_C = [H_2O (g)]_{eq}$
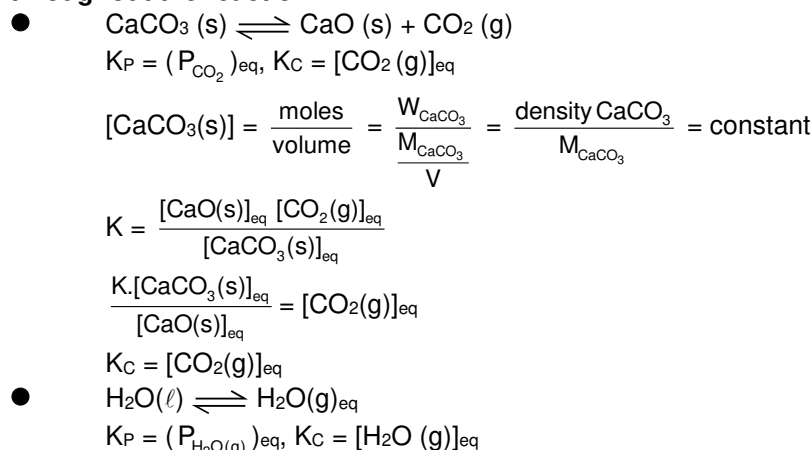
[For pure solid and pure liquid active mass is taken as unity i.e. = 1]

Section (I) : Degree of dissociation (α) and vapour density

It is the fraction of one mole dissociated into the products. (Defined for one mole of substance)

So, α = no. of moles dissociated / initial no. of moles taken

= fraction of moles dissociated out of 1 mole.

Note : % dissociation = $\alpha \times 100$

Suppose 5 moles of PCl_5 is taken and if 2 moles of PCl_5 dissociated then $\alpha = \dfrac{2}{5} = 0.4$

Let a gas A_n dissociates to give n moles of A as follows-

	$A_n(g) \rightleftharpoons$	nA(g)	
t = 0	a	0	
t = t_{eq}	a – x	n.x	$\alpha = \dfrac{x}{a} \Rightarrow$ x = aα.
	a – a α = a(1–α)	n a α	

Total no. of moles = a – a α + n a α = [1 + (n – 1) α] a

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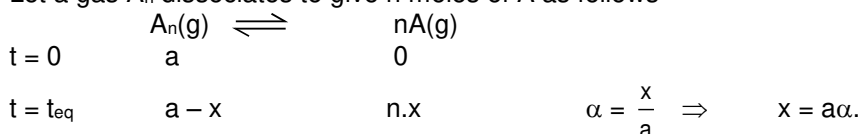
Significance of n

$$n = \frac{\text{sum of stoichiometric coefficient of product}}{\text{sum of coefficient of reactants}}$$

(i) for $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (n = 2)

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

(iii) for $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ (n = 1)

Solved Examples

Ex-5. Calculate the degree of dissociation and K_p for the following reaction.

	$PCl_5(g) \rightleftharpoons$	$PCl_3(g) +$	$Cl_2(g)$
t = 0	a	0	0
t = t	a –x	x	x

Since for a mole, x moles are dissociated

Sol. ∴ For 1 mole, $\dfrac{x}{a}$ moles = α are dissociated

∴ $x = a\,\alpha$

	$PCl_5(g) \rightleftharpoons$	$PCl_3(g) +$	$Cl_2(g)$
∴ At $t = t_{eq}$	$a - a\alpha$	$a\alpha$	$a\alpha$
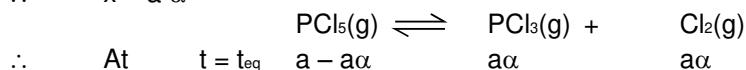
Total no. of moles at equilibrium = $a + a\alpha = a(1 + \alpha)$

$$P_{PCl_5} = \frac{a(1-\alpha)\,P}{a(1+\alpha)} \ , \quad P_{PCl_3} = \frac{a\,\alpha \cdot P}{a(1+\alpha)} \ , \quad P_{Cl_2} = \frac{a\,\alpha}{a(1+\alpha)} \cdot P$$

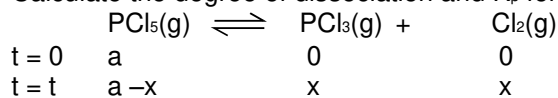$$K_P = \frac{\left\{ \left(\dfrac{\alpha P}{1+\alpha} \right) \right\}^2}{\left(\dfrac{1-\alpha}{1+\alpha} \right) P} \qquad K_P = \frac{\alpha^2 \cdot P}{1-\alpha^2} \ \text{(Remember)}$$

Observed molecular weight and Observed Vapour Density of the mixture

Observed molecular weight of $A_n(g)$ $= \dfrac{\text{molecular weight of } A_n(g)}{\text{total no. of moles at equilibrium}} = \dfrac{a.M_{th}}{a(1+(n-1)\alpha)}$

∴ $M_{obs} = \dfrac{M_{th}}{[1+(n-1)\alpha]}$

where M_{th} = theoritical molecular weight (n = atomicity)

$M_{mixture} = \dfrac{M_{A_n}}{[1+(n-1)\alpha]}$, M_{A_n} = Molar mass of gas A_n

Vapour density (V.D). : Density of the gas divided by density of hydrogen under same temp & pressure is called vapour density.

❍ D = vapour density without dissociation $= \dfrac{M_{A_n}}{2}$

d = vapour density of mixture = observed v.d. $= \dfrac{M_{mix}}{2}$

$\dfrac{D}{d} = 1 + (n - 1)\,\alpha$

∴ $\alpha = \dfrac{D-d}{(n-1) \times d} = \dfrac{M_T - M_o}{(n-1)M_0}$

Where M_T = The oritical molecular wt., M_0 = observed molecular wt. or molecular wt. of the mixture at equilibrium.

Note : It is not applicable for n = 1 eg. Dissociation of HI & NO (as the total number of don't change during the dissociation.)

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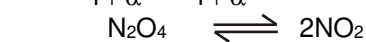Resonance® Educating for better tomorrow

Solved Examples

Ex-6. The vapour density of a mixture containing NO_2 and N_2O_4 is 38.3 at 33°C calculate the no. of moles of NO_2 if 100g of N_2O_4 were taken initially.

Sol. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$M_{mix} = 2 \times 38.3 = 76.6$

$M_{mix} = \dfrac{M_{th}}{1+\alpha} = \dfrac{92}{1+\alpha} \qquad \Rightarrow \qquad \alpha = 0.2$

$$N_2O_4 \rightleftharpoons 2NO_2$$

$t = 0 \qquad a \qquad\qquad 0$

$t = t \qquad a - a\alpha \qquad 2a\alpha$

no. of moles of $NO_2 = 2a\alpha = \dfrac{2 \times 100 \times 0.2}{92} = 0.435$

Section (J) : Thermodyanamics of equilibrium

For a general reaction, $\qquad mA + nB \rightleftharpoons pC + qD,\qquad \Delta G$ is given by-

$\Delta G = \Delta G^\circ + 2.303\ RT\ \log_{10}Q$

where $\Delta G =$ Gibb's Free energy change

$\Delta G^\circ =$ Standard Gibb's Free energy change

$Q =$ reaction quotient

Since, at equlibrium, $Q = K$

Here K is thermodynamic equilibrium constant replacing K_c or K_p

$$K = \dfrac{(a_C)^p\,(a_D)^q}{(a_A)^m\,(a_B)^n}\ ; \qquad \text{Here } a_X \text{ denotes the activity of X.}$$

In fact, 'a_x' is the ratio of the activity of substance at equilibrium and its activity in standard condition. That is why it is unitless and K is also unitless.

Note : (i) Themodynamic equilibrium constant is unitless since activity is unitless.

(ii) For pure solids & pure liquids, activity is unity.

(iii) For gases (ideal behaviour), the activity is its partial pressure (in atm).

(iv) For components in solution, activity is molar concentration.

At equilibrium, $\Delta G = 0$

$\Rightarrow \qquad\qquad \Delta G^\circ = -2.303\ RT\ \log_{10}K$

Now since, $\qquad \Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$

where $\qquad \Delta H^\circ =$ Standard enthalpy change of the reaction

$\Delta S^\circ =$ Standard entropy change

$\Rightarrow \qquad\qquad -2.303\ RT\ \log_{10}K = \Delta H^\circ - T\Delta S^\circ$

$\Rightarrow \qquad\qquad \log_{10}K = -\dfrac{\Delta H^\circ}{2.303} \cdot \dfrac{1}{RT} + \dfrac{\Delta S^\circ}{2.303R}$

If plot of ln k vs $\dfrac{1}{T}$ is plotted then it is a straight line with slope $= -\dfrac{\Delta H^\circ}{R}$ and intercept $= \dfrac{\Delta S^\circ}{R}$
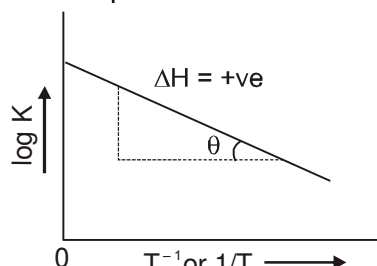
Endothermic reaction $\qquad\qquad$ Exothermic reaction

Slope $= \dfrac{-\Delta H^\circ}{2.303R} = \tan\theta$, $\qquad$ y intercept $= \dfrac{\Delta S^\circ}{2.303R}$

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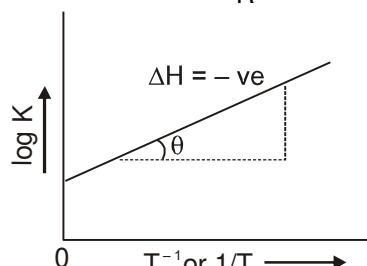
If at temperature T_1, equilibrium constant is K_1 and at T_2, it is K_2 then ;

$$\log_{10}K_1 = \frac{-\Delta H^{\circ}}{2.303R} \cdot \frac{1}{T_1} + \frac{\Delta S^{\circ}}{2.303R} \qquad \text{.......... (i)}$$

$$\log_{10}K_2 = \frac{-\Delta H^{\circ}}{2.303R} \cdot \frac{1}{T_2} + \frac{\Delta S^{\circ}}{2.303R} \qquad \text{.......... (ii)}$$

[Assuming ΔH° and ΔS° remains constant in this temperature range.]

Subtract eq. (ii) from (i) we get   **Vant Hoff equation-**

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

Note :   ❍ ΔH should be substituted with sign.

❍ Unit of $\Delta H/T$ and gas constant R should be same.

❍ For endothermic ($\Delta H > 0$) reaction value of the equilibrium constant increases with the rise in temperature

❍ For exothermic ($\Delta H < 0$) reaction, value of the equilibrium constant decreases with increase in temperature

Condition for spontaneity : $\Delta G < 0$ for spontaneous process or reaction.

Since, $\Delta G = \Delta H - T\Delta S$

$\Rightarrow$ $\Delta H - T\Delta S < 0$ $\Rightarrow$ $T > \Delta H/\Delta S$

* $\Delta G > 0$ for non-spontaneous process or reaction.

* $\Delta G = 0$ for equilibrium.

Solved Examples

Ex-7. Variation of equilibrium constant K with temperature T is given by van't Hoff equation,

$$\log K = \log A - \frac{\Delta H^{\circ}}{2.303\,RT}$$

A graph between log K and T^{-1} was a straight line as shown in the figure and having $\theta = \tan^{-1}(0.5)$ and OP = 10. Calculate :
(a) ΔH° (standard heat of reaction) when T = 300 K,
(b) A (pre-exponential factor),
(c) Equilibrium constant K, at 300 K,
(d) K at 900 K if ΔH° is independent of temperature.
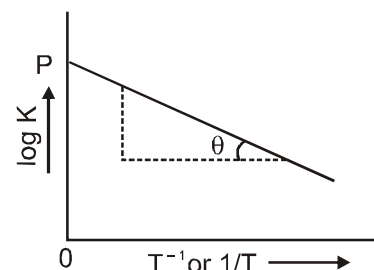
Sol.   (a) $\log_{10} K = \log_{10} A - \dfrac{\Delta H^{\circ}}{2.303\,RT}$

It is an equation of a straight line of the type y = c + mx

Slope 'm' = $\tan\theta = \dfrac{\Delta H^{\circ}}{2.303\,R}$

$0.5 = \dfrac{\Delta H^{\circ}}{2.303 \times 8.314}$ $\Rightarrow$ $\Delta H^{\circ} = 9.574$ J mol^{-1}

(b)   Intercept 'c' = $\log_{10} A = 10$ $\therefore$ $A = 10^{10}$

(c) $\log K = 10 - \dfrac{9.574}{2.303 \times 8.314 \times 298}$ $\Rightarrow$ $K = 9.96 \times 10^9$

(d) $\log\left(\dfrac{K_2}{K_1}\right) = \dfrac{\Delta H}{2.303R}\left\{\dfrac{1}{T_1} - \dfrac{1}{T_2}\right\}$

$\log\dfrac{K_2}{9.96 \times 10^9} = \dfrac{9.574}{2.303 \times 8.314}\left\{\dfrac{1}{298} - \dfrac{1}{798}\right\}$

On solving $K_2 = 9.98 \times 10^9$

Ans. (a) 9.574 J mol^{-1} ; (b) A = 10^{10} ; (c) 9.96 ×10^9 ; (d) 9.98 × 10^9

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Section (K) : Le-chatelier's principle

Le Chatelier's Principle:

If a change is applied to the system at equilibrium, then equilibrium will be shifted in that direction in which it can minimise the effect of change applied and the equilibrium is established again under new conditions.
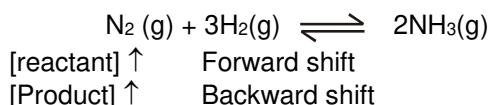
● **Effect of concentration :** If the concentration of a component is increased, reaction shifts in a direction which tends to decrease its concentration. e.g. In the following example.
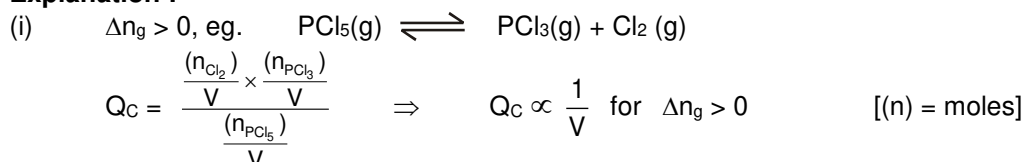
$$N_2 (g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$

[reactant] $\uparrow$ Forward shift

[Product] $\uparrow$ Backward shift

❍ If concentration of reactant is increased at equilibrium then reaction shifts in the forward direction.
❍ If concentration of product is increased then reaction shifts in the backward direction

Note : The addition of any solid component does not affect the equilibrium.

● **Effect of volume :**
❍ If volume is increased, pressure decreases hence reaction will shift in the direction in which pressure increases that is in the direction in which number of moles of gases increases and vice versa.
❍ If volume is increased then,   for
$\Delta n_g > 0$ reaction will shift in the forward direction
$\Delta n_g < 0$ reaction will shift in the backward direction
$\Delta n_g = 0$ reaction will not shift. eg. $H_2(g) + I_2(g)\ 2HI(g) \rightleftharpoons$ (No effect)

Explanation :

(i) $\Delta n_g > 0$, eg. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$Q_C = \frac{\frac{(n_{Cl_2})}{V} \times \frac{(n_{PCl_3})}{V}}{\frac{(n_{PCl_5})}{V}} \qquad \Rightarrow \qquad Q_C \propto \frac{1}{V} \text{ for } \Delta n_g > 0 \qquad [(n) = moles]$$

On incerasing V, Q_C, decreases.
Now, for $Q_C < K_C$ reaction will shift in forward direction.
Thus, if, Volume $\uparrow Q_C \downarrow$ (Forward shift)
      Volume $\downarrow Q_C \uparrow$ (Backward shift)

(ii) $\Delta n_g < 0$, eg. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q_C = \frac{\left\{\frac{(n_{NH_3})}{V}\right\}^2}{\left\{\frac{(n_{N_2})}{V}\right\}\left\{\frac{(n_{H_2})}{V}\right\}^3} \qquad \Rightarrow \qquad Q_C \propto V^2 \qquad \text{for } \Delta n_g < 0$$

$V \uparrow Q_C \uparrow$ (Backward shift)   ; $V \downarrow Q_C \downarrow$ (Forward shift)
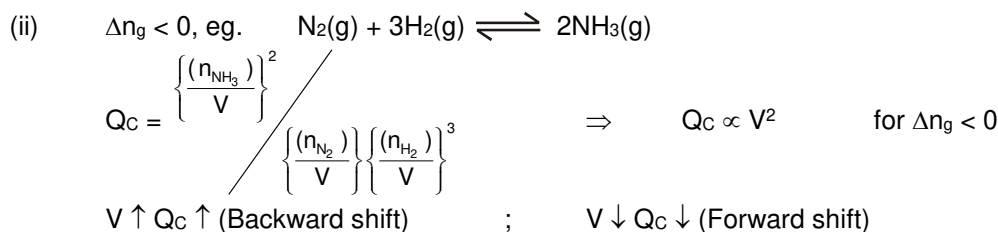
● **Effect of pressure :**
On increasing pressure, equilibrium will shift in the direction in which pressure decreases i.e. no. of moles in the reaction decreases and vice versa.
∵ $P \propto$ no. of moles
(i)   For $\Delta n_g = 0 \rightarrow$ No. effects
(ii)   For $\Delta n_g > 0$, $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

$$Q_p = \frac{(X_{PCl_3}P) \cdot (X_{Cl_2}P)}{(X_{PCl_5} \cdot P)} \qquad \Rightarrow \qquad Q_P \propto P \qquad [(\ ) = mole fraction]$$

$P \downarrow; Q_P \downarrow;$ (Forward shift)
$P \uparrow; Q_P \uparrow;$ (Backward shift)

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(iii) For $\Delta n < 0$, eg. $\qquad N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$$Q_P = \frac{\left[(X_{NH_3})P\right]^2}{[(X_{N_2}).P][(X_{H_2})P]^3} \qquad \Rightarrow \qquad Q_P \propto \frac{1}{P^2}$$

$P\uparrow$; $Q_P\downarrow$; (Forward shift) $\qquad$; $\qquad P\downarrow$; $Q_P\uparrow$; (Backward shift)

● **Effect of catalyst :**
Due to catalyst, the state of equilibrium is not affected i.e. no shift will occur as catalyst lowers the activation energy of both the forward & reverse reaction by same amount, thus altering the forward & reverse rate equally and hence, the <u>equilibrium will be attained faster</u> i.e time taken to reach the equilibrium is less.

● **Effect of inert gas addition :**
   (a) **At constant volume :** Inert gas addition has no effect at constant volume
   (b) **At constant pressure :** If inert gas is added then to maintain the pressure constant, volume is increased. Hence equilibrium will shift in the direction in which larger no. of moles of gas is formed
   (i) $\Delta n_g > 0$, reaction will shift in the forward direction
   (ii) $\Delta n_g < 0$, reaction will shift in the backward direction
   (iii) $\Delta n_g = 0$, no effect

● **Effect of temperature :**
   (i) **Exothermic reaction :** The reaction in which heat is evolved
   $\qquad\qquad A(g) + B(g) \rightleftharpoons C(g) + D(g) + \text{Heat} \qquad \Delta H = -\text{ve}$
   eg. $\quad N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$

   $T\uparrow \qquad \Rightarrow K'$ will decrease

   $\log \dfrac{K_1}{K_2} = \dfrac{\Delta H^\circ}{2.303R}\left(\dfrac{1}{T_2} - \dfrac{1}{T_1}\right)$ (from vant' hoff equation)

   $\log \dfrac{K_1}{K_2} < 0 \qquad \Rightarrow \qquad \log K_1 - \log K_2 > 0 \Rightarrow \quad \log K_1 > \log K_2 \Rightarrow \qquad K_1 > K_2$

   Reaction will shift in backward direction.
   $\qquad T\downarrow \qquad \Rightarrow K$ will increases.
   Reaction will shift in forward direction.

   (ii) **Endothermic reaction :** energy consumed.
   $\qquad\qquad A(g) + B(g) \rightleftharpoons C(g) + D(g) - \text{Heat} \qquad \therefore \Delta H = +\text{ve}$
   $\qquad\qquad T\uparrow \Rightarrow K\uparrow \qquad \Rightarrow \qquad \text{Forward} ; \qquad T\downarrow \Rightarrow K\downarrow \qquad \Rightarrow \qquad \text{Backward}$

Application of le chatelier's principle : Practical equilibrium situations :
Section (L) : Vapour pressure and Relative Humidity
● It is the pressure exerted by the vapours over it's liquid when it is in equilibrium with the liquid. Vapour pressure of water is also called **aqueous tension**.
   $\qquad\qquad H_2O\,(\ell) \rightleftharpoons H_2O\,(g)$; $K_P = P_{H_2O}$ = **constant at fixed temperature**

   Hence V.P. of liquid is independent of pressure, volume and concentration change.
   e.g. at 25°C, vapour pressure of water ≈ 24 mm of Hg

   Relative Humidity $= \dfrac{\text{Partial pressure of } H_2O \text{ vapours}}{\text{Vapour pressure of } H_2O \text{ at that temp.}}$

● **Formation of diamond :**
   $\qquad\qquad \text{C (graphite)} \rightleftharpoons \text{C (diamond)} - \text{Heat};\qquad\qquad \Delta H = +\text{ve}$
   $\qquad\qquad\qquad \downarrow \qquad\qquad\qquad\qquad \downarrow$
   $\qquad\qquad \text{Density Low} \qquad\qquad \text{Density High}$
   $\qquad\qquad \text{Volume High} \qquad\qquad \text{Volume Low}$
   Formation of diamond is favourable at high pressure and high temperature

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● **Melting of ice :**

$$H_2O \ (s) \quad \rightleftharpoons \quad H_2O \ (\ell) \ ; \qquad \Delta H = + \ ve$$

| Density Low | Density High |
| Volume High | Volume Low |

Melting of ice is favourable at high temperature and high pressure.

● **Boiling of water :**

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

| Density High | Density Low |
| Volume Low | Volume High |

On increasing pressure, equilibrium will shift in the direction in which volume is decreasing i.e. backward.

Hence, on increasing pressure, the boiling point increases.

● **Formation of ammonia by Haber's process :**

$N_2 \ (g) + 3 \ H_2 \ (g) \rightleftharpoons 2NH_3 \ (g) \quad \Delta H = -22.4 \ Kcal/mol.$
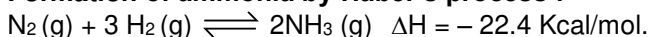
(i) The reaction will shift in the forward direction at low temperature, but at very low temperature the rate of reaction becomes very low; thus moderate temperature is used for this reaction.

(ii) At high pressure, reaction will shift in forward direction to form more product.

● **Manufacturing of SO_3 by contact process**

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g) + 45.2 \ kcal$$
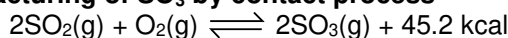
High pressure (1.5 to 1.7 atm), Low temperature (500°C), higher quantity of SO_2 and O_2 are favourable conditions for the formation of SO_3.

● **Manufacturing of NO by Birkeland–Eyde process**

$$N_2(g) + O_2(g) \rightleftharpoons 2 \ NO(g) - 43.2 \ kcal$$
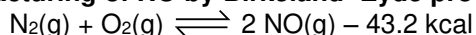
❍ No effect on change of pressure

❍ High temperature (1200°C to 2000°C), High concentration of N_2 and O_2 are favourable condition for the formation of NO.

Solved Examples

***Ex*-8.** The equilibrium constant of the reaction at 25°C

$$CuSO_4.5H_2O \ (s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$$
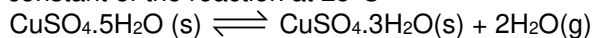
is $1.084 \times 10^{-4} \ atm^2$. Find out under what conditions of relative humidity, $CuSO_4.5H_2O$ will start loosing its water of crystallization according to above reaction. (Vapour pressure of water at 25°C is 24 mm of Hg).

Sol. $K_P = \left(P_{H_2O} \right)^2$ so $P_{H_2O} = \sqrt{1.084 \times 10^{-4}} = 1.041 \times 10^{-2}$ atm ≈ 8 mm of Hg

❍ If in a room, pressure of water is greater than 8 mm of Hg then $CuSO_4.3H_2O$ will absorb water from air and will form $CuSO_4.5H_2O$ & will keep absorbing until partial pressure of H_2O becomes 8 mm of Hg.

❍ If $P_{H_2O} < 8$ mm of Hg then $CuSO_4.5H_2O$ will loose water of crystallization and reaction will move in forward direction.

i.e. If relative humidity $< \dfrac{8}{24} < 33.33\%$ then $CuSO_4.5H_2O$ will loose water of crystallization.

Section (M) : Simultaneous equilibria

If in any container there are two or more equilibria existing simultaneously involving one or more than one common species. Then in both/all equilibrium the concentration of common species is the total concentration of that species due to all the equilibria under consideration.
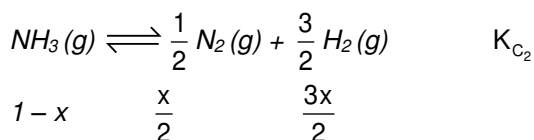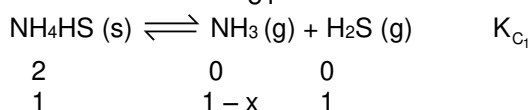
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e.g.

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

t = 0	a	0	0
t = t_{eq}	a – t	t	t + u

$$B(s) \rightleftharpoons Z(g) + Y(g)$$

b	0	0
b – u	u	u + t

$$K_{C_1} = t(u + t)$$

$$K_{C_2} = (u + t)u$$
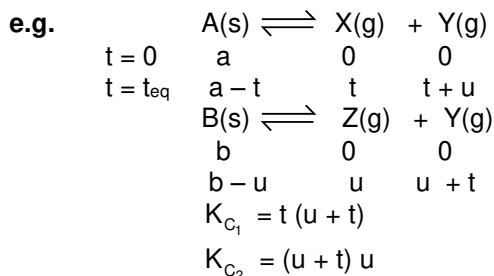
Solved Examples

Ex-9. 102 g of solid NH_4HS is taken in the 2L evacuated flask at 57°C. Following two equilibrium exist simultaneously

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g) \quad ; \quad NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g)$$
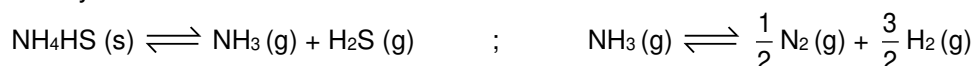
one mole of the solid decomposes to maintain both the equilibrium and 0.75 mole of H_2 was found at the equilibrium then find the equilibrium concentration of all the species and K_C for both the reaction.

Sol. Moles of $NH_4HS = \dfrac{102}{51} = 2$

$$NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g) \qquad K_{C_1}$$

2	0	0
1	1 – x	1

$$NH_3(g) \rightleftharpoons \frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \qquad K_{C_2}$$

1 – x	$\dfrac{x}{2}$	$\dfrac{3x}{2}$

Given that moles of $H_2 = \dfrac{3x}{2} = 0.75 \quad \Rightarrow \quad x = \dfrac{1}{2}$

$$K_{C_1} = \frac{1}{2}\frac{(1-x)}{2} = \frac{1}{8} \qquad \text{[Since V = 2 L]}$$

$$K_{C_2} = \frac{\left(\dfrac{3x}{4}\right)^{3/2}\left(\dfrac{x}{4}\right)^{\frac{1}{2}}}{\left(\dfrac{1-x}{2}\right)} = \frac{\left(\dfrac{3}{8}\right)^{3/2}\left(\dfrac{1}{8}\right)^{\frac{1}{2}}}{\dfrac{1}{4}} = (3)^{3/2}\frac{1}{64}\times\frac{4}{1} = \frac{(3)^{3/2}}{16}$$

SUMMARY

Chemical equilibrium is a dynamic state in which the concentration of reactants and products remain constant because the rates of the forward and the reverse reaction are equal. For the general reaction

$$a\ A(g) + b\ B\ (g) \rightleftharpoons c\ C(g) + d\ D(g)$$
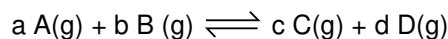
concentrations in the equilibrium mixture are related by the equilibrium equation :

$$K_C = \frac{[C]^c_{eq}[D]^d_{eq}}{[A]^a_{eq}[B]^b_{eq}}$$

The ratio on the right side of the equation is called the equilibrium constant expression. The equilibrium constant K_c is the number obtained when equilibrium concentrations (in mol/L) are substituted into the equilibrium constant expression. The value of K_c varies with temperature and depends upon the form of the balanced chemical equation.

The equilibrium constant K_p can be used for gas phase reactions. It is defined in the same way as K_c except that the equilibrium constant expression contains partial pressures (in atmospheres) instead of molar concentrations. The constants K_p and K_c are related by the equation,

$$K_p = K_c\ (RT)^{\Delta n_g}, \text{ where } \Delta n_g = (c + d) - (a + b).$$

Homogeneous equilibrium are those in which all reactants and products are in a single phase; heterogeneous equilibria are those in which reactants and products for heterogeneous equilibrium does not include concentrations of pure solids or pure liquids.

The value of the equilibrium constant for a reaction makes it possible to judge the extent of reaction, predict the direction of reaction, and calculate equilibrium concentrations (or partial pressures) from initial concentration (or partial pressures) . The farther the reaction proceed towards completion, the larger the value of K_c. The direction of a reaction not at equilibrium depends on the relative values of K_c and the reaction quotient Q_c which is defined in the same way as K_c except that the concentrations in the equilibrium constant expression are not necessarily equilibrium concentrations. If $Q_c < K_c$, net reaction goes from left to right to attain equilibrium; if $Q_c = K_c$, the system is at equilibrium.

The composition of an equilibrium mixture can be altered by changes in concentration, pressure (volume), or temperature. The qualitative effect of these changes is predicted by Le Chatelier's principle, which says that if a stress is applied to a reaction mixture at equilibrium, net reaction occurs in the direction that relieves the stress. Temperature changes affect equilibrium concentrations because K_c is temperature-dependent. As the temperature increases, K_c for an exothermic reaction decreases, and K_c for an endothermic reaction increases.
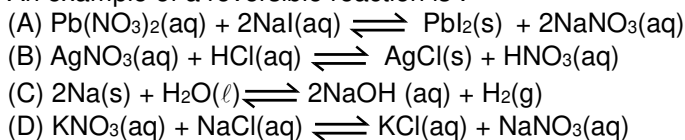
A catalyst increases the rate at which chemical equilibrium is reached, but it does not affect the equilibrium constant or the equilibrium concentration. The equilibrium constant for a single-step reaction equals the ratio of the rate constants for the forward and reverse reactions : $K_c = k_f / k_b$.

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Types of chemical reactions

REVERSIBLE REACTION
Bi-directional → Can attain → Equilibrium

IRREVERSIBLE REACTION
Unidirectional → Cannot attain equilibrium

Equilibrium → Mathematically → Law of mass action → Equilibrium equation

Under stress /Change → Le-Chaterlier principle → Shifts equilibrium to minimize stress/change

Equilibrium equation →

Reaction quotient $Q = \dfrac{[Conc]_{Product}}{[Conc]_{Reactant}}$ → Conc. Not at equilibrium → Direction of reaction

Equilibrium constant, $K = K_f/K_b$

Applications
- Direction of reaction
- Conc. Calculation
- Extent of reaction

Equilibrium constant, $K = K_f/K_b$ → Depends on
- Stoichiometry
- temperature → $\log \dfrac{K_2}{K_1} = \dfrac{H}{2.303\ R}\left[\dfrac{1}{T_1}\ \dfrac{1}{T_2}\right]$

Types
- K_x
- K_c
- K_p

Ratio of
- Mole Fraction.
- Molar Conc.
- Partial Pressure

Types
- Physical Equilibrium
- Chemical Equilibrium
  - Heterogeneous → At least two phase
  - Homogeneous → Single phase

MISCELLANEOUS SOLVED PROBLEMS (MSPs)

1. An example of a reversible reaction is :
(A) $Pb(NO_3)_2(aq) + 2NaI(aq) \rightleftharpoons PbI_2(s) + 2NaNO_3(aq)$
(B) $AgNO_3(aq) + HCl(aq) \rightleftharpoons AgCl(s) + HNO_3(aq)$
(C) $2Na(s) + H_2O(\ell) \rightleftharpoons 2NaOH(aq) + H_2(g)$
(D) $KNO_3(aq) + NaCl(aq) \rightleftharpoons KCl(aq) + NaNO_3(aq)$

Ans. **(D)**
Sol. Precipitation reactions, acid base reactions and reactions in which gases are liberated and are taking place in open container will be irreversible reactions.

2. For the reaction, $A + B \rightleftharpoons 3C$, if 'a' mol/litre of each 'A' & 'B' are taken initially then at equilibrium the incorrect relation is :
(A) $[A] - [B] = 0$ (B) $3[B] + [C] = 3a$ (C) $3[A] + [C] = 3a$ (D) $[A] + [B] = 3[C]$

Ans. **(D)**
Sol. At equilibrium :
$[A] = [B]$
$[A] + \dfrac{1}{3}[C] = a$

3. The equilibrium constant for the decomposition of water $H_2O(g) \rightarrow H_2(g) + \dfrac{1}{2}O_2(g)$ is given by :

(α = degree of dissociation of $H_2O(g)$; p = Total equilibrium pressure)

(A) $K = \dfrac{\alpha^2 p^{1/2}}{(1+\alpha)(2-\alpha)^{1/2}}$

(B) $K = \dfrac{\alpha^{3/2} p^{1/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

(C) $K = \dfrac{\alpha^3 p^{1/2}}{\sqrt{2}}$

(D) $K = \dfrac{\alpha^3 p^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

Ans. **(B)**

Sol : $H_2O(g) \rightarrow H_2(g) + \dfrac{1}{2}O_2(g)$

| 1 | 0 | 0 |
| $1-\alpha$ | α | $\alpha/2$ |
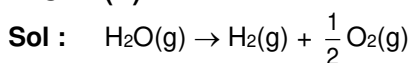
Total moles at equilibrium = $1 - \alpha + \alpha + \alpha/2 = 1 + \alpha/2$
Let the total pressure at equilibrium be = p

So, $p_{H_2O} = \dfrac{1-\alpha}{1+\alpha/2} \times p$

$p_{H_2} = \dfrac{\alpha}{1+\alpha/2} \times p$

$p_{O_2} = \dfrac{\alpha/2}{1+\alpha/2} \times p$

So $K_p = \dfrac{(p_{O_2})^{1/2}(p_{H_2})}{(p_{H_2O})}$

4. The reaction quotient Q for $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is given by $Q = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$. The reaction will proceed in backward direction, when:
(A) $Q = K_c$ (B) $Q < K_c$ (C) $Q > K_c$ (D) $Q = 0$

Ans. **(C)**
Sol. When Q > K, reaction will favour backward direction and when Q < K, it will favour forward direction.

5. 0.96 g of HI were heated to attain equilibrium $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$. The reaction mixture on titration requires 15.7 mL of N/10 hypo solution. Calculate degree of dissociation of HI.
Ans. 20.9%

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Sol. meq of $I_2 = \dfrac{w_{I_2}}{127} \times 1000 = 1.57$

$$w_{I_2} = \dfrac{127 \times 1.57}{1000} \qquad n_{I_2} = \dfrac{1.57}{2000}$$

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$
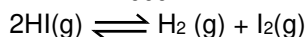
$$a - a\alpha \qquad \dfrac{a\alpha}{2} \qquad \dfrac{a\alpha}{2} \qquad \dfrac{0.96}{256} \times \alpha = \dfrac{1.57}{2000}$$

$$\alpha = 0.209 \qquad \textbf{Ans.}$$

6. Would 1% CO_2 by volume in air be sufficient to prevent any loss in weight when M_2CO_3 is heated at 120ºC ?

$$M_2CO_3(s) \rightleftharpoons M_2O(s) + CO_2(g)$$

$K_p = 0.0095$ atm at 120ºC. How long would the partial pressure of CO_2 have to be to promote this reaction at 120ºC ?

Ans. (No reactions)

Sol. For, $\qquad M_2CO_3(g)\,(s) \rightleftharpoons M_2O\,(s) + CO_2\,(g)$

$\because$ CO_2 is 1% in air ; $\qquad \therefore \qquad P'_{CO_2} = \dfrac{1}{100} \times P_{air} = \dfrac{1}{100} \times 1$ atm. $= 0.01$ atm.

Also for equilibrium $\qquad K_P = P'_{CO_2} = 0.0095$ atm.

$\because \qquad$ Given, $\qquad P'_{CO_2} = 0.01$ atm.

Since decomposition is carried out in presence of P'_{CO_2} of 0.01 atm and $K_P = 0.0095$ atm, thus, practically no decomposition of M_2CO_3. Thus, 1% CO_2 is sufficient to prevent any loss in weight.

If at all reaction is desired, the P'_{CO_2} must be lesser than 0.0095 atm as P'_{CO_2} at equilibrium cannot be more than 0.0095 atm.

Altrernate solution :

For $\qquad M_2CO_3\,(s) \rightleftharpoons M_2O\,(s) + CO_2\,(g)$
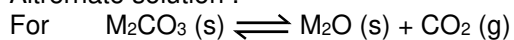
$$\left(\dfrac{1}{100} + P\right)$$

$\because \qquad K_P = P'_{CO_2}$ and the pressure of CO_2 already present in 1/100 atm. Let the decomposition of M_2CO_3 produces the CO_2 of pressure P, then

$\therefore \qquad K_P = \dfrac{1}{100} + P \qquad\qquad$ or $\qquad\qquad 0.0095 = P + 001 \qquad$ or $\qquad P = -0.0005.$

The value of pressure comes negative and thus, it may be concluded that M_2CO_3 will not dissociate in pressure of CO_2 of pressure 0.01 atm.

7. For the chemical equilibrium, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

ΔH_f° can be determined from which one of the following plots ?

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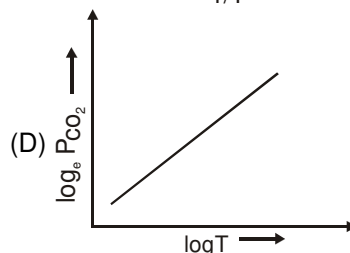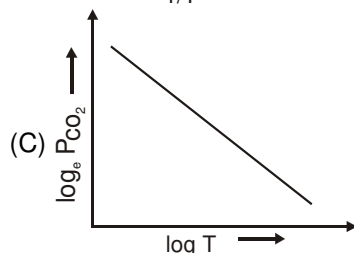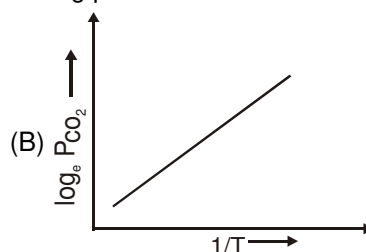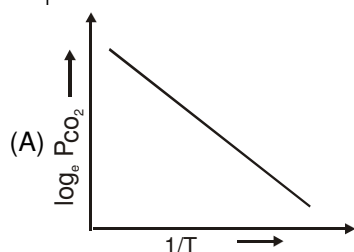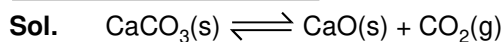
$K_p = P_{CO_2}$

$\log K_p = \log A - \dfrac{\Delta H_r^0}{2.303\,RT}$

$\log P_{CO_2} = \log A - \dfrac{\Delta H_r^\ominus}{2.303}\dfrac{1}{RT}$ .... (i)
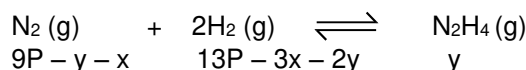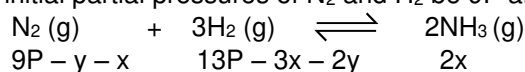
Graph (a) represents (i) and its slope will be used to determine the heat of the reaction.

So, Ans. (A).

8. 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 in the container

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$$
$$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$$
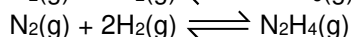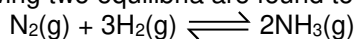
The total equilibrium pressure is found to be 3.5 atm while partial pressure of $NH_3(g)$ and $H_2(g)$ are 0.5 atm and 1 atm respectively. Calculate of equilibrium constants of the two reactions given above.

Sol. Let the initial partial pressures of N_2 and H_2 be 9P and 13 P respectively

$$\begin{array}{cccc} N_2\,(g) & + & 3H_2\,(g) & \rightleftharpoons & 2NH_3\,(g) \\ 9P - y - x & & 13P - 3x - 2y & & 2x \end{array}$$

$$\begin{array}{cccc} N_2\,(g) & + & 2H_2\,(g) & \rightleftharpoons & N_2H_4\,(g) \\ 9P - y - x & & 13P - 3x - 2y & & y \end{array}$$

Total pressure $= P_{N_2} + P_{H_2} + P_{NH_3} + P_{N_2H_4} = 3.5$ atm

$= (9P - x - y) + (13P - 3x - 2y) + 2x + y = 3.5$ atm ...(1)

$P_{NH_3} = 2x = 0.5$ atm ...(2)

$P_{H_2} = (13P - 3x - 2y) = 1$ atm ...(3)

from (1) $\Rightarrow$ $(9P - x - y) + 1$ atm $+ 0.5 + y = 3.5$

$\Rightarrow$ $(9P - x) = 2$ atm

so $9P = 2.25$

$P = 0.25$ atm

from (3) equation $2y = 1.5$

$y = 0.75$ atm

so $P_{N_2} = 9P - x - y = 1.25$ atm

$P_{H_2} = 1$ atm

$P_{NH_3} = 0.5$ atm

$P_{N_2H_4} = 0.75$ atm

So, $K_{P_1} = \dfrac{P_{NH_3}^2}{P_{H_2}^3 \cdot P_{N_2}} = \dfrac{0.5 \times 0.5}{1 \times 1 \times 1 \times 1.25} = 0.2$ atm^{-2}

$K_{P_2} = \dfrac{P_{N_2H_4}}{P_{N_2} \cdot P_{H_2}^2} = \dfrac{0.75}{1 \times 1 \times 1.25} = 0.6$ atm^{-2}

Exercise-1

✍ Marked questions are recommended for Revision.

PART - I : SUBJECTIVE QUESTIONS

Section (A) : Properties of equilibrium, active mass

A-1. In a reaction $A + B \rightleftharpoons C + D$ the rate constant of forward reaction & backward reaction is $k_f = 2 \times 10^{-4}$ M sec^{-1} and $k_b = 5 \times 10^{-5}$ M sec^{-1} then the equilibrium constant (k) for reaction is expressed as :

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

Section (B) : Homogeneous equilibrium : K_C in gaseous system

B-1.✍ 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 ?

B-2. The equilibrium constant of the reaction, $A_2 (g) + B_2 (g) \rightleftharpoons 2 AB (g)$ at 100ºC is 16. Initially equal moles of A_2 & B_2 are taken in 2L container. Then find mole % of A_2 in equilibrium mixture.

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

B-4.✍

The gas A_2 in the left flask allowed to react with gas B_2 present in right flask as
$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$; $K_c = 4$ at 27°C.
What is the concentration of AB when equilibrium is established?
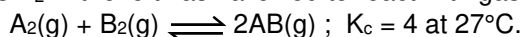
Section (C) : Homogeneous equilibrium : K_P in gaseous system

C-1.✍ 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.

C-2. The moles of N_2O_4 and NO_2 at equilirbrium are 1 and 2 respectively total pressure at equilibrium is 9 atm. Find K_P for the reaction $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$.

C-3.✍ 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 the equilibrium constant (K_C) at 400 K is $\frac{4}{27}$.
$N_2 (g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
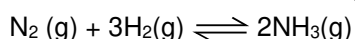
Section (D) : Relation between K_P and K_C

D-1. 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)

D-2.✍ 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.

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ADVCEQ - 20

D-3. 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.

Section (E) : Reaction quotient and Its applications

E-1. A mixture of 1.5 mol of N_2, 2 mole of H_2 and 8 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?

E-2. 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 $[NO_2] = 0.04$ M

         $[NO] = 0.30$ M $[SO_3] = 0.3$ 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?

Section (F) : Properties of equilibrium Constant

F-1. 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.

F-2. 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 $N_2 + 2O_2 \rightleftharpoons 2NO_2$?

F-3. 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

         $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ $K_1 = 2.1 \times 10^{-13}$

         $2CO_2(g) \rightleftharpoons 2CO(g) + O_2(g)$ $K_2 = 1.4 \times 10^{-12}$.

Section (G) : Homogenuous Equilibrium (liquid system)

G-1. 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 initial acid and alcohol moles.

	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)	X	Y	8/3

Section (H) : Heterogenuous equilibrium

**H-1.** Write the expressions for equilibrium constant K_C and K_P and classify in Homogeneous and Hetereogeneous equilibrium :

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

(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) $NH_4NO_2(s) \rightleftharpoons N_2(g) + 2H_2O(\ell)$

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H-2. For the reaction: $CaCO_3 \rightleftharpoons CaO(s) + CO_2(g)$; $K_p = 1$ atm at 927°C. If 20g of $CaCO_3$ were kept in a 10 litre vessel at 927°C, then calculate percentage of $CaCO_3$ remaining at equilibrium :

H-3. For the given reaction at equilibrium :

$$AgNO_3(s) \rightleftharpoons Ag(s) + NO_2(g) + \frac{1}{2} O_2(g)$$
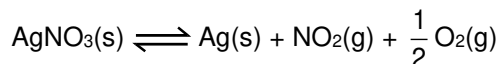
If total pressure at equilibrium is P, then calculate K_P for the given reaction.

Section (I) : Degree of dissociation (α) and vapour density

I-1. 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.

I-2. At temperature T, the compound AB_2 (g) dissociates according to the reaction; $2AB_2$ (g) $\rightleftharpoons$ 2 AB(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.

I-3. 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.

I-4. 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).

Section (J) : Thermodyanamics of equilibrium

J-1. For the reaction, SO_2 (g) + $1/2O_2$(g) $\rightleftharpoons$ SO_3(g)
$\Delta H^\circ_{298} = -98.32$ kJ/mole, $\Delta S^\circ_{298} = -95.0$ J/mole-K. Find the K_p for this reaction at 298K. (Given that $10^{.27} = 1.86$)

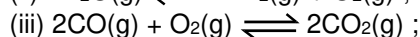**J-2.** From the following data :
(i) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$; $K_{2000K} = 4.4$
(ii) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$; $K_{2000K} = 5.31 \times 10^{-10}$
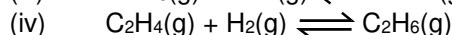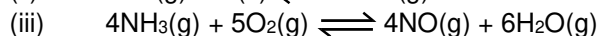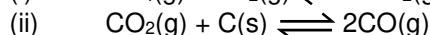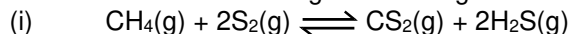(iii) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$; $K_{1000K} = 2.24 \times 10^{22}$
State whether the reaction (iii) is exothermic or endothermic?
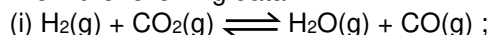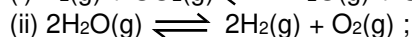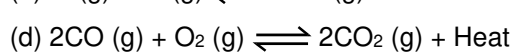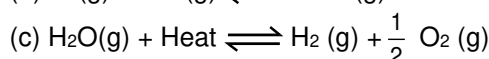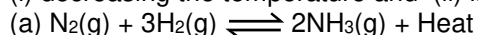
Section (K) : Le-chatelier's principle

K-1. 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 ?
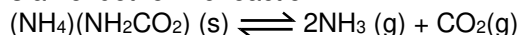(i) $CH_4(g) + 2S_2(g) \rightleftharpoons CS_2(g) + 2H_2S(g)$
(ii) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$
(iii) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(g)$
(iv) $C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g)$

K-2. 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) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ + Heat   (b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ + Heat

(c) $H_2O(g) +$ Heat $\rightleftharpoons H_2$ (g) + $\frac{1}{2}$ O_2 (g)   (d) $2CO$ (g) + O_2 (g) $\rightleftharpoons 2CO_2$ (g) + Heat

K-3. 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 0.3 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 ?

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      (i)   Adding CO_2 (ii)   Adding $(NH_4)(NH_2CO_2)$

      (iii)   Removing CO_2 (iv)   Increasing the total volume

      (v)   Adding neon (at constant volume)   (vi)   Increasing the temperature.

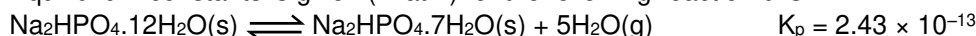**K-4.** Following equilibrium is established at temperature T.

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

at eq.   1M   2M   2M.
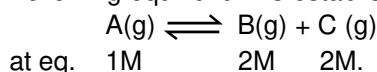
If volume of the vessel is doubled then find the equilibrium concentration of each species.

(Given that : $\sqrt{40} = 6.324$)

Section (L) : Vapour pressure and Relative Humidity

L-1. Equilibrium constants is given (in atm) for the following reaction 0ºC :

$Na_2HPO_4.12H_2O(s) \rightleftharpoons Na_2HPO_4.7H_2O(s) + 5H_2O(g)$ $K_p = 2.43 \times 10^{-13}$

The vapour pressure of water at 0ºC is 4.56 torr.

At what relative humidities will $Na_2HPO_4.12H_2O(s)$ be effloresent when exposed to air at 0ºC ?

L-2. Equilibrium constant for the following equilibrium is given at 0ºC.

$Na_2HPO_4.12H_2O(s) \rightleftharpoons Na_2HPO_4.7H_2O(s) + 5H_2O(g)$ $K_P = 31.25 \times 10^{-13}$
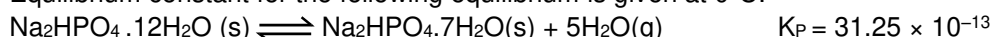
At equilibrium what will be partial pressure of water vapour :

Section (M) : Simultaneous equilibria

M-1. 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 60 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 39 mm

M-2. When NO & NO_2 are mixed, the following equilibria readily obtained;

        $2NO_2 \rightleftharpoons N_2O_4$ $K_p = 6.8$ atm^{-1}

        $NO + NO_2 \rightleftharpoons N_2O_3$ $K_p = ?$

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 $NO + NO_2 \rightleftharpoons N_2O_3$

PART - II : ONLY ONE OPTION CORRECT TYPE

Section (A) : Properties of equilibrium, active mass, homogeneous & heterogeneous equilibrium (theoritical)

A-1. A reversible reaction is one which

(A) Achieves equlibrium state   (B) Proceeds in both directions

(C) Does not occurs at all   (D) Both (A) and (B)

A-2. A chemical reaction is at equilibrium when

(A) Measurable properties becomes constant

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

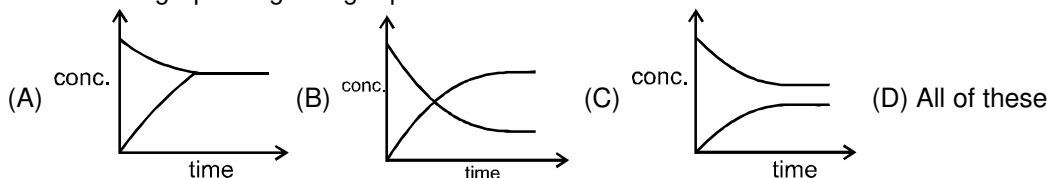(C) Net rate of reaction is zero

(D) All are correct

A-3. 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

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A-4. Find correct graph reagarding equlibrium state :

(A)

(B)

(C)

(D) All of these

A-5.
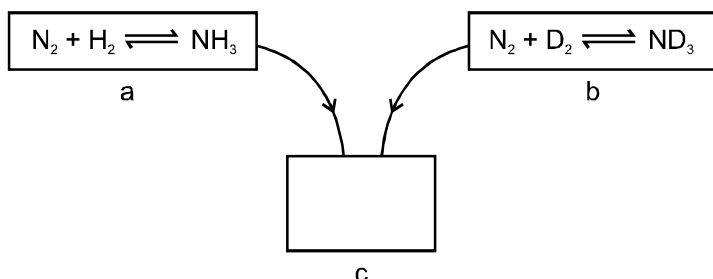
Initially the reactions in the container a & b are at equilibrium when the products & reactants are put together in a container c then at the equilibrium the total number of different chemical compounds are :
(A) 5   (B) 7   (C) 6   (D) 8

## Section (B) : Homogeneous equilibrium : K_c in gaseous system

B-1. 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) $\dfrac{k_1 a - k_2 b}{k_1 + k_2}$ (B) $\dfrac{k_1 a - k_2 b}{k_1 - k_2}$ (C) $\dfrac{k_1 a - k_2 b}{k_1 \, k_2}$ (D) $\dfrac{k_1 a + k_2 b}{k_1 + k_2}$

B-2. 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

B-3. 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 :
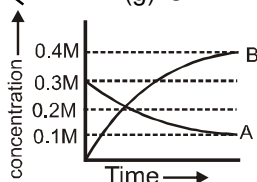
(A) $K_c > 1$ (B) $K_c < 1$ (C) $K_c = 1$ (D) data insufficient

B-4. $K_c = 9$ for the reaction, $A + B \rightleftharpoons C + D$, If one mole of each A and B are taken, then amount of C in equilibrium is :
(A) 1   (B) 0.25   (C) 0.75   (D) None of these

B-5. 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

B-6. An equilibrium mixture for the reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$ had 1 mol of H_2S, 0.2 mol of H_2 and 0.8 mol of S_2 in a 2 litre flask. The value of K_C in mol lit^{-1} is :
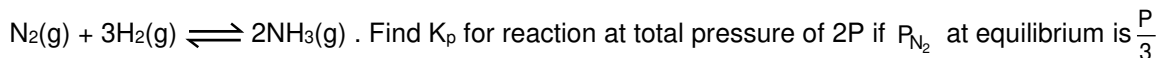(A) 0.08   (B) 0.016   (C) 0.004   (D) 0.160

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Section (C) : Homogeneous equilibrium : K_P in gaseous system

C-1. What is the unit of K_P for the reaction ?

$$CS_2 (g) + 4H_2 (g) \rightleftharpoons CH_4 (g) + 2H_2S (g)$$
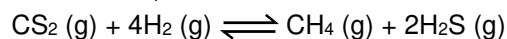
(A) atm   (B) atm^{-2} (C) atm^2 (D) atm^{-1}

C-2. N_2 and H_2 are taken in 1 : 3 molar ratio in a closed vessel to attained the following equilibrium
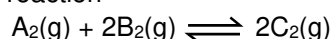
$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. Find K_p for reaction at total pressure of 2P if P_{N_2} at equilibrium is $\dfrac{P}{3}$

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

C-3. 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) 16.0atm   (B) 0.25 atm   (C) 1 atm   (D) 0.75 atm

C-4. For the reaction

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

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

C-5. $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ in the reversible reaction at equilibrium 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) $\dfrac{bc}{a}$ .RT   (B) $\dfrac{b}{(a+b+c)}$ .P   (C) $\dfrac{bc.P}{a\ (a+b+c)}$ (D) $\dfrac{c}{(a+b+c)}$ .P

C-6. 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:
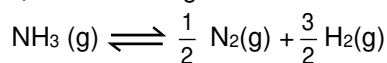
(A) 0.03   (B) 0.25   (C) 0.025   (D) 0.04

C-7. 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, $\dfrac{49}{150}$

Section (D) : Relation between K_p and K_c

D-1. At 527ºC, the reaction given below has $K_C = 4$

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

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

D-2. The value of K_p for the reaction, $2H_2O(g) + 2Cl_2(g) \rightleftharpoons 4HCl(g) + O_2(g)$ is 0.03 atm at 427º 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}

D-3. $\log + \dfrac{K_p}{K_c} \log RT = 0$ 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) $N_2 + 3H_2 \rightleftharpoons 2NH_3$

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ADVCEQ - 25

Section (E) : Reaction quotient and Its applications

E-1. 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).

E-2. 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

E-3.

For the equilibium $CH_3-CH_2-CH_2-CH_3(g) \rightleftharpoons CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-CH_3(g)$ 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
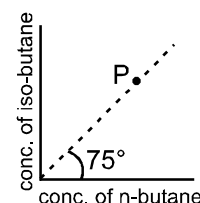
(A) Immediately, above equilibrium will be setup
(B) Above reaction will go in the forward direction till it attains equilibrium
(C) Above reaction will go in the backward direction till it attains equilibrium
(D) Nothing can be said

E-4. The reaction quotient Q for $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ is given by $Q = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$. The reaction will proceed in backward direction, when
(A) $Q = K_C$ 　　　 (B) $Q < K_C$ 　　　 (C) $Q > K_C$ 　　　 (D) A = 0
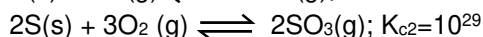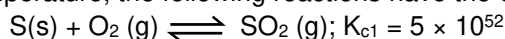
E-5. For the reaction,
$$2A + B \rightleftharpoons 3C \qquad \text{at 298 K,} \qquad K_C = 49$$
A 3L vessel contains 2, 1 and 3 moles of A, B and C respectively. The reaction at the same temperature
(A) must proceed in forward direction
(B) must proceed in backward direction
(C) must be equilibrium
(D) can not be predicted

E-6. When two reactants, A & B are mixed to give products C & D, the reaction quotient Q, at the initial stages of the reaction : **[JEE-2000, 1/35]**
(A) is zero
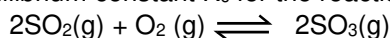(B) decrease with time
(C) is independent of time
(D) increases with time

Section (F) : Properties of equilibrium Constant

F-1. At a certain temperature, the following reactions have the equilibrium constant as shown below :
$$S(s) + O_2(g) \rightleftharpoons SO_2(g); \quad K_{c1} = 5 \times 10^{52}$$
$$2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g); \quad K_{c2} = 10^{29}$$
What is the equilibrium constant K_c for the reaction at the same temperature ?
$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$$
(A) 2.5×10^{76} 　　　 (B) 4×10^{23} 　　　 (C) 4×10^{-77} 　　　 (D) None of these

F-2. The equilibrium constant of the reaction $SO_2(g) + \frac{1}{2}O_2(g) \, SO_3(g) \rightleftharpoons$ 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

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F-3. 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
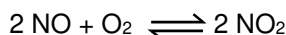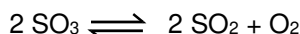
$2 SO_3 \rightleftharpoons 2 SO_2 + O_2$ is K_{C_3} then correct reaction is :

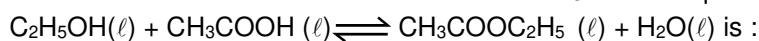(A) $K_{C_3} = K_{C_1} \times K_{C_2}$
(B) $K_{C_3} \times K_{C_1} \times K^2_{C_2} = 1$

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

Section (G) : Homogenuous Equilibrium (liquid system)

G-1. When alcohol (C_2H_5OH (ℓ)) and acetic acid (CH_3COOH (ℓ)) are mixed together in equimolar ratio at 27ºC , 33% of each is converted into ester. Then the K_C for the equilibrium

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

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

Section (H) : Heterogenuous equilibrium

H-1. 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 g

H-2. 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 :
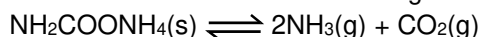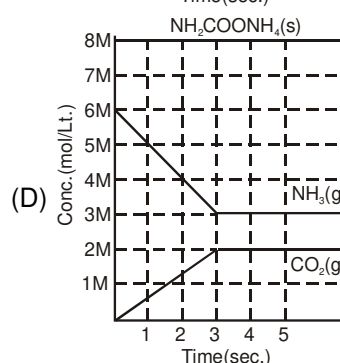
(A) 12 atm
(B) 16 atm
(C) 20 atm
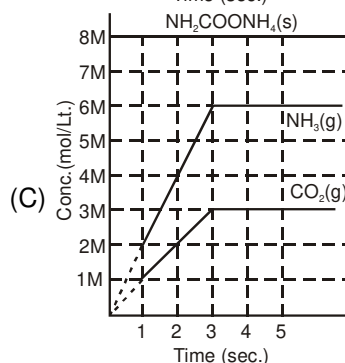(D) 24 atm

H-3. 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.
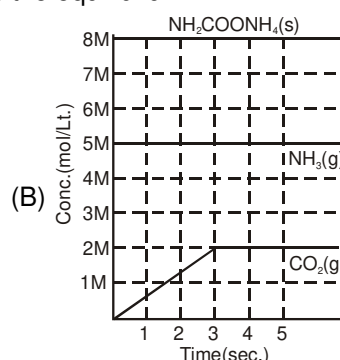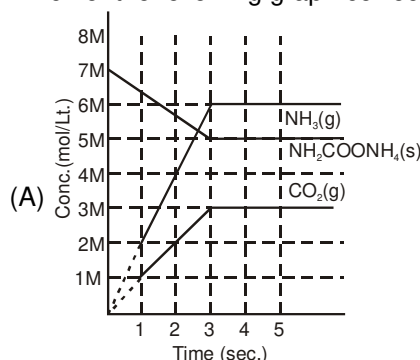
H-4. For $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ reaction started only with $NH_4HS(s)$, the observed pressure for reaction mixture in equilibrium is 1.2 atm at 106°C. What is the value of K_p for the reaction ?

(A) 1.44 atm^2
(B) 0.36 atm^2
(C) 0.16 atm^2
(D) 3.6 atm^2

H-5. Consider the decomposition of solid NH_4HS in a flask containing $NH_3(g)$ at a pressure of 2 atm. What will be the partial pressure of $NH_3(g)$ and $H_2S(g)$ after the equilibrium has been attained?
K_P for the reaction is 3.

(A) $p_{NH_3} = 6$ atm, $p_{H_2S} = \frac{1}{2}$ atm   (B) $p_{NH_3} = 1.732$ atm, $p_{H_2S} = 1.732$ atm

(C) $p_{NH_3} = 3$ atm, $p_{H_2S} = 1$ atm   (D) $p_{NH_3} = 1$ atm, $p_{H_2S} = 3$ atm

Section (I) : Degree of dissociation (α) and vapour density

I-1. For the dissociation reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, the degree of dissociation (α) in terms of K_p and total equilibrium pressure P is:

(A) $\alpha = \sqrt{\dfrac{4p + K_p}{K_p}}$ (B) $\alpha = \sqrt{\dfrac{K_p}{4p + K_p}}$ (C) $\alpha = \sqrt{\dfrac{K_p}{4p}}$ (D) None of these

I-2. 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:
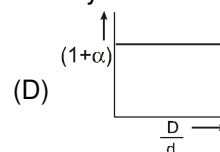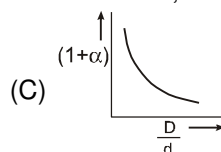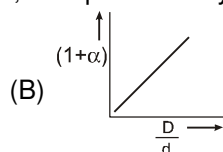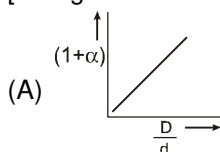
(A) $[(P_0\alpha^3)/2(1 - \alpha)^3]$ (B) $[(P_0\alpha^3)/(2+\alpha)(1 - \alpha)^2]$

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

I-3. In the dissociation of N_2O_4 into NO_2, $(1 + \alpha)$ values with the vapour densies ratio $\left(\dfrac{D}{d}\right)$ is as given by :

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

I-4. In the above question, α varies with $\dfrac{D}{d}$ according to :
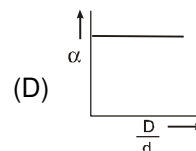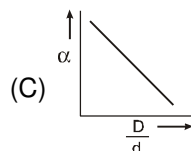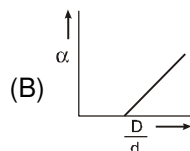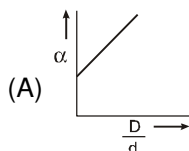
I-5. For the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, if percentage dissociation of N_2O_4 are 20%, 45%, 65% & 80%, then the sequence of observed vapour densities will be :

(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) $(d_{20} = d_{45}) > (d_{65} = d_{80})$

I-6. The degree of dissociation of PCl_5 (α) 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) $\alpha \propto \dfrac{1}{\sqrt{P}}$ (C) $\alpha \propto \dfrac{1}{P^2}$ (D) $\alpha \propto \dfrac{1}{P^4}$

I-7. 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 g/litre. The degree of dissociation is :

(A) 1/3   (B) 2/3   (C) l/4   (D) 1/5.

I-8. Consider the following hypothetical equilibrium $2B(g) \rightleftharpoons B_2(g)$. If d is observed vapour density and D is theoretical vapour density, then degree of association (α) will be :

(A) $\alpha = 2\left(\dfrac{D - d}{d}\right)$ (B) $\alpha = \dfrac{2D - d}{D}$ (C) $\alpha = 2 - \dfrac{2D}{d}$ (D) $\alpha = \dfrac{2D}{D - d}$

I-9. The degree of dissociation is 0.5 at 800 K and 2 atm for the gaseous reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Assuming ideal behaviour of all the gases.
Calculate the density of equilibrium mixture at 800 K and 2 atm.
(A) 4.232 g/L   (B) 6.4 g/L   (C) 8.4 g/L   (D) 2.2 g/L

I-10. $SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2} O_2(g)$

If observed vapour density of mixture at equilibrium is 35 then find out value of α
(A) 0.28   (B) 0.38   (C) 0.48   (D) 0.58

Section (J) : Thermodyanamics of equilibrium

**J-1.** The correct relationship between 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) $\Delta G^o = RT \ln K$

J-2. 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

J-3. 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

J-4. An exothermic reaction is represented by the graph :

(A)   (B)   (C)   (D)   None of these
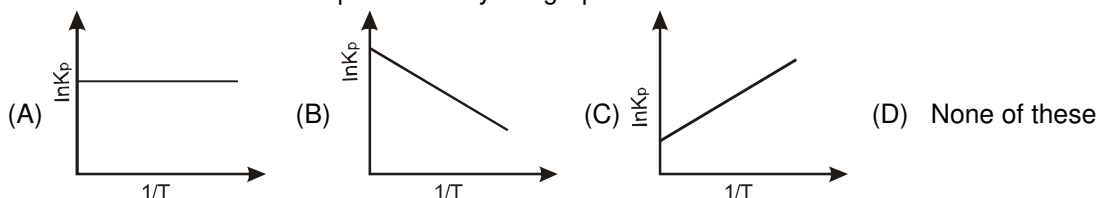
J-5. An endothermic reaction is represented by the graph :

(A)   (B)   (C)   (D) None of these
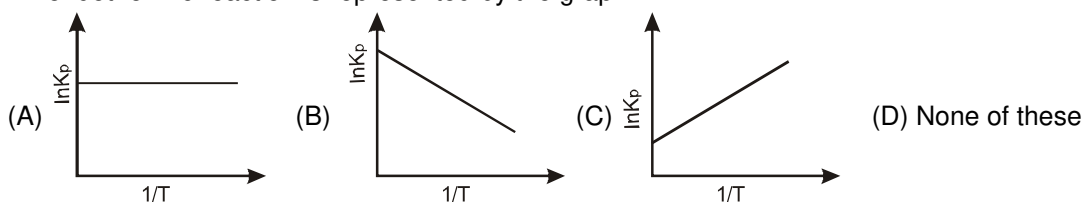
J-6. The value of $\Delta G°$ for a reaction in aqueous phase having $K_c = 1$, would be :
(A) $-RT$ (B) -1 (C) 0   (D) $+ RT$

J-7. The effect of temperature on equilibrium constant is expressed as $(T_2 > T_1)$

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

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

Section (K) : Le-chatelier's principle
K-1. 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)

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K-2. 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

K-3. 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

K-4. Densities of diamond and graphite are 3.5 and 2.3 g/mL.

        C (diamond) $\rightleftharpoons$ C (graphite) $\Delta_rH = -1.9$ 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

K-5. 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 $\Delta n_g = 0$

K-6. For an equilibrium $H_2O(s) \rightleftharpoons H_2O(\ell)$ 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 degree of advancement of the reaction do not depend on pressure.

K-7. A reaction in equilibrium is represented by the following equation –

$2A(s) + 3B(g) \rightleftharpoons 3C(g) + D(g) + O_2$ 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

Section (L) : Vapour pressure and Relative Humidity

L-1. What is the relative humidity of air at 1 bar pressure and 313 K temperature if partial pressure of water in air is 19.355 mmHg.for any data use the table given below :

(in mmHg)	V.P. of H_2O	25.2	31.8	42.2	55.3	71.9	92.5
(in K)	Temp.	298	303	308	313	318	323

(A) 35%   (B) 25%   (C) 75%   (D) 5%

L-2. (a) $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4.3H_2O$ (s) + $2H_2O$ (g) $K_P = 4 \times 10^{-4}$ atm^2

      (b) $Na_2SO_4.10H_2O(s) \rightleftharpoons Na_2SO_4.5H_2O$ (s) + $5H_2O$ (g) $K_P = 2.43 \times 10^{-8}$ atm^5

      (c) $Na_2S_2O_3.5H_2O(s) \rightleftharpoons Na_2S_2O_3.2H_2O$ (s) + $3H_2O$ (g) $K_P = 6.4 \times 10^{-5}$ atm^3

What is order of partial pressure of water vapours at equilibrium and relative humidity respectively.

(A) c > b > a   Partial pressure   (B) c < b < a   Partial pressure

     c > b > a   Relative humidity   c > b > a   Relative humidity

(C) a > c > b   Partial pressure   (D) a > c > b   Partial pressure

     a > c > b   Relative humidity   a < c < b   Relative humidity

L-3. $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$ $K_P = 4 \times 10^{-4}$ atm^2

and vapour pressure of water is 22.4 torr at 298 K. Then find out realative humidity

(A) 74.46%   (B) 78.46%   (C) 67.85%   (D) 70.46%

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Section (M) : Simultaneous equilibria

M-1. 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).

M-2. 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) $\dfrac{y}{x}(y-x)^2$ 　　(B) $\dfrac{y^2(x+y)}{x}$ 　　(C) $\dfrac{y^2(x+y)}{x}$ 　　(D) $\dfrac{y}{x}(x-y)$

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

M-3. 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

PART - III : MATCH THE COLUMN

1. 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 = 300ºC)	(p)	$\Delta n_g > 0$
(B)	$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (t = 50ºC)	(q)	$K_p < K_c$
(C)	$C(s) + H_2O(g) \rightleftharpoons CO(g) + H_2(g)$	(r)	K_p not defined
(D)	$CH_3COOH(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$	(s)	$P_{initial} > P_{eq.}$

2. **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 $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, Cl_2 is removed at equilibrium.	(s)	Final pressure is more than initial pressure

Exercise-2

✎ **Marked questions are recommended for Revision.**

PART - I : ONLY ONE OPTION CORRECT TYPE

1.✎ If K_1, K_2, K_3 are equilibrium constant for formation of AD, AD_2, AD_3 respectively as follows $A + D \rightleftharpoons AD$, $AD + D \rightleftharpoons AD_2$, $AD_2 + D \rightleftharpoons AD_3$. 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) $\log K_1 + \log K_2 = \log K_3 + \log K$

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2. 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 $P_{O_2} \gg P_{O_3}$ 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

3. 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. $S(s) + S^{2-}(aq) \rightleftharpoons S_2^{2-}(aq)$ $K_1 = 12$ & $2S(s) + S^{2-}(aq) \rightleftharpoons S_3^{2-}(aq)$ $K_2 = 132$. 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

4. 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.

5. 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

6. A 10 L container at 300 K 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 $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ $K_p = 0.800$ atm

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

7. In the system, $LaCl_3(s) + H_2O(g) + heat \rightleftharpoons LaClO(s) + 2HCl(g)$, 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) $\sqrt{5}$

8. 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

9. 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

10. For reaction, assuming large volume of water.
$H_2O(\ell) \rightleftharpoons H_2O(g)$;   at temp. T K   Choose correct options :
(A) On introduction of an inert gas at constant temperature pressure in the container remains same at equilibrium.
(B) For this system % relative humidity always remains 100% at constant temperature at equilibrium
(C) If steam at temperature '2T' is passed into given system, after equilibrium is attained relative humidity changes.
(D) This is a special case of equilibrium where pressure of $H_2O(g)$ remains same always due to unique structural feature of H_2O.

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11. 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 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.

12. Addition of water to which of the following equilibria causes it to shift in the backward direction?
(A) CH_3NH_2 (aq) + H_2O (ℓ) $\rightleftharpoons$ $CH_3NH_3^{\oplus}$ (aq) + OH^- (aq)
(B) $AgCl$ (s) $\rightleftharpoons$ Ag^+ (aq) + Cl^- (aq)
(C) HCN (aq) + H_2O (ℓ) $\rightleftharpoons$ H_3O^+ (aq) + CN^- (aq)
(D) $[Cr(dien)_2]^{3+}$ (aq) + $3H_2O$ (ℓ) + $3Cl^-$ (aq) $\rightleftharpoons$ $[Cr(H_2O)_3Cl_3]$ (aq) + 2 dien (aq)

13. 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 pressure
(A) will increase the dissociation of PCl_5 as well as N_2O_4
(B) observed molecular weight of PCl_5 increases at equilibrium.
(C) Concentration NO_2 increases at equilibrium.
(D) will not disturb the equilibrium of the reactions

14. An equilibrium mixture [$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$] 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.

15. $CaCl_2.6H_2O(s) \rightleftharpoons CaCl_2(s) + 6H_2O(g)$ $K_p = 6.4 \times 10^{-17}$ atm^6
Excess solid $CaCl_2.6H_2O$ & $CaCl_2$ are taken in a container containing some water vapours at a pressure of 1.14 torr at a particular temp.
(A) $CaCl_2(s)$ acts as drying agent under given condition.
(B) $CaCl_2(s)$ acts as hygroscopic substance given condition.
(C) $CaCl_2.6H_2O(s)$ acts as effluoroscent substance.
(D) Mass of $CaCl_2.6H_2O(s)$ increases dueto some reaction.

16. $A(s) \rightleftharpoons B(g) + C(g)$ $K_P = 40$ atm^2
$X(s) \rightleftharpoons B(g) + E(g)$
Above equilibrium is allowed to attain in a closed container and pressure of B was found to be 10 atm.
Calculate standard Gibb's free energy change for $X(s) \rightleftharpoons B(g) + E(g)$ at 300 K (take R = 2 cal/K/mol)
(A) 3.5 Kcal/mol (B) 3 Kcal/mol (C) 2.5 Kcal/mol (D) 2 Kcal/mol

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

1. How many of the following reactions are homogenous reversible reactions ?
(1) $CH_3COOH(\ell) + C_2H_5OH(\ell) \rightleftharpoons CH_3COOC_2H_5(\ell) + H_2O(\ell)$
(2) $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g)$
(3) $CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$
(4) $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$
(5) $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
(6) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
(7) $CO_2(g) + C(s) \rightleftharpoons 2CO(g)$
(8) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
(9) $NO(g) + \frac{1}{2} Br_2(\ell) \rightleftharpoons 2NOBr(g)$

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2. $A(g) + B(g) \rightleftharpoons C(g) + D(g)$ 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, $C(g) + D(g) \rightleftharpoons A(g) + B(g)$.

3. 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 :

4. For the reaction, $N_2O_5(g) \rightleftharpoons 2NO_2(g) + 1/2\ O_2(g)$, calculate the mole fraction of $N_2O_5(g)$ decomposed at a constant volume & temperature, if the initial pressure is 600 mm Hg & the pressure at any time is 960 mm Hg. Assume ideal gas behaviour. If answer is x then report 10x.

5. Consider the equilibrium
$Ni(s) + 4CO(g) \rightleftharpoons Ni(CO)_4(g)$; $K_p = 0.125$ 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 ?

6. K_p is 9 atm^2 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 $LiCl.3NH_3$? Multiply the obtained answer by 100. Round off the answer to the nearest integer.

7. Consider the reaction, $2Cl_2(g) + 2H_2O(g) \rightleftharpoons 4HCl(g) + O_2(g)$; $\Delta H^\circ = +113$ kJ
The four gases, Cl_2, H_2O, HCl and O_2, are mixed and the reaction is allowed to come to equilibrium. Each operation is to be considered separately. Temperature and volume are constant unless stated otherwise. Report the number of operations in the left column which lead to increase in the equilibrium value of the quantity in the right column.
(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

8. For given simultaneous reaction :
$X(s) \rightleftharpoons A(g) + B(s) + C(g)$ $K_{P_1} = 500$ atm^2
$Y(s) \rightleftharpoons D(g) + A(g) + E(s)$ $K_{P_2} = 2000$ atm^2
If total pressure = x, then write your answer after dividing by 25.

9. For equilibrium $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the observed vapour density of N_2O_4 is 40 at 350 K. Calculate percentage dissociation of $N_2O_4(g)$ at 350K.

10. The vapour density of N_2O_4 at a certain temperature is 30.67. The % dissociation of N_2O_4 at this temperature is :

11. Solid ammonium carbamate dissociates to give ammonia and carbon dioxide as follows:
$NH_2 COONH_4 (s) \rightleftharpoons 2NH_3 (g) + CO_2 (g)$
At equilibrium, ammonia is added such that partial pressures of NH_3 at new equilibrium equals the original total pressure (at previous equilibrium). If the ratio of the total pressures now to the original total pressure is a/b then report a + b.

## PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

1. 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

2. 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

3. Which of the following statement/s is/are correct :
(A) At equilibrium, vapour pressure of solution and refractive index of eq. mixture becomes constant.
(B) Equilibrium can be attained in both homogenous and heterogenous reaction.
(C) Approach to the equilibrium is fast in initial state but gradually it decreases.
(D) Equilibrium is dynamic in nature

4. Equilibrium constant for following reactions respectively K_1, K_2 and K_3
$N_2 + 3H_2 \rightleftharpoons 2NH_3$ K_1
$N_2 + O_2 \rightleftharpoons 2NO$ K_2
$H_2 + \dfrac{1}{2} O_2 \rightleftharpoons H_2O$ K_3

$2NH_3 + \dfrac{5}{2} O_2 \rightleftharpoons 2NO + 3H_2O$ K_4

Which of the following relation is correct.

(A) $K_1 = \dfrac{K_2 \times (K_3)^3}{K_4}$ (B) $K_4 = K_1 \times K_2/(K_3)^3$ (C) $K_2 = \dfrac{K_4 \times K_1}{(K_3)^3}$ (D) $K_4 = \dfrac{K_2 \times (K_3)^3}{K_1}$

5. If $\log \dfrac{k_c}{k_p} - \log \dfrac{1}{RT} = 0$, then above is true for the following equilibrium reaction

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

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

6. The reaction for which, $K_P = K_C$ is satisfied
(A) $A(g) + 2B(g) \rightleftharpoons 3C(g)$ (B) $A(s) \rightleftharpoons B(g)$
(C) $2A(g) \rightleftharpoons B(g) + C(g)$ (D) $A(s) + B(g) \rightleftharpoons C(s) + 2D(g)$

7. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$, $K_c = 4$. This reversible reaction is studied graphically as shown in figure. Select the correct statements.
(A) Reaction quotient has maximum value at point A
(B) Reaction proceeds left to right at a point when $[N_2O_4] = [NO_2] = 0.1$ M
(C) $K_c = Q$ when point D or F is reached :
(D) None of these
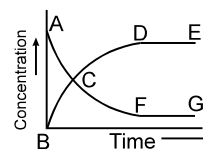
8. If reaction $A + B \rightleftharpoons C + D$, take place in 5 liter close vessel, the rate constant of forward reaction is nine times of rate of backward reaction.
If initially one mole of each reactant present in the container, then find the correct option/s.

(A) $\dfrac{[C]}{[B]} = \dfrac{3}{1}$ (B) $\log K_P = \log K_C$
(C) $[D]_{eq} = 15 \times 10^{-2}$ mole L^{-1} (D) $K_{eq} = 9$

9. Consider the following equilibrium $2AB(g) \rightleftharpoons A_2(g) + B_2(g)$
The vapour density of the equilibrium mixture does not depend upon
(A) Temperature   (B) Initial concentration
(C) Volume of contain   (D) Pressure of equilibrium mixture

10. Vapour density of equilibrium $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ is decreased by
(A) increasing temperature (B) decreasing pressure
(C) increasing pressure (D) decreasing temperature

11. $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4(s) + 5H_2O(g)$ $K_p = 10^{-10}$ (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 = $\dfrac{1}{12}$ 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}

12. $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$ $K_P = 0.4 \times 10^{-3}$ atm^2
Which of following statement are correct :
(A) $\Delta G^\circ = - RT \ln P_{H_2O}$ where P_{H_2O} = Partial pressure of H_2O at equilibrium.
(B) At vapour pressure of H_2O = 15.2 torr relative humidity of $CuSO_4.5H_2O$ is 100%.
(C) In presence of aqueous tension of 24 torr, $CuSO_4.5H_2O$ can not loss moisture.
(D) In presence of dry atmosphere in open container $CuSO_4.5H_2O$ will completely convert into $CuSO_4.3H_2O$

13. 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.

14. 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

15. Which of the following reaction will shift in forward direction. When the respective change is made at equilibrium :
(A) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ increase in pressure at eq.
(B) $H_2O(s) \rightleftharpoons H_2O(\ell)$ addition of inert gas at constant volume
(C) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ addition of inert gas at constant pressure
(D) $H_2 + I_2 \rightleftharpoons 2HI$ increase in temperature

16. $2CaSO_4(s) \rightleftharpoons 2CaO(s) + 2SO_2(g) + O_2(g)$, $\Delta H > 0$
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.
$2CaSO_4(s) \rightleftharpoons 2CaO(s) + 2SO_2(g) + O_2(g)$, $\Delta H > 0$

17. 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

PART - IV : COMPREHENSION

Read the following passage 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 nullify 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.

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 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. $Au(s) \rightleftharpoons Au(\ell)$
   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

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 # 2

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

$\Delta G^\circ = -2.30\ RT\ logk$ .... (1) ΔG° : Standard free energy change

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

From (1) & (2)

$-2.3\ RT\ logk = \Delta H^\circ - T\Delta S^\circ$ ΔS° : Standard entropy change

$\Rightarrow\quad logK = -\dfrac{\Delta H^\circ}{2.3RT} + \dfrac{\Delta S^\circ}{2.3\ R}$ .... (3)

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

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

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:

$\Rightarrow$ $\log K_1 = -\dfrac{\Delta H^\circ}{2.3\ R\ T_1} + \dfrac{\Delta S^\circ}{2.3\ R}$ .... (4)

$\Rightarrow$ $\log K_2 = -\dfrac{\Delta H^\circ}{2.3\ R\ T_2} + \dfrac{\Delta S^\circ}{2.3\ R}$ .... (5)

Substracting (4) from (5) we get

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

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.

4.   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

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

(A)   (B)   (C) logk   (D)
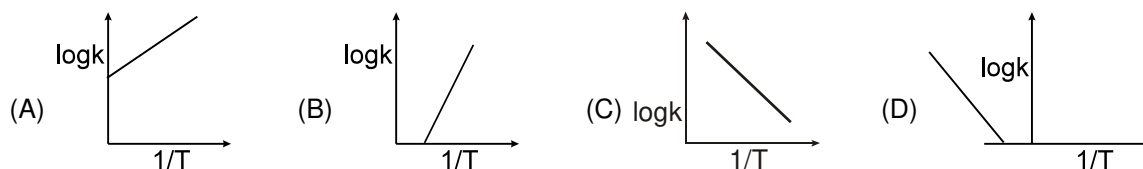
6.   If for a particular reversible reaction $K_C = 57$ at 355ºC and $K_C = 69$ at 450ºC then :
(A) $\Delta H < 0$ (B) $\Delta H > 0$
(C) $\Delta H = 0$ (D) ΔH whose sign can't be determined

Comprehension # 3
Answer Q.7, Q.8 and Q.9 by appropriately matching the information given in the three columns of the following table.

Equilibrium is a state in which there are no observable changes as time goes by. When a chemical reaction has reached the equilibrium state, the concentrations of reactants and products remain constant over time and there are no visible changes in the system. However, there is much activity at the molecular level because reactant molecules continue to from product molecules while product molecules react to yield reactant molecules. If a change is applied to the system at equilibrium, then equilibrium will be shifted in that direction in which it can minimise the effect of change applied and the equilibrium is established again under new conditions.

	Column-1		Column-2		Column-3
(I)	$2NH_{3(g)} \rightleftharpoons N_{2(g)} + 3H_{2(g)}$	(i)	Homogeneous	(P)	If $\alpha = \dfrac{1}{2}$ & $P_{total\ at\ equilibrium} = 1$ atm $k_P \leq 1$
(II)	$N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$	(ii)	$k_P > k_C$ (T = 298k)	(Q)	On Increasing Temperature yield of reaction increases
(III)	$2O_{3(g)} \rightleftharpoons 3O_{2(g)}$	(iii)	degree of dissociation is not affected by pressure	(R)	On increasing pressure vapour density of equilibrium mixture decreases
(IV)	$2HI_{(g)} \rightleftharpoons H_{2(g)} + I_{2(g)}$	(iv)	$M_{theoritical} \geq M_{experimental}$	(S)	Products are paramagnetic in nature

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7.* Incorrect combination is
(A) (I) (i) (p)   (B) (II) (ii) (Q)   (C) (III) (iii) (Q)   (D) (IV) (iv) (S)

8. Correct combination is
(A) (IV) (ii) (Q)   (B) (III) (i) (S)   (C) (II) (iv) (R)   (D) (II) (iii) (S)

9.* Correct combination is
(A) (I) (iii) (R)   (B) (II) (iv) (S)   (C) (III) (iv) (Q)   (D) (IV) (iii) (P)

Exercise-3

* Marked Questions may have more than one correct option.

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

1. For a chemical reaction $3X(g) + Y(g) \rightleftharpoons X_3Y(g)$, the amount of X_3Y at equilibrium is affected by
(A) temperature and pressure   (B) temperature only
(C) pressure only   (D) temperature, pressure and catalyst **[JEE-1999, 2/80]**

2. For the reversible reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$ at 500°C, the value of K_P is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of K_C, with concentration in mole litre^{-1}, is **[JEE 2000, 1/35]**

(A) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$ (B) $\dfrac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$ (C) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^2}$ (D) $\dfrac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$

3. When two reactants, A & B are mixed to give products C & D, the reaction quotient Q, at the initial stages of the reaction. **[JEE-2000, 1/35]**
(A) is zero   (B) decrease with time
(C) is independent of time   (D) increases with time

4. At constant temperature, the equilibrium constant (K_P) for the decomposition reaction $N_2O_4 \rightleftharpoons 2NO_2$ is

expressed by $K_P = \dfrac{(4x^2 \ P)}{(1-x^2)}$, where P = pressure, x = extent of decomposition. Which one of the following

statements is true? **[JEE 2001, 1/35]**
(A) K_P increases with increase of P   (B) K_P increases with increase of x
(C) K_P increases with decrease of x   (D) K_P remains constant with change in P and x

5. Consider the following equilibrium in a closed container **[JEE 2002, 3/90]**
$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$
At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements holds true regarding the equilibrium constant (K_P) and degree of dissociation (α)?
(A) neither K_P nor α changes   (B) both K_P and α change
(C) K_P changes, but α does not change   (D) K_P does not change but α changes

6. The value of $\log_{10}K$ for a reaction $A \rightleftharpoons B$ is : (Given : $= \Delta_r H_{298K}^\circ$ -54.07 kJ mol^{-1}, $\Delta_r S_{298K}^\circ = 10$ JK^{-1} mol^{-1} and R = 8.314 JK^{-1} mol^{-1}; $2.303 \times 8.314 \times 298 = 5705$) **[JEE 2007, 3/162]**
(A) 5   (B) 10   (C) 95   (D) 100

7.* The thermal dissociation equilibrium of $CaCO_3(s)$ is studied under different conditions.
$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$
For this equilibrium, the correct statement(s) is (are) : **[JEE(Advanced) 2013, 3/120]**
(A) ΔH is dependent on T
(B) K is independent of the initial amount of $CaCO_3$
(C) K is dependent on the pressure of CO_2 at a given T
(D) ΔH is independent of the catalyst, if any

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Paragraph 1

Thermal decomposition of gaseous X_2 to gaseous X at 298 K takes place according to the following equation :

$$X_2(g) \rightleftharpoons 2X(g)$$
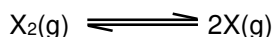
The standard reaction Gibbs energy, $\Delta_r G^\circ$, of this reaction is positive. At the start of the reaction, there is one mole of X_2 and no X. As the reaction proceeds, the number of moles of X formed is given by β. Thus. $\beta_{equilibrium}$ is the number of moles of X formed at equilibrium. 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})

8. The equilibrium constant K_p for this reaction at 298 K, in terms of $\beta_{equilibrium}$, is

    [JEE(Advanced) 2016, 3/124]

    (A) $\dfrac{8\beta_{equilibrium}^2}{2-\beta_{equilibrium}}$
    (B) $\dfrac{8\beta_{equilibrium}^2}{4-\beta_{equilibrium}^2}$
    (C) $\dfrac{4\beta_{equilibrium}^2}{2-\beta_{equilibrium}}$
    (D) $\dfrac{4\beta_{equilibrium}^2}{4-\beta_{equilibrium}^2}$

9. The **INCORRECT** statement among the following, for this reaction, is   **[JEE(Advanced) 2016, 3/124]**
    (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) $\beta_{equilibrium}$ = 0.7
    (D) K_C < 1

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

OFFLINE JEE-MAIN

1. Change in volume of the system does not alter the number of moles in which of the following equilibriums:
    [AIEEE 2002, 3/225]

    (1) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
    (2) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
    (3) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$
    (4) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

2. In which of the following reactions, increase in the volume at constant temperature don't effect the number of moles of at equilibrium :   **[AIEEE 2002, 3/225]**
    (1) $2NH_3 \rightleftharpoons N_2 + 3H_2$
    (2) $C(g) + (1/2) O_2(g) \rightleftharpoons CO (g)$
    (3) $H_2 (g) + O_2 (g) \rightleftharpoons H_2O_2 (g)$
    (4) none of these.

3. For the reaction CO (g) + (1/2) O_2 (g) $\rightleftharpoons$ CO_2 (g), K_c/K_p is :   **[AIEEE 2002, 3/225]**
    (1) RT
    (2) $(RT)^{-1}$
    (3) $(RT)^{-1/2}$
    (4) $(RT)^{1/2}$

4. Consider the reaction equilibrium
    $$2SO_2 (g) + O_2 (g) \rightleftharpoons 2SO_3 (g) ; \Delta H^\circ = -198 \text{ kJ}.$$
    On the basis of Le Chatelier's principle, the condition favourable for the forward reaction is :
    [AIEEE 2003, 3/225]

    (1) lowering of temperature as well as pressure
    (2) increasing temperature as well as pressure
    (3) lowering the temperature and increasing the pressure
    (4) any value of temperature and pressure.

5. For the reaction equilibrium, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ the concentrations of N_2O_4 and NO_2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol L^{-1} respectively. The value of K_c for the reaction is   **[AIEEE 2003, 3/225]**
    (1) 3.3×10^2 mol L^{-1}
    (2) 3×10^{-1} mol L^{-1}
    (3) 3×10^{-3} mol L^{-1}
    (4) 3×10^3 mol L^{-1}

6. What is the equilibrium constant expression for the reaction :   **[AIEEE 2004, 3/225]**
    $$P_4 (s) + 5O_2 (g) \rightleftharpoons P_4 O_{10} (s) ?$$
    (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) $K_C = [P_4O_{10}] / 5[P_4] [O_2]$

7. For the reaction, CO(g) + Cl_2 (g) $\rightleftharpoons$ $COCl_2$ (g) then K_p / K_c is equal to :   **[AIEEE 2004, 3/225]**
   (1) 1/RT
    (2) 1.0
    (3) $\sqrt{RT}$
    (4) RT

8. 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 :

[AIEEE 2004, 3/225 & JEE(Main) 2012, 4/120]

(1) 2.5×10^2 (2) 0.02   (3) 4×10^{-4} (4) 50

9. 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, 3/225]**
(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

10. The exothermic formation of ClF_3 is represented by the equation $Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g); \Delta_r H = -329$ J which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2, F_2 and ClF_3.

[AIEEE 2005, 3/225]

(1) Adding F_2 (2) Increasing the volume of container
(3) Removing Cl_2 (4) Increasing the temperature

11. 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, 4½/225]**
(1) 0.11   (2) 0.17   (3) 0.18   (4) 0.30

12. 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, 3/165]**

(1) $\left(\dfrac{x}{x+1}\right)P$ (2) $\left(\dfrac{2x}{1-x}\right)P$ (3) $\left(\dfrac{x}{x+1}\right)P$ (4) $\left(\dfrac{x}{1-x}\right)P$

13. 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, 3/165]**
(1) 416   (2) 2.40×10^{-3} (3) 9.8×10^{-2} (4) 4.9×10^{-2}

14. 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, 3/105]**
(1) $K_2 K_3 = K_1$ (2) $K_3 = K_1 K_2$ (3) $K_3 K_2^3 = K_1^2$ (4) $K_1\sqrt{K_2} = K_3$

15. 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, 3/105]**
(1) 1 : 1   (2) 1 : 3   (3) 1 : 9   (4) 1 : 36

16. 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, 4/120]

(1) 1.8 atm   (2) 3 atm   (3) 0.3 atm   (4) 0.18

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17. 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, 4/120]**

(1) 0.02   (2) 2.5×10^2 (3) 4×10^{-4} (4) 50.0

18. 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, 4/120]**

(1) –1   (2) $-\frac{1}{2}$ (3) $\frac{1}{2}$ (4) 1

19. The standard Gibbs energy change at 300 K for the reaction $2A \rightleftharpoons B + C$ is 2494.2 J. 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 :

[R = 8.314 J/K/mol, e = 2.718] **[JEE(Main) 2015, 4/120]**
(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 $Q < K_C$

20. 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 1 M each, then equilibrium concentration of D (in mol L^{-1}) will be :

[JEE(Main) 2016, 4/120]

(1) 0.818   (2) 1.818   (3) 1.182   (4) 0.182

21. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction ?

[JEE(Main) 2018, 4/120]

(1) C and D
(2) A and D
(3) A and B
(4) B and C
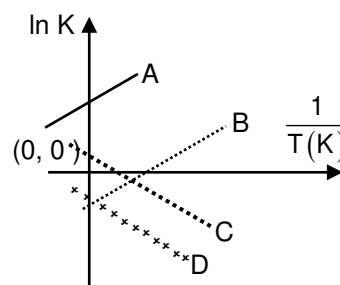
ONLINE JEE-MAIN

1. At a certain temperature, only 50% HI is dissociated into H_2 and I_2 at equilibrium. The equilibrium constant is: **[JEE(Main) 2014 Online (09-04-14), 4/120]**
(1) 1.0   (2) 3.0   (3) 0.5   (4) 0.25

2. What happens when an inert gas is added to an equilibrium keeping volume unchanged ?
[JEE(Main) 2014 Online (12-04-14), 4/120]
(1) More product will form   (2) Less product will form
(3) More reactant will form   (4) Equilibrium will remain unchanged

3. For the decomposition of the compound, represented as $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$ the $K_p = 2.9 \times 10^{-5}$ atm^3. If the reaction is started with 1 mol of the compounds, the total pressure at equilibrium would be : **[JEE(Main) 2014 Online (19-04-14), 4/120]**
(1) 1.94×10^{-2} atm   (2) 5.82×10^{-2} atm
(3) 7.66×10^{-2} atm   (4) 38.8×10^{-2} atm

4. Gaseous N_2O_4 dissociates into gaseous NO_2 according to the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ at 300 K and 1 atm pressure, the degree of dissociation of N_2O_4 is 0.2. If one mole of N_2O_4 gas is contained in a vessel, then the density of the equilibrium mixture is : **[JEE(Main) 2015 Online (10-04-15), 4/120]**
(1) 3.11 g/L   (2) 4.56 g/L   (3) 1.56 g/L   (4) 6.22 g/L

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5. The increase of pressure on ice $\rightleftharpoons$ water system at constant temperature will lead to :
[JEE(Main) 2015 Online (11-04-15), 4/120]
(1) a decrease in the entropy of the system
(2) an increase in the Gibbs energy of the system
(3) no effect on the equilibrium
(4) a shift of the equilibrium in the forward direction

6. A solid XY kept in an evacuated sealed container undergoes decomposition to form a mixture of gases X and Y at temperature T. The equilibrium pressure is 10 bar in this vessel. K_P for this reaction is :
[JEE(Main) 2016 Online (10-04-16), 4/120]
(1) 25   (2) 5   (3) 10   (4) 100

7. The following reaction occurs in the Blast Furnace where iron ore is reduced to iron metal :
$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(\ell) + 3CO_2(g)$
Using the Le Chatelier's principle, predict which one of the following will **not** disturb the equilibrium ?
[JEE(Main) 2017 Online (09-04-17), 4/120]
(1) Addition of Fe_2O_3 (2) Removal of CO_2 (3) Removal of CO   (4) Addition of CO_2

8. In which of the following reactions, an increase in the volume of the container will favour the formation of products ?   **[JEE(Main) 2018 Online (15-04-18), 4/120]**
(1) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(\ell)$ (2) $2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$
(3) $3O_2(g) \rightleftharpoons 2O_3(g)$ (4) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

9. At a certain temperature in a 5 L vessel, 2 moles of carbon monoxide and 3 moles of chlorine were allowed to reach equilibrium according to the reaction,
$CO + Cl_2 \rightleftharpoons COCl_2$
At equilibrium if one mole of CO is present then equilibrium constant K_C for reaction is :
[JEE(Main) 2018 Online (15-04-18), 4/120]
(1) 2   (2) 2.5   (3) 3   (4) 4

10. At 320 K, a gas A_2 is 20 % dissociated to A(g). The standard free energy change at 320 K and 1 atm in J mol^{-1} is approximately : (R = 8.314 JK^{-1} mol^{-1} ; ln 2 = 0.693 ; ln 3 = 1.098)
[JEE(Main) 2018 Online (16-04-18), 4/120]
(1) 1844   (2) 2068   (3) 4281   (4) 4763

11. The gas phase reaction $2NO_2(g) \rightarrow N_2O_4(g)$ is an exothermic reaction. The decomposition of N_2O_4, in equilibrium mixture of $NO_2(g)$ and $N_2O_4(g)$, can be increased by :
[JEE(Main) 2018 Online (16-04-18), 4/120]
(1) addition of an inert gas at constant pressure.   (2) lowering the temperature
(3) increasing the pressure   (4) addition of an inert gas at constant volume.

12. Consider the following reversible chemical reactions :

$A_2(g) + B_2(g) \overset{K_1}{\rightleftharpoons} 2AB(g)$ ......(1)

$6AB(g) \overset{K_2}{\rightleftharpoons} 3A_2(g) + 3B_2(g)$ ......(2)

The relation between K_1 and K_2 is :   **[JEE(Main) 2019 Online (09-01-19), 4/120]**

(1) $K_1K_2 = \dfrac{1}{3}$ (2) $K_2 = K_1^{-3}$ (3) $K_1K_2 = 3$ (4) $K_2 = K_1^3$

13. The values of K_P/K_C for the following reactions at 300 K are, respectively : (At 300 K, RT = 24.62 dm^3 atm mol^{-1})

         $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$
         $N_2O_4(g) \rightleftharpoons 2NO_2(g)$
         $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

[JEE(Main) 2019 Online (10-01-19), 4/120]

(1) 1,4.1 × 10^{-2} dm^{-3} atm^{-1} mol, 606 dm^6 atm^2mol^{-2}
(2) 1,24.62 dm^3 atm^{-1} mol^{-1}, 1.65 × 10^{-3} dm^{-6} atm^2mol^{-2}
(3) 24.62 dm^3 atm mol^{-1} 606.0 dm^6 atm^2 mol^{-2}, 1.65 × 10^{-3} dm^{-6} $atm^{-2}mol^2$
(4) 1,24.62 dm^3 atm mol^{-1}, 606.0 dm^6 atm^2mol^{-2}

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14. 5.1 g NH_4SH is introduced in 3.0 L evacuated flask at 327°C. 30% of the solid NH_4SH decomposed to NH_3 and H_2S as gases. The K_p of the reaction at 327°C is (R = 0.082 L atm $mol^{-1}K^{-1}$, molar mass of S = 32 g mol^{-1}, molar mass of N = 14 g mol^{-1}) **[JEE(Main) 2019 Online (10-01-19), 4/120]**
(1) 4.9×10^{-3} atm^2 (2) 0.242×10^{-4} atm^2 (3) 1×10^{-4} atm^2 (4) 0.242 atm^2

15. Consider the reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$. The equilibrium constant of the above reaction is K_P. If pure ammonia is left to dissociate, the partial pressure of ammonia at equilibrium is given by (Assume that $p_{NH_3} \ll p_{total}$ at equilibrium) **[JEE(Main) 2019 Online (11-01-19), 4/120]**

(1) $\dfrac{3^{3/2}K_p^{1/2}P^2}{16}$ (2) $\dfrac{3^{3/2}K_p^{1/2}P^2}{4}$ (3) $\dfrac{K_p^{1/2}P^2}{4}$ (4) $\dfrac{K_p^{1/2}P^2}{16}$

16. In a chemical reaction, $A + 2B \underset{}{\overset{K}{\rightleftharpoons}} 2C+D$, the initial concentration of B was 1.5 times of the concentration of A, but the equilibrium concentrations of A and B were found to be equal. The equilibrium constant (K) for the aforesaid chemical reaction is : **[JEE(Main) 2019 Online (12-01-19), 4/120]**
(1) 16   (2) 1   (3) 1/4   (4) 4

17. Two solids dissociate as follows

$A(s) \rightleftharpoons B(g) + C(g)$; $K_{P_1} = x\,atm^2$

$D(s) \rightleftharpoons C(g) + E(g)$; $K_{P_2} = y\,atm^2$

The total pressure when both the solids dissociate simultaneously is :

[JEE(Main) 2019 Online (12-01-19), 4/120]
(1) $\sqrt{x+y}$ atm   (2) $(x + y)$ atm   (3) $x^2 + y^2$ atm   (4) $2\left(\sqrt{x+y}\right)$ atm

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Answers

EXERCISE - 1

PART - I

A-1. 4   **A-2.** 0.044 M.   **B-1.** (a) 0.1 (b) 0.4   **B-2.** $\dfrac{100\%}{6}$

B-3. 1/3M   **B-4.** 0.66   **C-1.** $\dfrac{P(n+y/2)(n+y)^2}{(3n+y/2)(n-y)^2}$ **C-2.** $K_P = 12$

C-3. $[NH_3] = 0.76$ M   **D-1.** $K_C = \dfrac{4x^2V^2}{(a-x)(b-3x)^3}$; $K_P = \dfrac{(a+b-2x)^2.4x^2}{P^2(a-x)(b-3x)^3}$

D-2. $[A]_{eq} = [B]_{eq} = [C]_{eq} = 1/2$ M, $K_p = 12.3$ atm, $K_c = 0.5$ M (unitless).

D-3. (i) $K_c = \dfrac{20000}{343}$ = 58.3 mol^{-2} L^2, $K_P = \dfrac{58.3}{41 \times 41}$ = 0.035 atm^{-2} (ii) P = 8.2 atm

E-1. The reaction is $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

$Q_c = \dfrac{[NH_3]^2}{[N_2][H_2]^3} = \dfrac{8 \times 8 \times 20 \times 20}{\dfrac{3}{2} \times 2 \times 2 \times 2} = \dfrac{64}{3} \times 10^2$

As $Q_c \neq K_c$, the reaction mixture is not in equilibrium.
As $Q_c > K_c$, the net reaction will be in the backward direction.

E-2. $[SO_2] = 0.034$ M ; $[NO_2] = 0.034$ M ; $[NO] = 0.306$ M ; $[SO_3] = 0.306$ M

F-1. (i) No change   (ii) 1/k   (iii) No change   (iv) Change the equilibrium constant

F-2. For the required reaction, $K = K_1 \times K_2$.   **F-3.** 2.58

G-1. X = 4, Y = 4

H-1. (i)   Homogeneous equilibrium $K_C = \dfrac{[NO_2]^2}{[N_2O_4]}$ $K_P = \dfrac{(P_{NO_2})^2}{(P_{N_2O_4})}$

     (ii)   Hetereogeneous equilibrium $K_C = \dfrac{[H_2]^4}{[H_2O]^4}$ $K_P = \dfrac{(P_{H_2})^4}{(P_{H_2O})^4}$

     (iii)   Hetereogeneous equilibrium $K_C = [NH_3][H_2S]$ $K_P = (P_{NH_3})(P_{H_2S})$

     (iv)   Homogeneous equilibrium $K_C = \dfrac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$ but K_P is not define for liquid system

     (v)   Hetereogeneous equilibrium $K_C = [CO_2]$ $K_P = (P_{CO_2})$

     (vi)   Homogeneous equilibrium $K_C = \dfrac{[H_2]^2[S_2]}{[H_2S]^2}$ $K_P = \dfrac{(P_{H_2})^2(P_{S_2})}{(P_{H_2S})^2}$

     (vii)   Homogeneous equilibrium $K_C = \dfrac{[SO_3][NO]}{[SO_2][NO_2]}$ $K_P = \dfrac{(P_{SO_3})(P_{NO})}{(P_{SO_2})(P_{NO_2})}$

     (viii)   Hetereogeneous equilibrium $K_C = [N_2]$ $K_P = (P_{N_2})$

H-2. 50%   **H-3.** $K_P = \dfrac{2}{3^{3/2}} P^{3/2}$

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I-1. (i) 0.266 atm (ii) 63.25%　　　　**I-2.** $x = \left[\dfrac{2 \ K_P}{P}\right]^{1/3}$

I-3. (i) 76.66, (ii) 0.2, (iii) 33.33 %, (iv) 1/3　　　**I-4.** 2.55 atm^3　　**J-1.** $K_P = 1.86 \times 10^{12}$ atm$^{-1/2}$

J-2. $\Rightarrow$ reaction (iii) is exothermic.

K-1. (i) unaffected; no shift　　(ii) affected; left direction.　　(iii) affected; left　　(iv) affected; right

K-2. (i) When decreasing temperature
(a) Forward　　　　(b) Forward　　　　(c) Backward　　　　(d) Forward
(ii) Increasing the pressure
(a) Forward　　　　(b) No change　　　(c) Backward　　　　(d) Forward

K-3. (a) 4×10^{-3} (b) (i) decrease (ii) no change (iii) increase (iv) increase (v) no change (vi) increase

K-4. [A] = 0.34 M, [B] = 1.16 M, [C] = 1.16 M.　　**L-1.** below 50%

L-2. 5×10^{-3} atm.　　**M-1.** (a) $K_{p_1} = 625$ mm^2, $K_{p_2} = 900$ mm^2 (b) $\dfrac{25}{36}$

M-2. (a) 1.05 atm,　　　(b) 3.43 atm^{-1}

PART – II

A-1. (D)　　**A-2.** (D)　　**A-3.** (B)　　**A-4.** (D)　　**A-5.** (D)

B-1. (A)　　**B-2.** (A)　　**B-3.** (A)　　**B-4.** (C)　　**B-5.** (B)

B-6. (B)　　**C-1.** (B)　　**C-2.** (B)　　**C-3.** (B)　　**C-4.** (A)

C-5. (C)　　**C-6.** (C)　　**C-7.** (A)　　**D-1.** (C)　　**D-2.** (A)

D-3. (B)　　**E-1.** (D)　　**E-2.** (B)　　**E-3.** (C)　　**E-4.** (C)

E-5. (A)　　**E-6.** (D)　　**F-1.** (C)　　**F-2.** (D)　　**F-3.** (B)

G-1. (B)　　**H-1.** (A)　　**H-2.** (B)　　**H-3.** (C)　　**H-4.** (B)

H-5. (C)　　**I-1.** (B)　　**I-2.** (B)　　**I-3.** (A)　　**I-4.** (B)

I-5. (A)　　**I-6.** (B)　　**I-7.** (B)　　**I-8.** (C)　　**I-9.** (A)

I-10. (A)　　**J-1.** (A)　　**J-2.** (B)　　**J-3.** (A)　　**J-4.** (C)

J-5. (B)　　**J-6.** (C)　　**J-7.** (A)　　**K-1.** (D)　　**K-2.** (B)

K-3. (B)　　**K-4.** (C)　　**K-5.** (B)　　**K-6.** (B)　　**K-7.** (B)

L-1. (A)　　**L-2.** (A)　　**L-3.** (C)　　**M-1.** (D)　　**M-2.** (A)

M-3. (C)

PART – III

1. (A - q, s) ; (B - p) ; (C - p) ; (D - r)　　**2.** (A - r) ; (B - r) ; (C - q) ; (D - p)

EXERCISE – 2

PART – I

1.	(B)	**2.**	(B)	**3.**	(A)	**4.**	(A)	**5.**	(C)
6.	(B)	**7.**	(B)	**8.**	(B)	**9.**	(A)	**10.**	(B)
11.	(D)	**12.**	(D)	**13.**	(A)	**14.**	(A)	**15.**	(C)
16.	(C)								

PART – II

1.	05	**2.**	3	**3.**	7	**4.**	4	**5.**	4
6.	78 mole	**7.**	5	**8.**	4	**9.**	15	**10.**	50
11.	58								

PART – III

1.	(ABC)	**2.**	(ABD)	**3.**	(ABCD)	**4.**	(ACD)	**5.**	(AB)
6.	(AC)	**7.**	(BC)	**8.**	(ABCD)	**9.**	(ABCD)	**10.**	(AB)
11.	(BD)	**12.**	(BCD)	**13.**	(ABCDE)	**14.**	(BCD)	**15.**	(ABC)
16.	(ACD)	**17.**	(BD)						

PART – IV

1.	(D)	**2.**	(C)	**3.***	(AB)	**4.**	(B)	**5.**	(B)
6.	(B)	**7.***	(CD)	**8.**	(B)	**9.***	(BD)		

EXERCISE – 3

PART - I

1.	(A)	**2.**	(D)	**3.**	(D)	**4.**	(D)	**5.**	(D)
6.	(B)	**7.***	(ABD)	**8.**	(B)	**9.**	(C)		

PART – II

OFFLINE JEE-MAIN

1.	(1)	**2.**	(4)	**3.**	(4)	**4.**	(3)	**5.**	(3)
6.	(2)	**7.**	(1)	**8.**	(4)	**9.**	(4)	**10.**	(1)
11.	(1)	**12.**	(1)	**13.**	(1)	**14.**	(2)	**15.**	(4)
16.	(1)	**17.**	(4)	**18.**	(2)	**19.**	(2)	**20.**	(2)
21.	(3)								

ONLINE JEE-MAIN

1.	(4)	**2.**	(4)	**3.**	(2)	**4.**	(1)	**5.**	(4)
6.	(1)	**7.**	(1)	**8.**	(2)	**9.**	(2)	**10.**	(3)
11.	(1)	**12.**	(2)	**13.**	(2)	**14.**	(4)	**15.**	(1)
16.	(4)	**17.**	(4)							

Additional Problems for Self Practice (APSP)

✎ **Marked questions are recommended for Revision.**

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Time : 1 Hr.   **Max. Marks : 120**

Important Instructions
1. The test is of **1 hour** duration.
2. The Test Booklet consists of **30** questions. The maximum marks are **120.**
3. Each question is allotted **4 (four)** marks for correct response.
4. Candidates will be awarded marks as stated above in Instructions No. 3 for correct response of each question.
   ¼ (one fourth) marks will be deducted for indicating incorrect response of each question. No deduction from the total score will be made if no response is indicated for an item in the answer sheet.
5. There is only one correct response for each question. Filling up more than one response in any question will be treated as wrong response and marks for wrong response will be deducted accordingly as per instructions 4 above.

1. 1 mole of N_2 and 2 moles of H_2 are allowed to react in a 1 dm³ vessel. At equilibrium, 0.8 mole of NH_3 is formed. The concentration of H_2 in the vessel is :
   (1) 0.6 mole   (2) 0.8 mole   (3) 0.2 mole   (4) 0.4 mole

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

   [k represents rate constant]

   (1) $\dfrac{K_A.K_B}{K_C.K_D}$ (2) $\dfrac{K_A.K_D}{K_B.K_C}$ (3) $\dfrac{K_B.K_D}{K_A.K_C}$ (4) $\dfrac{K_A.K_C}{K_B.K_D}$

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

   (1) $MX_3 \rightleftharpoons MX_2 + \dfrac{1}{2} X_2$ (2) $2MX_3 \rightleftharpoons 2MX_2 + X_2$

   (3) $2MX_2 + X_2 \rightleftharpoons 2MX_3$ (4) $MX_2 + \dfrac{1}{2} X_2 \rightleftharpoons MX_3$.

4. ✎ 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?
   (1) 64   (2) 0.30   (3) 42   (4) 8.5

5. 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 :
   (1) 32   (2) 64   (3) 16   (4) 4

6. 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 :
   (1) 1   (2) 10   (3) 5   (4) 0.33

7. 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 :
   (1) H_2, more then 1 mole   (2) CO, H_2O, H_2 less then 1 mole
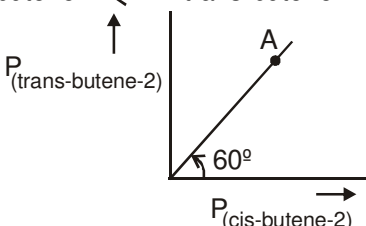   (3) CO_2 & H_2O both more than 1 mole   (4) All of these

8. 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 :
(1) 20000 R   (2) 0.02 R   (3) 5×10^{-5} R   (4) $5 \times 10^{-5} \times R^{-1}$

9. In which of the following reactions is $K_p < K_c$?
(1) $CO(g) + Cl_2(g) \rightleftharpoons COCl_2 (g)$ (2) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g)$
(3) $2BrCl(g) \rightleftharpoons Cl_2(g) + Br_2(g)$ (4) $I_2(g) \rightleftharpoons 2I(g)$

10. K for the synthesis of HI is 50. K for dissociation of HI is :
(1) 50   (2) 5   (3) 0.2   (4) 0.02

11. The equilibrium constant of the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ is 64. If the volume of the container is reduced to one fourth of its original volume, the value of the equilibrium constant will be
(1) 16   (2) 32   (3) 64   (4) 128

12. In equilibrium $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H_3O^+$
The equilibrium constant may change when
(1) CH_3COO^- is added   (2) CH_3COOH is added
(3) Catalyst is added   (4) Mixture is heated

13. 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 be respectively :
(1) 0.75 mol/litre, 0.55 mole/litre   (2) 0.50 mole/litre, 0.75 mole/litre
(3) 0.25 mole/litre, 0.50 mole/ litre   (4) 0.25 mole/litre, 1.0 mole/litre

14. In the following reaction started only with A_8, $2A_8(g) \rightleftharpoons 2A_3(g) + 3A_2(g) + A_4(g)$ 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 :
(1) 0.28   (2) 0.72   (3) 0.18   (4) None of these

15. 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 :
(1) $\dfrac{1}{(18)^2}$ (2) $\dfrac{1}{(8)^2}$ (3) $\dfrac{1}{16}$ (4) $\dfrac{1}{32}$

16. For the given reaction at constant pressure,
$$n A (g) \rightleftharpoons A_n (g)$$
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
(1) $\left[\dfrac{n-1}{n}\right]\left[\dfrac{d_f - d_i}{d_f}\right] = \alpha$ (2) $\dfrac{n}{n-1}\dfrac{\left[d_f - d_i\right]}{d_f} = \alpha$
(3) $\left[\dfrac{n-1}{n}\right]\left[\dfrac{d_i - d_f}{d_i}\right] = \alpha$ (4) $\dfrac{1}{(n-1)}\left[\dfrac{d_i - d_f}{d_i}\right] = \alpha$

17. 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
(1) P atm   (2) P^2 atm^2 (3) $P^2 / 4$ atm^2 (4) 2P atm

18. 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
(1) is exothermic   (2) is endothermic
(3) is difficult to predict   (4) no relation between ΔH and K

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ADVCEQ - 49

19. Calculate $\Delta G°$ for conversion of oxygen to ozone $3/2\ O_2(g) \longrightarrow O_3(g)$ at 298 K, if K_p for this conversion is 2.47×10^{-29}
(1) 163 kJ mol^{-1} (2) 2.4×10^2 kJ mol^{-1} (3) 1.63 kJ mol^{-1} (4) 2.38×10^6 kJ mol^{-1}

20. For the reaction, $4\ NH_3(g) + 5\ O_2(g) \rightleftharpoons 4\ NO(g) + 6\ H_2O(\ell)$, ΔH = positive .
At equilibrium which factor will not effect the concentration of NH_3 is :
(1) change in pressure   (2) change in volume   (3) catalyst   (4) None of these

21. The effect of adding krypton (Kr) gas on position of equilibrium, keeping the volume of the system constant is
(1) If $\Delta n = 0$, backward reaction is favoured.   (2) If, $\Delta n = +ve$, forward reaction is favoured
(3) If $\Delta n = -ve$, forward reaction is favoured   (4) No effect whatever be the value of Δn

22. Le-Chatelier's principle is applicable only to a
(1) System in equilibrium   (2) Irreversible reaction
(3) Homogeneous reaction   (4) Heterogeneous reaction

23. '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:
(1) 2.5   (2) 1.0   (3) 0.5   (4) None

24. The value of $\Delta G°$ for the phosphorylation of glucose in glycolysis is 15 kJ/mole. Find the value of K_c at 300 K.

(1) e^6 (2) $10^{-\frac{6}{2.303}}$ (3) $\dfrac{1}{e^{-6}}$ (4) $10^{\frac{2.303}{6}}$

25. Which of the following statements is correct for a reversible process in a state of equilibrium ?
(1) $\Delta G = 2.30\ RT \log K$ (2) $\Delta G° = -2.30\ RT \log K$
(3) $\Delta G° = 2.30\ RT \log K$ (4) $\Delta G = -2.30\ RT \log K$

26. For the following isomerisation reaction
cis-butene-2 $\rightleftharpoons$ trans-butene-2 $K_P = 1.732$

Which of the following statement is true at point 'A' ?
(1) $Q > K_P$ (2) $Q < K_P$ (3) $Q = K = 1$ (4) $Q = K = 1.732$

27. The following equilibrium exists in a saturated solution of NH_4Cl.
$NH_4Cl_{(S)} \rightleftharpoons NH_4^+{}_{(aq)} + Cl^-{}_{(aq)}$; $\Delta H_{25°C} = 3.5$ kcal mol^{-1}
A change that will shift the equilibrium to the right is
(1) decrease in temperature
(2) increase in temperature
(3) addition of NH_4Cl crystals to the reaction mixture
(4) addition of NH_4OH solution to the reaction mixture.

28. For the reaction : $PCl_5 (g) \rightleftharpoons PCl_3 (g) + Cl_2 (g)$
The backward reaction at constant temperature is favoured by
(1) introducing chlorine gas at constant volume
(2) introducing an inert gas at constant pressure
(3) increasing the volume of the container
(4) introducing PCl_5 at constant volume

29. Find out $\ln K_{eq}$ for the formation of NO_2 from NO and O_2 at 298 K

$$NO_{(g)} + \frac{1}{2}O_2 \rightleftharpoons NO_2 \, g$$
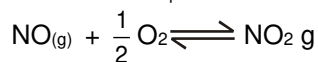
Given : ΔG_f° (NO_2) = 52.0 KJ/mole

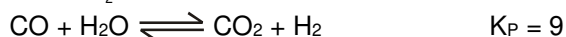ΔG_f° (NO) = 87.0 KJ/mole

ΔG_f° (O_2) = 0 KJ/mole

(1) $\dfrac{35 \times 10^3}{8.314 \times 298}$ (2) $-\dfrac{35 \times 10^3}{8.314 \times 298}$ (3) $\dfrac{35 \times 10^3}{2.303 \times 8.314 \times 298}$ (4) $\dfrac{35 \times 10^3}{2 \times 298}$

30. If a reaction vessel at 400ºC is charged with equimolar mixture of CO and steam such that $P_{CO} = P_{H_2O}$ = 4 bar what will be that partial pressure of H_2 at equilibrium

$$CO + H_2O \rightleftharpoons CO_2 + H_2 \qquad K_P = 9$$

(1) 0.3 bar (2) 0.4 bar (3) 0.2 bar (4) 0.1 bar

Practice Test-1 (IIT-JEE (Main Pattern))
OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25	26	27	28	29	30
Ans.										

PART - II : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE-I

1. If the equilibrium constant for the reaction 0.125. **[NSEC-2000]**

$$P_{4(g)} + 6Cl_{2(g)} \rightleftharpoons 4 PCl_{3(g)}$$

The value of equilibrium for this reaction $4PCl_{3(g)} \rightleftharpoons P_{4(g)} + 6Cl_{2(g)}$.

(A) 0.25 (B) 8 (C) 0.125 (D) 6

2. The free energy change for a reversible reaction at equilibrium is : **[NSEC-2000]**

(A) very large positive (B) positive (C) zero (D) negative

3. Pure ammonia is placed in a vessel at a temperature where its dissociation constant is appreciable. At equilibrium : **[NSEC-2001]**

(A) concentration of ammonia does not change with pressure.

(B) its degree of dissociation, a does not change with pressure.

(C) K_p does not change significantly with pressure.

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

4. One mole of ethyl alcohol was treated with one mole of acetic acid at 25ºC. Two-third of the acid changes into ester at equilibrium. The equilibrium constant for the reaction will be : **[NSEC-2001]**

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

5. The relationship between equilibrium constants K_p and K_c for a gaseous reaction is : **[NSEC-2001]**

(A) $K_p = K_c . R(T)^{\Delta n}$ (B) $K_c = K_p . (RT)^{\Delta n}$ (C) $K_p = K_c . (RT)^{\Delta n}$ (D) $K_p = K_c / RT^{\Delta n}$

6. For the gaseous reaction, $C_2H_4 + H_2 \rightleftharpoons C_6H_6$, the equilibrium constant has the units : **[NSEC-2001]**

(A) $mol^2 dm^{-3}$ (B) $dm^3 mol^{-1}$ (C) $dm^3 mol^{-2}$ (D) $mol.dm^{-3}$

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7. The equilibrium constant for the reaction $H_2 + Br_2 \rightleftharpoons 2HBr$ is 67.8 at 300ºK. The equilibrium constant for the dissociation of HBr is : **[NSEC-2001]**
(A) 0.0147   (B) 67.80   (C) 33.90   (D) 8.349

8. The equilibrium constant (K) for the reaction, $A + 2B \rightleftharpoons 2C + D$ is : **[NSEC-2001]**
(A) $\dfrac{[C]^2[D]}{[A][2B]}$ (B) $\dfrac{[2C][D]}{[A][2B]}$ (C) $\dfrac{[C][D]}{[A][B]}$ (D) $\dfrac{[C]^2[D]}{[A][B]^2}$

9. The following pictures represents the equilibrium state for three different reactions of the type **[NSEC-2002]**

$$A_2 + X_2 \rightleftharpoons 2AX \ (X = B, C \text{ or } D)$$

[$A_2 + B_2 \rightleftharpoons 2AB$]   [$A_2 + C_2 \rightleftharpoons 2AC$]   [$A_2 + D_2 \rightleftharpoons 2AD$]
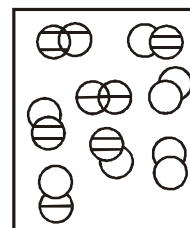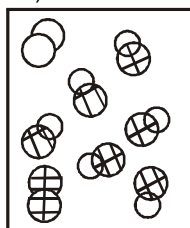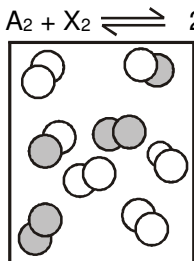
Which reaction has the largest equilibrium constant ?
(A) $A_2 + B_2 \rightleftharpoons 2AB$ (B) $A_2 + C_2 \rightleftharpoons 2AC$
(C) $A_2 + D_2 \rightleftharpoons 2AD$ (D) none of these

10. Methanol (CH_3OH) is manufactrued by reaction of carbon monoxide with hydrogen in the presence of ZnO/Cr_2O_3 catalyst. **[NSEC-2002]**
$$CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH_{(g)} \ ; [\Delta H^o = -91 \text{ kJ}]$$
What happen to the amount of methanol when an equilibrium mixtrue of reactants and products is subjected to rise in temperature ?
(A) Amount of methanol will increase
(B) Amount of methanol will decrease
(C) Amount of methanol remain the same
(D) None of these

11. For the reversible reaction, $A + B \rightleftharpoons C$, the specific reaction rates for forward and reverse reactions are 1.25×10^{-3} and 2.75×10^{-5} respectively. The equilibrium constant for the reaction is : **[NSEC-2002]**
(A) 45.45   (B) 0.022   (C) 2.20   (D) 0.4545

12. The equilibrium constant for the gaseous reaction $H_2 + Cl_2 \rightleftharpoons 2HCl$ is given by **[NSEC-2002]**
(A) $K = \dfrac{[H_2][Cl_2]}{[HCl]^2}$ (B) $K = \dfrac{[H_2][Cl_2]}{2[HCl]}$ (C) $K = \dfrac{[HCl]^2}{[H_2][Cl_2]}$ (D) $K = \dfrac{2[HCl]}{[H_2][Cl_2]}$

13. For the reaction, $N_2 + 3H_2 \rightleftharpoons 2NH_3$, the units of K_c and K_p respectively are : **[NSEC-2003]**
(A) $mol^{-2} L^2$ and bar^{-2} (B) $mol^{-2} L^2$ and bar^{-1} (C) $mol^{-1} L$ and bar^{-2} (D) $mol^{-1} L^{-1}$ and bar^{-1}

14. The equilibrium constant for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is 70 at a certain temperature. Hence, equilibrium constant for the reaction $NH_3 \rightleftharpoons \dfrac{1}{2}N_2 + \dfrac{3}{2}H_2$ of the same temperature will be approximately **[NSEC-2004]**
(A) 1.4×10^{-2} (B) 1.2×10^{-1} (C) 2.0×10^{-4} (D) 2.9×10^{-2}.

15. For the reaction $4NH_{3 (g)} + 7O_{2(g)} \rightleftharpoons 4NO_{2(g)} + 6H_2O_{(g)}$, K_p is related to K_c by **[NSEC-2005]**
(A) $K_p = K_c (RT)$ (B) $K_p = K_c$ (C) $K_p = K_c (RT)^3$ (D) $K_p = K_c (RT)^{-1}$.

16. When $K_c > 1$ for a chemical reaction, **[NSEC-2005]**
(A) the equilibrium would be achieved rapidly
(B) the equilibrium would be achieved slowly
(C) product concentrations would be much greater than reactant concentrations at equilibrium
(D) reactant concentrations would be much greater then product concentrations at equilibrium.

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17. Increased pressure shifts the equilibrium of the reaction : $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ so as to

[NSEC-2006]

(A) form more ammonia gas
(B) produce more $N_2(g)$ and $H_2(g)$
(C) keep the conversion to ammonia unaltered
(D) produce more $H_2(g)$.

18. In which of the following reactions will an increase in volume of the reaction system favor the formation of the products ? **[NSEC-2007]**

(A) $C_{(s)} + H_2O_{(g)} \rightleftharpoons CO_{(g)} + H_{2(g)}$ (B) $H_{2(g)} + I_{2(g)} \rightleftharpoons H_{2(g)}$
(C) $4NH_{3(g)} + 5O_{2(g)} \rightleftharpoons 4NO_{(g)} + 6H_2O$ (D) $3O_{2(g)} \rightleftharpoons 2O_{3(g)}$

19. Which of the following changes the value of the equilibrium constant? **[NSEC-2007]**
(A) change in concentration   (B) change in pressure
(C) change in volume   (D) none of these

20. Consider the equilibrium reaction: **[NSEC-2007]**
$4NH_{3(g)} + 3O_{2(g)} \rightleftharpoons 2N_{2(g)} + 6H_2O_{(g)}$ ($\Delta H = -1268$ KJ)
Which change will cause the reaction to shift to the right?
(A) Increase the temperature
(B) Decrease the volume of the container.
(C) Add a catalyst to speed up the reaction.
(D) Remove the gaseous water by allowing it to react and be absorbed by KOH.

21. At a given temperature the equilibrium constants of the gaseous reactions

$NO_{(g)} + 1/2\, O_{2(g)} \xrightleftharpoons{K_1} NO_{2(g)}$

$2NO_{2(g)} \xrightleftharpoons{K_1} 2NO_{(g)} + O_{2(g)}$ are related as : **[NSEC-2008]**

(A) $K_1 = 2K_2$ (B) $K_1 = 1/K_2$ (C) $K_1 = \sqrt{1}\, K_2$ (D) $K_1 = \sqrt{K_2}$

22. For the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ **[NSEC-2009]**
(A) $K_p = K_c$ (B) $K_p > K_c$ (C) $K_p < K_c$ (D) $K_c = \sqrt{K_p}$

23. If the equilibrium constants of the reactions, **[NSEC-2009]**

$2SO_3 \rightleftharpoons 2SO_2 + O_2$ and $SO_2 + \dfrac{1}{2} O_2 \rightleftharpoons SO_3$

are K_1 and K_2 respectively, the correct relation between the two equilibrium constant is,

(A) $K_2 = (K_1)^{-1}$ (B) $K_2 = \sqrt{\dfrac{1}{K_1}}$ (C) $K_2 = \left(\dfrac{1}{K_1}\right)^2$ (D) $\sqrt{K_1}$

24. The equilibrium constant K_c for the reaction, **[NSEC-2009]**
$2NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(l)$

(A) $K_c = \dfrac{[Na_2CO_3][CO_2][H_2O]}{[NaHCO_3]^2}$ (B) $K_c = \dfrac{[Na_2CO_3]}{[NaHCO_3]^2}$
(C) $K_c = [CO_2][H_2O]$ (D) $K_c = p_{CO2} \times p_{H2O}$

25. For the following reaction, the value of K changes with **[NSEC-2010]**
$N_2(g) + O_2(g) \rightleftharpoons 2\,NO(g)$ $\Delta H = +180$ kJ mol^{-1}
(A) change in pressure   (B) change in concentration of oxygen
(C) introduction of NO(g)   (D) change in temperature

26.* The formation of ammonia from nitrogen and hydrogen gases can he written by the following two equations

(a) $\dfrac{1}{2} N_2(g) + \dfrac{3}{2} H_2(g) \rightleftharpoons NH_3(g)$ (b) $\dfrac{1}{3} N_2(g) + H_2(g) \rightleftharpoons \dfrac{2}{3} NH_3(g)$

The two equations have equilibrium constants K_1 and K_2, respectively. The relationship between the equilibrium constants is **[NSEC-2010]**
(A) $K_1 = K_2^2$ (B) $K_1^3 = K_2^2$ (C) $K_1^{2/3} = K_2$ (D) $K_1 = K_2^{3/2}$

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27. For the reaction $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, K_c is 26 at 250°C. K_p at the same temperature is
($R = 8.314 \ JK^{-1}mol^{-1}$) **[NSEC-2011]**
(A) 4.6×10^{-3} (B) 5.7×10^{-3} (C) 6.0×10^{-3} (D) 8.3×10^{-3}

28. At 445ºC, K_c for the following reaction is 0.020.
$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$
A mixture of H_2, I_2 and HI in a vessel at 445º C has the following concentrations : **[NSEC-2011]**
[HI] = 2.0M, [H_2] = 0.50M and [I_2] = 0.10M. The statement that is true concerning the reaction quotient, Q_c is:
(A) $Q_c = K_c$; the system is at equilibrium
(B) Q_c is less than K_c; more H_2 and I_2 will be produced
(C) Q_c is less than K_c; more HI will be produced
(D) Q_c is greater than K_c; more H_2 and I_2 will be produced

29. The oxidation of SO_2 by O_2 is an exothermic reaction. The yield of SO_3 can be maximized if :
(A) temperature is increased and pressure is kept constant **[NSEC-2012]**
(B) temperature is decreased and pressure is increased
(C) both temperature and pressure are increased
(D) both temperature and pressure are decreased

30. The K_P/K_C ratio for the reaction $4NH_3(g) + 7O_2(g) \rightleftharpoons 4\ NO(g) + 6\ H_2O(g)$, at 127ºC is: **[NSEC-2013]**
$4NH_3(g) + 7O_2(g) \rightleftharpoons 4\ NO(g) + 6\ H_2O(g)$
(A) 0.0301   (B) 0.0831   (C) 1.0001   (D) 33.26

31. K_P for the reaction given below is 1.36 at 499 K. Which of the following equaitons can be used to calculate K_c for this reaction ? **[NSEC-2013]**
$N_2O_5(g) \longrightarrow N_2O_3(g) + O_2(g)$
(A) $K_c = \dfrac{[(0.0821) \times (499)]}{[1.36]}$ (B) $K_c = \dfrac{[(1.36) \times (0.0821)]}{[499]}$
(C) $K_c = \dfrac{[1.36]}{[(0.0821) \times (499)]}$ (D) $K_c = \dfrac{[(1.36) \times (499)]}{[0.0821]}$

32. At 700 K, for the reaction $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ the K_p is 3.2×10^4. At the same temperature the K_P for the reaction $SO_3(g) \rightleftharpoons SO_2(g) + 0.50O_2(g)$ is : **[NSEC-2014]**
(A) 3.125×10^{-5} (B) 5.59×10^{-3} (C) 1.79×10^4 (D) 1.79×10^{-2}

33. For the following reaction, formation of the product is favored by **[NSEC-2015]**
$A_2(g) + 4B_2(g) \rightleftharpoons 2AB_4(g)$, $\Delta H < 0$
(A) Low temperature and high pressure
(B) High temperature and low pressure
(C) Low temperature and low pressure
(D) High temperature and high pressure

34. The equilibrium constant of the following isomerisation reaction at 400K and 298 K are 2.07 and 3.42 respectively.
$$\text{cis-butene} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{trans-butene}$$
Which of the following is/are correct ? **[NSEC-2017]**
I. The reaction is exothermic
II. The reaction is endothermic
III. At 400K 50% of cis-butene and 50% of trans-butene are present of equilibrium
IV. Both at 298K and 400K, $k_1 = k_{-1}$
(A) I and IV   (B) II and IV   (C) I and III   (D) I only

35. Acetic acid (CH_3COOH) is partially dimerised to ($CH_3COOH)_2$ in the vapour phase. At a total pressure of 0.200 atm, acetic acid is 92.0% dimerized at 298 K.
The value of equilibrium constant of dimerisation under these conditions is **[NSEC-2017]**
(A) 57.5   (B) 9.7   (C) 97   (D) 194

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PART - III : HIGH LEVEL PROBLEMS (HLP)

SUBJECTIVE QUESTIONS

1. In a vessel, two equilibrium are simultaneously established at the same temperature as follows:

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) \qquad ...(1)$$
$$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g) \qquad ...(2)$$
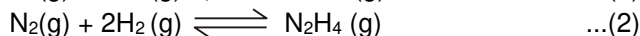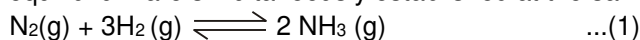
Initially the vessel contains N_2 and H_2 in the molar ratio of 9 : 13. The equilibrium pressure is $7P_0$, in which pressure due to ammonia is P_0 and due to hydrogen is $2P_0$. Find the values of equilibrium constants (K_P's) for both the reactions

ONLY ONE OPTION CORRECT TYPE

2. 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

3. 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) $X + Y \rightleftharpoons 4Z$
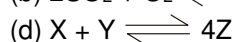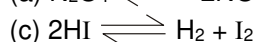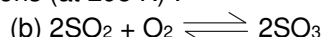
   Highest and lowest value of $\dfrac{K_p}{K_c}$ will be shown by the equilibrium

   (A) d, b   (B) a, c   (C) a, b   (D) b, c7

4. For a container containing A(g), B(g), C(g) & D(g) with rigid walls, an experiment is carried upon. This experiment involves increase in temperature of container in steps of 1ºC and system is allowed to attain equilibrium, followed by calculation of K_1 & K_2 at each step, where K_1 & K_2 are equilibrium constants for reaction (1) & (2) respectively.

   $$A(g) + 2B(g) \rightleftharpoons C(g) + D(g) \qquad ...(1)$$
   $$C(g) + D(g) \rightleftharpoons A(g) + 2B(g) \qquad ...(2)$$
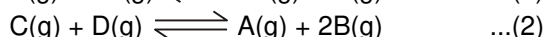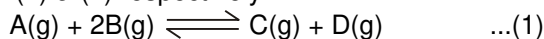
   Select the graph showing correct relationship –
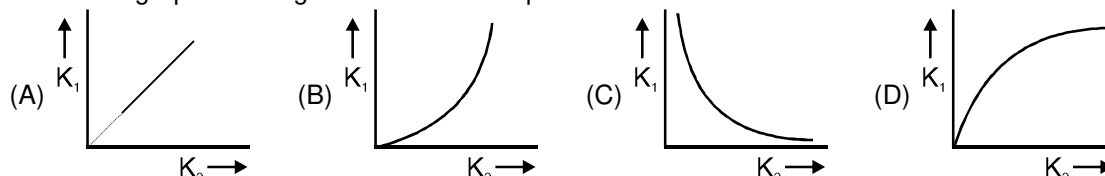
5. If $CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4.3H_2O(s) + 2H_2O(g)$ $K_P = 4 \times 10^{-4}$ atm^2

   at 25ºC. The efflorescent nature of $CuSO_4.5H_2O$ can be noticed when vapour pressure of H_2O in atmosphere is
   (A) > 15.2 mm   (B) < 15.2 mm   (C) $\leq$ 15.2 mm   (D) = 15.2 mm

6. 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.

7. The equilibrium, $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$ is attained at 25ºC in a closed container and inert gas helium is introduced isothermally. Which of the following statement(s) is/are correct ?
   I.   Concentrations of SO_2, Cl_2 and SO_2Cl_2 change
   II. More chlorine is formed
   III. Concentration of SO_2 is reduced
   IV. More SO_2Cl_2 is formed.
   (A) I, II, III   (B) II, III, IV   (C) III, IV   (D) None

8. C(s) + CO$_2$(g) $\rightleftharpoons$ 2CO(g) K_P = 1 atm

CaCO$_3$(s) $\rightleftharpoons$ CaO(s) + CO$_2$(g) K_P = 4 × 10^{-2}

Solid C, CaO and CaCO$_3$ are mixed and allowed to attain equilibrium. Calculate final pressure of CO.

(A) 0.4 atm   (B) 0.2 atm   (C) 8 atm   (D) 0.01 atm

9. 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

10. 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

11. For equilibrium ZnSO$_4$.7H$_2$O(s) $\rightleftharpoons$ ZnSO$_4$.2H$_2$O(s) + 5H$_2$O(g), K_P = 56.25 × 10^{-10} atm^5 and vapour pressure of water is 22.8 torr at 298 K. ZnSO$_4$.7H$_2$O(s) is efflorescent (lose water) when relative humidity is [$\sqrt[5]{56.25}$ = 2.23]

(A) more than 80.60%   (B) less than 74.60%

(C) Above than 74.60%   (D) Above than 70.60%

12. 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 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

13. X(s) $\rightleftharpoons$ Y(g) + 2Z(g)

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

Consider both these equilibrium to be established simultaneously in a closed container.

At equilibrium, pressure of Z and B were found to be same and sum of pressure of Z & B is 10 atm more than that of species Y. Find ratio of standard gibb's energy of two reactions.

(A) 20   (B) 2.303 log$_{10}$20   (C) log$_{10}\sqrt[3]{144}$ (D) $\dfrac{3+\log 12}{2+\log 6}$

14. In one experiment, certain amount of NH$_4$I(s) was heated rapidly in a closed container at 375ºC. The following equilibrium was established :

NH$_4$I(s) $\rightleftharpoons$ NH$_3$(g) + HI(g)

Excess of NH$_4$I(s) remained unreacted in the flask and equilibrium pressure was 304 mm of Hg. After some time, the pressure started increasing further owing to the dissociation of HI.

2HI(g) $\rightleftharpoons$ H$_2$(g) + I$_2$(g) K_C = 0.010 calculate final pressure.

(A) 328 mm Hg   (B) 331 mm Hg

(C) 662 mm Hg   (D) 151 mm Hg

15. A(s) $\rightleftharpoons$ B(g) + C(g) K_{P_1} = 36 atm^2

E(s) $\rightleftharpoons$ B(g) + D(g) K_{P_2} = 64 atm^2

Both solids A & E were taken in a container of constant volume at a given temperature. Total pressure in the container after equilibrium is

(A) 6 atm   (B) 5 atm   (C) 10 atm   (D) 20 atm

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16. In a closed container following equilibrium will be attained –

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

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

On adding He gas (inert) to the above system at constant pressure & temperature

(A) Amount of AB(g) will be increased surely.   (B) Amount of B(g) will be decreased surely.

(C) Amount of C(g) will be decreased surely.   (D) Amount of BC(g) will be decreased surely.

17. $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ in a V lit container total x mol at eq.

$N_2H_4(g) \rightleftharpoons N_2 + 2H_2(g)$ in V lit (other) container total y mol at eq.

If both are taken in same container (V lit) then at new equation total mols will be

(A) x + y   (B) > x + y   (C) < x + y   (D) No prediction is possible.

SINGLE AND DOUBLE VALUE INTEGER TYPE

18. 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.

19. If the equilibrium constant of the reaction $2HI(g) \rightleftharpoons H_2(g) + I_2(g)$ is 0.25, find the equilibrium constant of the reaction $\frac{1}{2} H_2(g) + \frac{1}{2} I_2(g) \rightleftharpoons HI(g)$.

20. $A_2(g)$ and $B_2(g)$ having partial pressures 60 mm of Hg & 42 mm of Hg respectively, are present in a closed vessel. At equilibrium, partial pressure of AB(g) is 28 mm of Hg. If all measurements are made under similar condition, then calculate percentage of dissociation of AB (g).
(Round of answers to nearest integer).

21. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ K_{P_1}

$NH_3(g) \rightleftharpoons \frac{1}{2} N_2(g) + \frac{3}{2} H_2(g)$ K_{P_2}

2 mol $NH_4HS(s)$ is taken & 50% of this is dissociated till at equilibrium in 1 litre container. Find $\dfrac{K_{P_2}^2}{K_{P_1}^6}$ if 0.25 moles of N_2 are found finally.

22. Consider :   (I) $C(s) + O_2 \rightleftharpoons CO_2(g)$ $K_{p_1} = \dfrac{7}{8}$

                 (II) $2 C(s) + O_2 \rightleftharpoons 2 CO(g)$ $K_{p_2} = 12.5$ atm

As 100 L of air (80 % N_2, 20% O_2 by volume) is pased over excess heated coke to establish these equilibrium the equilibrium mixture is found to measure 105 L at constant temperature & pressure (105 atm). Assuming no other reaction, find the sum of partial pressure of CO and CO_2 in the final equilibrium mixture.

23. Two solid compounds A and C dissociate into gaseous product at temperature T as follows :

(i) $A(s) \rightleftharpoons B(g) + D(g)$ $Kp_1 = 625$ $(atm)^2$

(ii) $C(s) \rightleftharpoons E(g) + D(g)$ $Kp_2 = 975$ $(atm)^2$

Both solid are present in same container then calculate total pressure over the solid mixture.

24. ✎ If a mixture 0.4 mole H_2 and 0.2 mole Br_2 is heated at 700 K at equilibrium, the value of equilibrium constant is 0.25×10^{10} then find out the ratio of concentrations of (Br_2) and (HBr) (Report your answer as $\dfrac{Br_2}{HBr} \times 10^{11}$)

25. 2 mole of PCl_5 were heated in a 5 liter vessel. It dissociated. 80% at equilibrium find out the value of equilibrium constant. Report your answer as $K_C \times 50$.

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26. Two solids A and D dissociates into gaseous products as follows

$A(s) \rightleftharpoons B(g) + C(g)$; $K_{P_1} = 300$; $D(s) \rightleftharpoons E(g) + C(g)$ $K_{P_2} = 600$
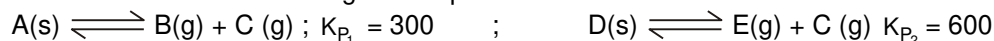
at 27ºC , then find the total pressure of the solid mixture.

ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

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

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

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

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

28. A 2 lit vessel is filled by 1 mole of each gas A & B. If K_C for reaction $A(g) \rightleftharpoons B(g)$ is 1.5 at temp. T. [Atomic mass of A is 40 & B is 20]. Which are correct option.

(A) [A] vs time is graph I   (B) [B] vs time is graph I
(C) [A] vs time is graph II   (D) [B] vs time is graph II
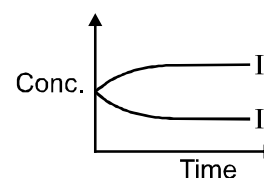
29. The equilibrium constant for some reactions are given below against each of the reaction

(i) $2N_2 + 5O_2 \rightleftharpoons 2N_2O_5$; $K = 5 \times 10^{-27}$
(ii) $N_2 + O_2 \rightleftharpoons 2NO$; $K = 2 \times 10^{-15}$
(iii) $N_2 + 2O_2 \rightleftharpoons 2NO_2$; $K = 1.5 \times 10^{-29}$

Which of the following statement is correct

(A) The least stable oxide is NO_2
(B) The most stable oxide is NO
(C) The stability order is $N_2O_5 > NO_2 > NO$
(D) The stability order is $NO_2 > NO > N_2O_5$

30. Sufficient amount of a solid X is taken in a rigid vessel at T°C where it attained the equilibrium :

$X(s) \rightleftharpoons Y(g) + 2Z(g)$
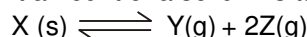
Total pressure was measured. Now the vessel is evacuated and filled with sufficient amount of another solid V under same conditions where it attained the equilibrium :

$V(s) \rightleftharpoons W(g) + 2Z(g)$
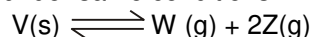
Total pressure measured now is found to be double that of previous value. Now, if both X & V solids are allowed to attain their respective equilibrium together in the same vessel at same temperature, select the correct statement(s) :

(A) K_P for decompostion reaction of V (s) = 8 × K_P for decomposition reaction of X (s).

(B) In the 3rd case (when both solids are simultaneously estabilishing their equilibrium), $P_Y = \dfrac{1}{8} P_W$.

(C) P_Y in 3rd case $= \dfrac{1}{3\sqrt{3}} \times P_Y$ in 1st case.

(D) In the 3rd case, $P_W : P_Z = 4:9$

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

$CO_2(g) \rightleftharpoons CO(g) + \dfrac{1}{2} O_2(g)$
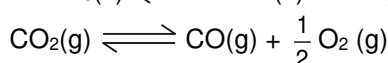
For above simultaneous equilibrium if CO_2 is added from out side at equilibrium then :

(A) P_{CO_2} will increase   (B) P_{CO_2} will decrease
(C) No shift in 2nd equilibrium   (D) Backward shift in 1st equilibrium

32. For the reaction $SnO_2(s) + 2H_2(g) \rightleftharpoons 2H_2O(g) + Sn(s)$. If at 900 K, equilibrium mixture contains 45% H_2 by volume and at 1100 K it contains 24% H_2 by volume then which of the statements is/are correct.
(A) Reaction is endothermic in nature
(B) At higher temperature, the efficiency of reduction of tin oxide will increase
(C) Reaction is exothermic in nature
(D) At lower temperature, the efficiency of reduction of tin oxide decreases.

33. Consider equilibrium $H_2O(\ell) \rightleftharpoons H_2O(g)$. Choose the correct direction of shifting of equilibrium with relative humidity.
(A) R.H. > 1, rightward   (B) R.H. < 1, rightward
(C) R.H. > 1, leftward   (D) R.H. < 1, leftward

34. 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

PART - IV : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr.   **Max. Marks : 60**
Important Instructions :
A.   General :
1.   The test is of 1 hour duration.
2.   The Test Booklet consists of 20 questions. The maximum marks are 60.
B.   Question Paper Format
3.   Each part consists of five sections.
4.   Section-1 contains 7 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
5.   Section-2 contains 4 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
6.   Section-3 contains 6 questions. The answer to each of the questions is a single-digit integer, ranging from 0 to 9 (both inclusive).
7.   Section-4 contains 1 paragraphs each describing theory, experiment and data etc. 2 questions relate to paragraph. Each question pertaining to a partcular passage should have only one correct answer among the four given choices (A), (B), (C) and (D).
8.   Section 5 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

C.   Marking Scheme
9.   For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (– 1) mark will be awarded.
10.   For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
11.   For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.
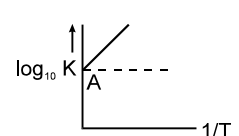
SECTION-1 : (Only One option correct Type)
This section contains 7 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.
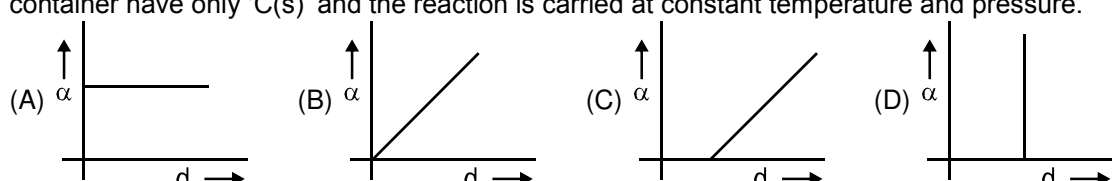
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1. Which of the following is correct for the equilibrium of the reaction

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

    (A) $p_{H_2} \propto p_{H_2O}$ (B) $p_{H_2} \propto \sqrt{p_{H_2O}}$ (C) $p_{H_2} \propto p_{H_2O}^2$ (D) $p_{H_2} \propto \dfrac{p_{H_2O}^2}{p_{CO}}$

2. For the reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2$; 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) $\dfrac{1}{4}$ times (C) 2 times (D) $\dfrac{1}{4}$ times

3. A vessel of 10 L was filled with 6 mole of Sb_2S_3 and 6 mole of H_2 to attain the equilibrium at 440°C as :

    $Sb_2S_3(s) + 3H_2(g) \rightleftharpoons 2Sb(s) + 3H_2S(g)$

    After equilibrium the H_2S formed was analysed by dissolving it in water and treating with excess of Pb^{2+} to give 708 g of PbS as precipitate. What is value of K_c of the reaction at 440°C ? (At. weight of Pb = 206).

    (A) 0.08 (B) 0.8 (C) 0.4 (D) 0.04

4. Variation of $\log_{10} K$ with $\dfrac{1}{T}$ 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

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

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

6. The value of k_p for the reaction at 27°C

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

    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 $Br_2(\ell)$ is also 0.1 atm. Then what will be minimum moles of $Br_2(\ell)$ to be added to 1 mole of Cl_2, initially, to get above equilibrium situation :

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

7. $C(s) \rightleftharpoons 2A(g) + B(s)$

    If the dissociation of C(s) is 'α' and d is the density of the gaseous mixture in the container. Initially container have only 'C(s)' and the reaction is carried at constant temperature and pressure.

Section-2 : (One or More than one options correct Type)
This section contains 4 multipole choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

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8. For which reaction at 298 K, the value of $\dfrac{K_p}{K_c}$ 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) $A + 3B \rightleftharpoons 7C$

9. For the equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$, $\Delta H = -198$ kJ, the equilibrium concentration of SO_3 will be affected by
(A) doubling the volume of the reaction vessel
(B) increasing the temperature at constant volume
(C) adding more oxygen to the reaction vessel
(D) adding helium to the reaction vessel at constant volume

10. ✎ $AB(s) \rightleftharpoons A(g) + B(g)$ $K_p = 4$, $\Delta H = +ve$
In a container, A (g) and B (g) are filled to partial pressure of 1 atm each. Now AB (s) is added (in excess quantity). Which of the following is **CORRECT** ? (No other gas is present in container) :
(A) At equilibrium, the total pressure in the container is 4 atm.
(B) Equilibrium pressure decreases uniformly on increasing the volume by container.
(C) At equilibrium, the total pressure in the container is more than 4 atm, if temperature is increased.
(D) None of these

11. ✎ Following two equilibria are established seperately in 2 different containers of unequal volume.
$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$
$COCl_2(g) \rightleftharpoons CO(g) + Cl_2(g)$
Now the containers are connected together by a thin tube of negligible volume.
Select incorrect statements. (Assume T constant)
(A) Degree of dissociation of both $PCl_5(g)$ & $COCl_2(g)$ will decrease
(B) Degree of dissociation of both $PCl_5(g)$ & $COCl_2(g)$ will increase
(C) Degree of dissociation of $PCl_5(g)$ may increase ; decrease or remain the same irrespective of effect on degree of dissociation of $COCl_2(g)$.
(D) Degree of dissociation of $PCl_5(g)$ may increase, decrease or remain the same, but the effect would be same as that on degree of dissociation of $COCl_2$.

Section-3 : (One Integer Value Correct Type.)
This section contains 6 questions. Each question, when worked out will result in one integer from 0 to 9 (both inclusive)

---

12. If 1 mole of CH_3COOH and 1 mole of C_2H_5OH are taken in 1 litre flask, 50% of CH_3COOH is converted into ester as ;
$CH_3COOH_{(\ell)} + C_2H_5OH_{(\ell)} \rightleftharpoons CH_3COOC_2H_{5(\ell)} + H_2O_{(\ell)}$
There is 33% conversion of CH_3COOH into ester, if CH_3COOH and C_2H_5OH have been taken initially in molar ratio x : 1, find x.

13. Solid ammonium carbamate (NH_2COONH_4) was taken in excess in closed container of volume 5 Litre according to the following reaction $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$. If equilibrium partial pressure of ammonia is 4 atm, it's equilibrium constant K_p is x atm^3. If the above equilibrium mixture is transferred to another vessel of volume 10 Litre, total equilibrium pressure is y atm. Calculate the value of (x + y). Assuming temperature is constant during the whole experiment.

14. Find the percentage dissociation of ammonia into N_2 and H_2 if the dissociation is carried out at constant pressure and the volume at equilibrium is 20% greater than initial volume. (Initially, equal moles of NH_3 and N_2 are present with no hydrogen)

15. ✎ $A_2B(g)$ is introduced in a vessel at 1000 K. If partial pressure of $A_2B(g)$ is 1 atm initially and K_P for reaction $A_2B(g) \rightleftharpoons 2A(g) + B(g)$ is 81×10^{-6} then calculate percentage of dissociation of A_2B.

16. Consider the following two equilibrium established together in a closed container
$A(s) \rightleftharpoons 2B(g) + 3C(g)$; K_{P_1}
$A(s) \rightleftharpoons 3D(g)$; K_{P_2}
Starting with only A(s), molar ratio of B(g) & D(g) at equilibrium is found to be in a ratio 1 : 6 determine $\dfrac{K_{P_2}}{8K_{P_1}}$.

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17. 0.1 mol each of ethyl alcohol and acetic acid are allowed to react and at equilibrium the acid was exactly neutralised by 100 ml of 0.75 N NaOH. If no hydrolysis of ester is supposed to have undergo find K_C in terms $(x)^{\frac{-1}{10}}$.

SECTION-4 : Comprehension Type (Only One options correct)
This section contains 1 paragraphs, each describing theory, experiments, data etc. 2 questions relate to the paragraph. Each question has only one correct answer among the four given options (A), (B), (C) and (D)

Paragraph for Question Nos. 18 to 19

There are different types of equilibria depending on the composition of equilibrium mixture. Homogenous equilibrium contains all the species in same phase and heterogeneous equilibrium contains different phases. If heterogeneous equilibrium involves pure solid or liquid, then their concentration or pressure term is not included in K_C or K_P respectively.

18. 05 moles of $NH_4HS(s)$ are ta1ken in a container having air at 1 atm. On warming the closed container to 50ºC the pressure attained a constant value of 1.5 atm, with some NH_4HS (s) remaining unreacted. The K_P of reaction $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$ at 50°C is :

(A) 0.25   (B) 0.625   (C) 0.025   (D) 0.0625

19. How many moles of water are in vapour phase present inside the vessel containing 1 L water after sufficient time? (Vapour pressure of water at 27ºC = 3000 Pa, R = $\frac{25}{3}$ J/mol–K)

(A) 5×10^{-4} (B) 120   (C) 1.2×10^{-3} (D) None of these

SECTION-5 : Matching List Type (Only One options correct)
This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

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20. In given setup, container I has double the volume to that of container II. Container I & II are connected by a narrow tube with two knobs.
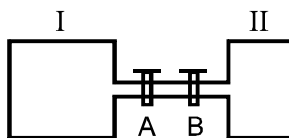
Knob A :   Closed – No gas is allowed to pass through
                 Open – All gases can pass
Knob B :   Closed – A thin filter of Pd is introduced on complete cross section of tube
                 Open – All gases can pass.
Initially both knobs are closed. In container I, some amount of NH_3 gas is introduced which sets up equilibrium according to following reaction :

       $2NH_3(g) \rightleftharpoons N_2(g) + H_2(g)$
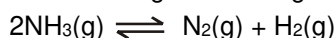
Match the actions in column I to corresponding value in column II and select the correct answer using the code given below the column. Assume each action from initial stage.

	Column I		Column II
P.	A & B are closed, $p_{H_2} / p_{N_2} = ?$	1.	1/3
Q.	A is open & B is closed, $n^I_{H_2} / n^I_{N_2} = ?$	2.	3
R.	A is open & B is open, $n^I_{N_2} / n^{II}_{H_2} = ?$	3.	2
S.	A & B are left open for long time; now B is closed & volume of container II is halved. $(n^I_{N_2} + n^{II}_{N_2})/(n^I_{H_2} + n^{II}_{H_2}) = ?$	4.	2/3

Code :

	P	Q	R	S		P	Q	R	S
(A)	4	2	3	1	(B)	2	3	4	1
(C)	2	1	3	4	(D)	1	2	3	4

Practice Test-2 (IIT-JEE (ADVANCED Pattern))
OBJECTIVE RESPONSE SHEET (ORS)

Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										

APSP Answers

PART - I

1.	(2)	2.	(4)	3.	(3)	4.	(2)	5.	(3)
6.	(1)	7.	(2)	8.	(4)	9.	(1)	10.	(4)
11.	(3)	12.	(4)	13.	(1)	14.	(1)	15.	(1)
16.	(2)	17.	(3)	18.	(1)	19.	(1)	20.	(3)
21.	(4)	22.	(1)	23.	(3)	24.	(2)	25.	(2)
26.	(4)	27.	(2)	28.	(1)	29.	(1)	30.	(1)

PART - II

1.	(B)	2.	(C)	3.	(C)	4.	(D)	5.	(C)
6.	(B)	7.	(A)	8.	(D)	9.	(B)	10.	(B)
11.	(A)	12.	(C)	13.	(A)	14.	(B)	15.	(D)
16.	(C)	17.	(A)	18.	(A)	19.	(D)	20.	(D)
21.	(D)	22.	(A)	23.	(B)	24.	(A)	25.	(D)
26.	(BC)	27.	(C)	28.	(B)	29.	(B)	30.	(A)
31.	(C)	32.	(B)	33.	(A)	34.	(D)	35.	(D)

PART - III

1.	$K_{P_1} = \dfrac{1}{20P_0^2}$, $K_{P_2} = \dfrac{3}{20}\dfrac{}{P_0^2}$	2.	(D)	3.	(A)	4.	(C)
5.	(B)	6.	(A)	7.	(D)	8.	(B)	9.	(B)
10.	(B)	11.	(B)	12.	(A)	13.	(D)	14.	(A)
15.	(D)	16.	(D)	17.	(C)	18.	4	19.	2
20.	72 %	21.	27	22.	15	23.	80 atm	24.	80
25.	64	26.	80 atm.	27.	(ABC)	28.	(BC)	29.	(AB)
30.	(ABCD)	31.	(CD)	32.	(AB)	33.	(BC)	34.	(AC)

PART - IV

1.	(B)	2.	(A)	3.	(A)	4.	(B)	5.	(D)
6.	(C)	7.	(D)	8.	(BD)	9.	(ABC)	10.	(ACD)
11.	(ABD)	12.	2	13.	38	14.	40	15.	3
16.	8	17.	1	18.	(D)	19.	(A)	20.	(B)

APSP Solutions

PART – I

1. N_2 + $3H_2$ $\rightleftharpoons$ $2\,NH_3$
t = 0   1 mole   2 mole   0
t = eq   1–x   2–3x   2x = 0.8
         x = 0.4
         mole of N_2 = 0.6
         mole of H_2 = 0.8
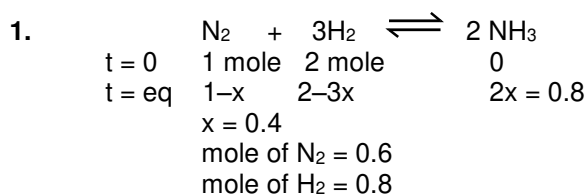
2. $\dfrac{K_A}{K_B} = \dfrac{[PQ]}{[P]\,[Q]}$ ..... (i)

$\dfrac{K_C}{K_D} = \dfrac{[R]}{[PQ]}$ ..... (ii)

On multiply equation (i) and (ii) we get

$\dfrac{K_A.K_C}{K_B.K_D} = \dfrac{[R]}{[P][Q]}$

4. $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

$K_C = \dfrac{[SO_3]^2}{[SO_2]^2[O_2]}$ Concentration in gram mole/litre, therefore

$[SO_3] = \dfrac{48}{80\times1}$ (Where 80 is molecular weight of SO_3)

$[SO_2] = \dfrac{128}{64\times1}$ (Where 64 is molecular weight of SO_2)

$[O_2] = \dfrac{9.6}{32\times1}$ (Where 32 is molecular weight of O_2)

Thus, $K_C = $ = 0.30
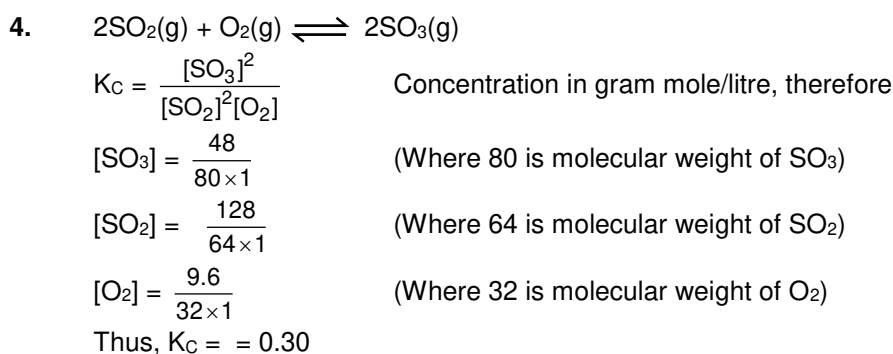
5. Since, K_p is temperature dependent only.

6. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
t = 0   4.5   4.5   0
t = teq. 4.5 – x 4.5 – x   2x
put   x = 1.5
         4.5 – 1.5   4.5 – 1.5   2 × 1.5 = 3
            ↓   ↓   ↓
            3   3   3

$K_C = \dfrac{(3)^2}{3\times3} = 1$

7. $Co + H_2O \rightleftharpoons CO_2 + H_2$
t = 0   1   1   1   0
t = teq   1 – x 1 – x 1 + x x
at equilibrium, only CO_2 has (1 + x) moles.
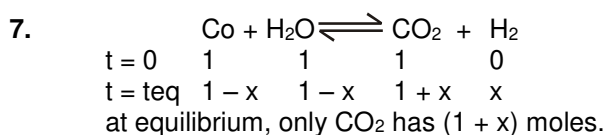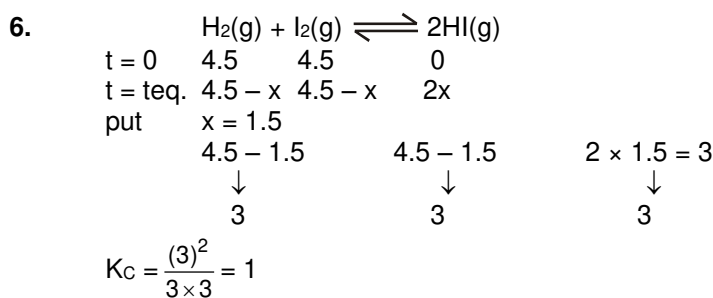
8. $K_p = K_c (RT)^{\Delta n}$, $\Delta n = 4 – 3 = 1$
0.05 = K_c R × 1000
$K_c = 5 \times 10^{-5} \times R^{-1}$

13. N_2 + O_2 $\rightleftharpoons$ 2NO   2x = 1.0 mole/litre
a   b   0   x = 1.0/2 mole/litre = 0.50 mole/litre
(a – x)   (b–x)   2x
If a – x = 0.25, b – x = 0.05
$[N_2]$ = a = a – x + x = 0.25 + 0.50 = 0.75 mole/litre

14.

$$2A_8 \rightleftharpoons 2A_3 + 3A_2 + A_4$$

t = 0   2   0   0   0

t = t_{eq} $2 - 2\alpha$ 2α 3α α
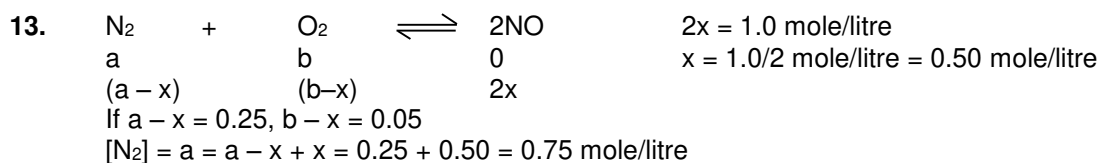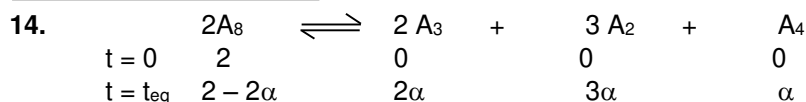
$n_T = 2 + 4\alpha$

given mole fraction of A_2 is = 0.36.

$$0.36 = \frac{3\alpha}{2+4\alpha} \quad \Rightarrow \quad \alpha = 0.46$$

Mole fraction of $A_8 = \dfrac{2-2\alpha}{2+4\alpha} = \dfrac{2-2\times0.46}{2+4\times0.46} = 0.28$

15.

$$2NO \rightleftharpoons N_2 + O_2 \qquad \alpha = 10\%$$

t = 0 $4 - .4$ .2   .2

        3.6   0.2   0.2
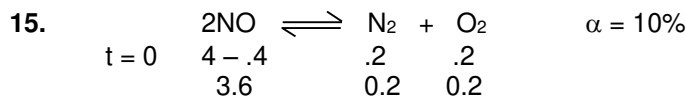
$\Delta n = 0$,

$\therefore K_P = K_C$, $K_C = \dfrac{(.2/V)^2}{(3.6/V)^2} = \dfrac{4}{36\times36}$

16. Total moles at equilibrium = $1 - \alpha + \alpha/n = 1 + \left[\dfrac{1}{n}-1\right]\alpha$

So using $\dfrac{d_i}{d_f} = 1 + \left[\dfrac{1}{n}-1\right]\alpha$.

17. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$
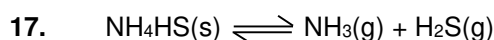
Total pressure is P

So, $P_{NH_3} = P_{H_2S} = \dfrac{P}{2}$

       $K_p = P_{NH_3} \times P_{H_2S} = \dfrac{P^2}{4}$.

18. At room temperature, K = 4.32 and at 425°C, equilibrium constant become 1.24×10^{-4} i.e. it is decreases with increase in temperature. So, it is exothermic reaction.

20. Catalyst can't disturb the state of the equilibrium.

23.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

at t = 0   a   0   0

t = t_{eq} $a - x$ x   x

       $P_{PCl_3} = X_{PCl_3} \times P_T = .25 \times 2 = .5$ atm

       $P_{PCl_3} = P_{Cl_2} = .5$ atm
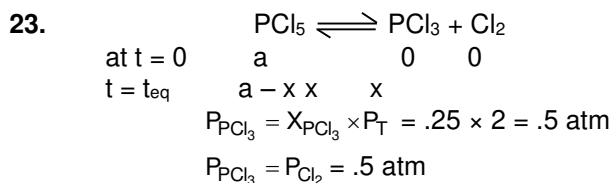
24. $\Delta G^\circ = -RT \ln K_{eq}$ $\ln K_{eq} = -6$

$15000 = -\dfrac{25}{3} \times 300 \ln K_{eq}$ $K_{eq} = e^{-6}$

$\ln K_{eq} = -\dfrac{15000}{2500} = 6$

25. $\Delta G^\circ = -2.303 \, RT \log K$

26. At point A,   Q = tan 60ºC

              Q = 1.732

    $\therefore$ Q = K = 1.732

28. According to $K_P = \dfrac{P_{PCl_3 \, (g)} \times P_{Cl_2 \, (g)}}{P_{PCl_5 \, (g)}} = \dfrac{(n_{PCl_3 \, (g)})_{eq.} \times (n_{Cl_2 \, (g)})_{eq.}}{V \times (n_{PCl_5 \, (g)})_{eq.}}$

and on adding inert gas at constant pressure effect on equilibrium will be similar to as if volume of container has been increased.

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29. $NO + \dfrac{1}{2} O_2 \rightleftharpoons NO_2$
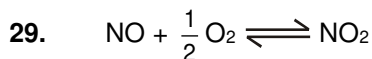
$\Delta G^{\circ}_{R \times H} = 52 - 87 = -35 \text{ kJ}$

$\Delta G^{\circ} = -RT \ln K_{eq}$

$\ln K_{eq} = \dfrac{35000}{8.314 \times 298}$.

30. $CO + H_2O \rightleftharpoons CO_2 + H_2$
  0.4   0.4
  0.4 – x   0.4 – x   x   x
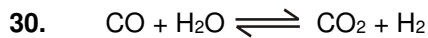
$\dfrac{x}{0.4 - x} = 3$

$1.2 - 3x = x$

$1.2 = 4x$

$x = \dfrac{1.2}{4} = 0.3$

$x = 0.3$

PART - III

1.
$\quad N_2(g) \quad + \quad 3H_2(g) \quad \rightleftharpoons \quad 2NH_3 (g)$
$\quad 9P - x - y \quad 13P - 3x - 2Y \quad\quad 2x$
$\quad N_2(g) \quad + \quad 2H_2(g) \quad \rightleftharpoons \quad N_2H_4(g)$
$\quad 9P - x - y \quad 13p - 3x - 2Y \quad\quad Y$

given $\quad 9P - x - y + 13P - 3x - 2y + 2x + y = 7P_o$

$\Rightarrow \quad 22P - 2x - 2y = 7P_o \quad\quad ....(1)$

then $\quad 2x = P_o \quad\quad\quad ....(2)$

and $\quad 13P - 3x - 2y = 2P_o \quad\quad ....(3)$

$\quad\quad 22P - 2y = 5P_o$

$\quad\quad \dfrac{-13P + 2y = \frac{7}{2}P_o}{9P = \frac{9}{2}P_o} \quad P = \dfrac{P_o}{2}$

$9P - x - y = \dfrac{9P_o}{2} - \dfrac{P_o}{2} - \dfrac{3P_o}{2} = \dfrac{5P_o}{2} \quad\quad\quad 2y = \dfrac{13-7}{2} P_o = 3P_o$

$13P - 3x - 2y = \dfrac{13P_o}{2} - \dfrac{3P_o}{2} - \dfrac{6P_o}{2} = 2P_o \quad\quad y = \dfrac{3}{2} P_o$

$K_1 = \dfrac{(2x)^2}{(9p - x - y)(13p - 3x - 2y)^3} = \dfrac{P_o{}^2}{\dfrac{5}{2}P_o \cdot (2P_o)^3} = \dfrac{1}{20P_o{}^2}$

$K_2 = \dfrac{\dfrac{3}{2}P_o}{\left(\dfrac{5}{2}P_o\right)(2P_o)^2} = \dfrac{3}{20P_o{}^2}$

2. $N_2O_4 \rightleftharpoons 2NO_{2(g)}$

$\Delta n = 2 - 1 = 1, \quad K_P = K_C \text{ (given)}$

We know, $K_P = K_C (RT)^{\Delta n}$

$\quad\quad 1 = RT, \quad T = \dfrac{1}{.0821} = 12.19 \text{ K}$

4. $K_1 = \dfrac{1}{K_2} \quad\quad$ for same value of T.

$\Rightarrow \quad K_1 K_2 = 1 \quad\quad$ similar to yx = const.

5. An efflorescent salt is one that loss of H_2O to atmosphere.

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

$$K_P = (P_{H_2O}^{'})^2 = 4 \times 10^{-4}$$

$$P_{H_2O}^{'} = 2 \times 10^{-2} \text{ atm} = 15.2 \text{ mm Hg}$$

If $P_{H_2O}^{'}$ at 25ºC < 15.2 mm only then reaction will proceed in forward direction.

6. $2AB_4(g) \rightleftharpoons A_2(g) + 4B_2(g)$ $\sum n = 1 + \dfrac{3\alpha}{2} \simeq 1$

$1 - \alpha$ $\dfrac{\alpha}{2}$ $2x$ $1 - \alpha \simeq 1$

$$K_P = \dfrac{\left(\dfrac{\alpha}{2}P\right)\left(\dfrac{2\alpha}{1} \times P\right)^4}{(P)^2} = 8P^3\alpha^5$$

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

$$K_P = \dfrac{(P_{CO})^2}{P_{CO_2}^{'}} = 1.0$$

At equilibrium, $P_{CO_2} = K_P = 4 \times 10^{-2}$ remain constant

$$\dfrac{(P_{CO})^2}{4 \times 10^{-2}} = 1$$

$$P_{CO} = \sqrt{4 \times 10^{-2}} = 0.2 \text{ atm}$$

9. $P_1 = 15$ atm   ; $T_1 = 300$ K.

Equilibrium temperature is 300ºC that is 573 K.

So first of all we have to calculate pressure of NH_3 at 573 K.

$$\dfrac{P_1}{T_1} = \dfrac{P_2}{T_2} = \dfrac{15}{300} = \dfrac{P_2}{573}$$

P_2 = 28.65 atm at 300ºC.

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

t = 0   28.65 atm   0   0

t = t_eq.   [28.65–x] $\dfrac{x}{2}$ atm $\dfrac{3}{2}$ x

But according to question.

P_{total} = 28.65 – x $+\dfrac{x}{2}$ $+\dfrac{3}{2}$ x

Or   28.65 + x = 40.11.

x = 11.46.

Degree of dissociation of $NH_3 = \dfrac{11.46}{28.65} = 0.4$.

10. (1) $A(s) \rightleftharpoons D(g) + C(g)$ $K_p = (20)^2$

                    20 atm 20 atm

(2) $B(s) \rightleftharpoons E(g) + F(g)$ $K_p = (30)^2$

                    30 atm 30 atm

(3) container K_p is same so on doubling the volume partial pressure does not change but moles of C, D, E, F will change to maintain their partial pressure. So total pressure = 40 + 60 = 100 atm.

11. $K_P = (P_{H_2O})^5 = 56.25 \times 10^{-10}$

$(P_{H_2O}) = (56.25 \times 10^{-10})^{1/5} = (56.25)^{1/5} \times 10^{-2} = 2.23 \times 10^{-2} \times 760 = 17.01$ torr

% Relative humidity = $\dfrac{\text{Parital pressure}}{\text{Vapour pressure}}$ × 100 = $\dfrac{17.01}{22.8}$ × 100 = 74.60%   (less than 74.60%)

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12. A(s) $\rightleftharpoons$ X + Y

              α $\alpha + \beta$

B(s) $\rightleftharpoons$ Y + Z

           $\beta + \alpha$ β

$\Rightarrow K_{P_1} = \alpha(\alpha + \beta)$

    $K_{P_2} = \beta(\alpha + \beta)$

$P_{total} = (\alpha + \beta) + \alpha + \beta = 2(\alpha + \beta)$

$\Rightarrow$ $2(\alpha + \beta) = 50$ $\Rightarrow$ $\alpha + \beta = 25$

$\Rightarrow$ $250 = 25\alpha$ $\Rightarrow$ $\alpha = 10$, $\beta = 15$

$\Rightarrow$ $K_{P_2} = \beta(\alpha + \beta) = 15 \times 25 = 375$
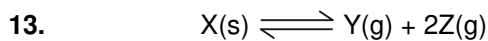
13.

X(s) $\rightleftharpoons$ Y(g) + 2Z(g)	A(s) $\rightleftharpoons$ Y(g) + B(g)

t = eq.   (a+b) 2a   t = eq.   (a+b)   b

Given $p_Z = p_B$

             $2a = b$ and $p_Z + p_B = p_Y + 10$

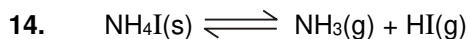 $(2a + b) = (a + b) + 10$

             $a = 10$ atm $\therefore$ $b = 20$ atm

$K_{P_1} = (a + b)(2a)^2 = (30)(400) = 12000$
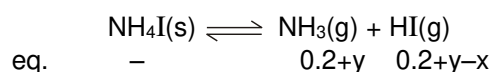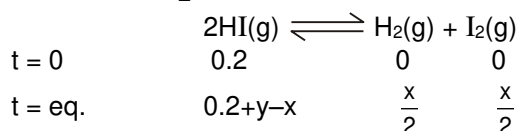
$K_{P_2} = (a + b)(b) = (30)(20) = 600$

$\Delta G = -RT\ln K$

$\dfrac{\Delta G_1}{\Delta G_2} = \dfrac{\ell n K_1}{\ell n K_2} = \dfrac{\log 12000}{\log 600} = \dfrac{3 + \log 12}{2 + \log 6}$
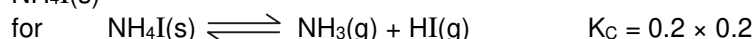
14. $NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$

at eq. total pressure = 304 mm of Hg

$p_{NH_3} = p_{HI} = \dfrac{304}{2} = 152$ mm of Hg = 0.2 atm

	$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$				$NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$	
t = 0	0.2	0	0	eq.	–	0.2+y 0.2+y–x
t = eq.	0.2+y–x	$\dfrac{x}{2}$	$\dfrac{x}{2}$			

We assumed that x atm of HI is used for dissociation which results formation of y atm of HI from $NH_4I(s)$

for $NH_4I(s) \rightleftharpoons NH_3(g) + HI(g)$ $K_C = 0.2 \times 0.2$

in other case $K_P = (0.2 + y)(0.2 + y - x)$

            $(0.2 + y)(0.2 + y - x) = 0.2 \times 0.2$ ...(i)

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

      $K_C = K_P = \dfrac{(x/2)(x/2)}{(0.2 + y - x)^2} = 0.010$ ...(ii)
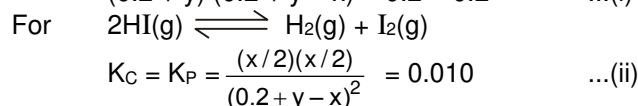
on solving the equation :   x = 0.036 & y = 0.016

total pressure at eq. = $p_{NH_3} + p_{HI} + p_{H_2} + p_{I_2}$

                          = 0.432 atm = 328 mm of Hg

15. A(s) $\rightleftharpoons$ B(g) + C(g) ,   E(s) $\rightleftharpoons$ B(g) + D(g)

      ($P_1 + P_2$) P_1 ($P_1 + P_2$) P_2

Total pressure = $2(P_1 + P_2) = 2\sqrt{K_{sp_1} + K_{sp_2}} = 20$ atm

16. On addign inert gas at content temperature & pressure 2nd reaction will be shifted in backward direction.

17. On mixing, P(N$_2$) & P(H$_2$) will add up. This will shift both the equilibrium backwards thereby decreasing the number of moles.

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18.
$$SO_2(g) + \frac{1}{2} O_2(g) \rightleftharpoons SO_3(g)$$

No. of mole   2   1   4

conc. $\frac{2}{4}$ $\frac{1}{4}$ $\frac{4}{4}$

$$K_C = \frac{[SO_3]}{[SO_2][O_2]^{1/2}} = \frac{1}{(1/2)\ (1/4)^{1/2}} = \frac{1}{(1/2)\times(1/2)} = \textbf{4 Ans.}$$

19. For reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ $K' = \dfrac{1}{0.25} = 4$

For reaction, $\dfrac{1}{2} H_2 + \dfrac{1}{2} I_2 \rightleftharpoons HI(g)$ $K'' = \sqrt{4}$

20.
$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$

at t = 0   60   42   0

at eq.   (60–x)   (42–x)   (2x)

(Partial pressures)

$\Rightarrow 2x = 28$ $\Rightarrow$ x = 14

$$K_p = \frac{(P_{AB})^2}{(P_{A_2})(P_{B_2})} = \frac{(28)^2}{(46)(28)} = \frac{14}{23}$$

For $\Delta n_g = 0$; $K_p = K_{C_1} = \dfrac{14}{23}$

Let degree of dissociation for AB is 'x' , then

$$2AB(g) \rightleftharpoons A_2(g) + B_2(g) \left(K_{C_2} = \frac{1}{K_{C_1}} = \frac{23}{14} \right)$$
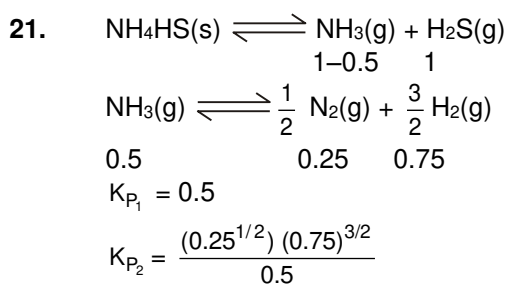
at t = 0   (1 – x)   x   x

$$\frac{\left(\dfrac{x}{2}\right)\left(\dfrac{x}{2}\right)}{(1-x)^2} = \frac{23}{14} \rightarrow \qquad \alpha = 0.719$$

Hence percentage of dissociatin = 0.719 × 100 = 72 %

21. $NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$
                      1–0.5   1

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

0.5   0.25   0.75

$K_{P_1} = 0.5$

$$K_{P_2} = \frac{(0.25^{1/2})\ (0.75)^{3/2}}{0.5}$$
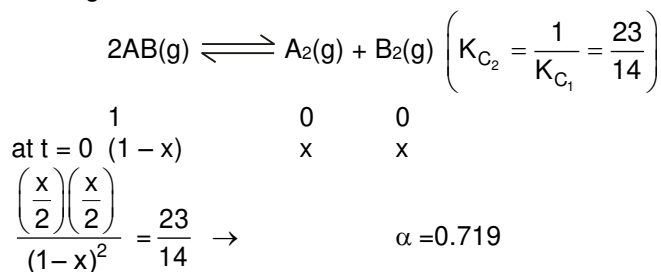
22. Since (I) causes no change in volume due to reaction change from 100 L is due to (II) only.
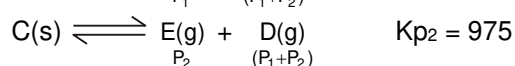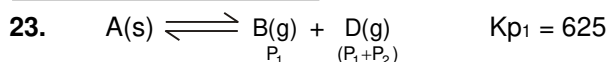
∴ v (CO) finally = 10 L

$$P(O) \text{ finally} = \left(\frac{10}{105}\right)\times 105 = 10 \text{ L}$$

$$\therefore P(O_2) = P_{CO}^2 / K_{p_2} = \frac{10^2 \text{ atm}^2}{125\,\text{atm}} = \text{solutions}$$

Also, $K_{P_1} = \dfrac{P_{CO_2}}{P_{O_2}} = \dfrac{7}{8} \times$ solution = 7 atm   ∴ $P(CO_2) = KP_1. P(O_2)$

∴ $P(CO) + P(CO_2)$ finally is 8 + 7 = 15 atm

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23.
$$A(s) \rightleftharpoons \underset{P_1}{B(g)} + \underset{(P_1+P_2)}{D(g)} \qquad K_{p_1} = 625$$

$$C(s) \rightleftharpoons \underset{P_2}{E(g)} + \underset{(P_1+P_2)}{D(g)} \qquad K_{p_2} = 975$$

$K_{p_1} + K_{p_2} = (p_1^2 + p_2^2 + 2p_1p_2) = (p_1 + p_2)^2 = (625 + 975) \Rightarrow (p_1 + p_2) = 40$

so total pressure $= 2[p_1 + p_2] = 80$ atm.

24.
$$H_2 + Br_2 \rightleftharpoons 2HBr$$

$t = 0 \qquad 0.4 \qquad 0.2 \qquad\qquad -$

$t = t_{eq.} \qquad 0.2 \qquad y \qquad\qquad 0.4$

$\qquad\qquad\qquad\qquad\quad = $ negligible $= y$
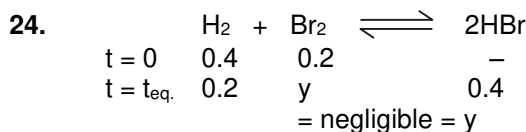
$\therefore \quad \dfrac{1}{4} \times 10^{10} = \dfrac{0.4 \times 0.4}{0.2 \times y}$

$\qquad y = 3.2 \times 10^{-10}$

$\qquad \dfrac{Br_2}{HBr} \times 10^{11} = \dfrac{3.2}{0.4} \times 10^{-10} \times 10^{11} = 80$

25.
$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$\quad 2 \qquad\qquad - \qquad - \qquad\qquad K_C = a\alpha = 2 \times 0.8 = 1.6$

$2-1.6$

$= 0.4 \qquad \dfrac{1.6}{5} \quad 1.6 \quad 1.6$
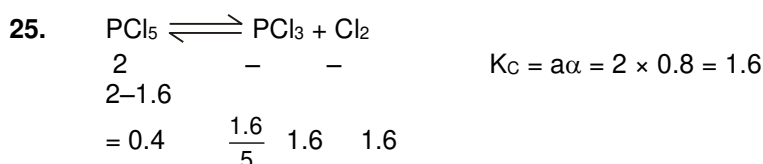
$\dfrac{0.4}{5} \qquad \dfrac{1.6}{5} \qquad \dfrac{1.6}{5} \qquad K_C = \dfrac{\dfrac{1.6}{5} \times \dfrac{1.6}{5}}{\dfrac{0.4}{5}}$

$K_C = \dfrac{4 \times 1.6}{5} = \dfrac{64}{50} \qquad$ Ans. is $\dfrac{64}{50} \times 50 = 64$

26.
$$A(s) \rightleftharpoons B(g) + C(g) \qquad\qquad K_{P_1} = 300$$

$\qquad - \qquad\qquad P_1 \quad (P_1+P_2) \qquad\qquad K_{P_1} = P_1(P_1+P_2)$

$$D(s) \rightleftharpoons E(g) + C(g) \qquad\qquad K_{P_2} = 600$$
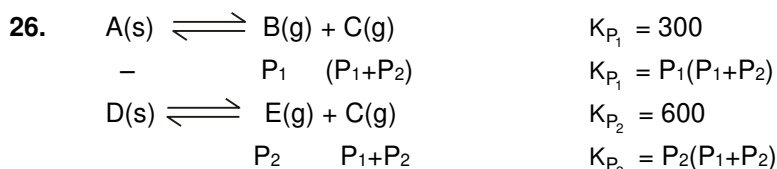
$\qquad\qquad\qquad P_2 \quad P_1+P_2 \qquad\qquad K_{P_2} = P_2(P_1+P_2)$

$\left(\dfrac{Kp_1}{Kp_2}\right) = \dfrac{P_1(P_1+P_2)}{P_2(P_1+P_2)}$

$\dfrac{300}{600} = \left(\dfrac{P_1}{P_2}\right)$

$\dfrac{P_1}{P_2} = \dfrac{1}{2} \qquad P_2 = 2P_1$

$K_{P_1} = P_1(P_1+P_2) \qquad \Rightarrow \qquad K_{P_1} = P_1(P_1+2P_1) \qquad \Rightarrow \qquad 300 = P_1(3P_1)$

$P_1^2 = 100 \qquad (P_1 = 10)$

$P_2 = 20$ atm

Now Total pressure

$P_B + P_E + P_C$

$(P_1+P_2) + (P_1+P_2) = (10 + 20) + (30) $ **= 60 atm.**

27. From given reactions.

(i) $= -$ (iii) $\qquad ; \qquad \dfrac{1}{2}$ (i) $= -$ (iv) $\qquad ; \qquad \dfrac{1}{2}$ (iii) $= -$ (ii)

29. Higher is the value of equilibrium const, higher will be the stability of products.

31. Second equilibrium will not be affected by CO_2 addition only first will shift backward.

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32. Since ↑ in temperature results in shifting of equilibria in forward direction hence reaction is endothermic in nature. Endothermic reaction is driven in forward direction upon increase in temperature.

33. R.H. > 1 ⇒ > V.P. ⇒ Q > K ⇒ leftward shift
R.H. < 1 ⇒ < V.P. ⇒ Q < K ⇒ Rightward shift

34. Addition of solids have no effect on equilibrium and temperature favours endothermic direction while increasing pressure will shift equilibrium in backward direction as Δn_g is +ve.

PART - IV

1. $K_P = \dfrac{P_{CO(g)} \cdot P_{H_2(g)}}{P_{H_2O(g)}} = \dfrac{(P_{H_2(g)})^2}{P_{H_2O(g)}}$ (as $P_{CO(g)} = P_{H_2(g)}$)

3. Mole of PbS = 708 / 236 = 3 mole = mole of H_2S

$$Sb_2S_3(s) + 3H_2(g) \rightleftharpoons 2Sb(s) + 3H_2S(g)$$

initial	6	6	0	0
at eq.	5	3	2	3

$K_C = \dfrac{(3/10)^3 \times (2/10)^2}{(5/10) \times (3/10)^3} = \dfrac{4}{50} = 0.08$

4. $K = A\, e^{-\Delta H/RT}$

$\log K = \log A - \dfrac{\Delta H}{2.303RT}$.

$\log K = \log A - \dfrac{\Delta H}{2.303 \; R} \times \dfrac{1}{T}$.

$\log K = \left[-\dfrac{\Delta H}{2.303 \; R}\right] \times \dfrac{1}{T} + \log A$.

$\dfrac{-\Delta H}{2.303 \; R} = 1$.

$\Delta H = -2.303\,R = -4.606$ cal.

5. $aA + bB \rightleftharpoons cC + dD$
At high temp. & low pressure equilibrium is shifting in backward direction. It means (a + b) > (c + d) & heat will reaction in the formation of producers is $\Delta H < 0$.

6. $$Br_2(\ell) + Cl_2(g) \rightleftharpoons 2BrCl(g)$$

t = 0		1	0
		(1 − x)	2x

$k_p = \dfrac{(P_{BrCl})^2}{P_{Cl_2}} = 1$ so, $P_{Cl_2} = (P_{BrCl})^2 = 0.01$ atm

then at equilibrium, $\dfrac{n_{BrCl}}{n_{Cl_2}} = \dfrac{0.1}{0.01} = 10 = \dfrac{2x}{1-x}$

So, $10 - 10x = 2x$ or $x = \dfrac{10}{12} = \dfrac{5}{6}$ moles

Moles of $Br_2(\ell)$ required for maintaining vapour pressure of 0.1 atm

$= 2 \times \dfrac{5}{6}$ moles $= \dfrac{10}{6}$ moles = moles of BrCl(g).

Moles required for taking part in reaction = moles of Cl_2 used up $= \dfrac{5}{6}$ moles.

Hence total moles required $= \dfrac{5}{6} + \dfrac{10}{6} = \dfrac{15}{6}$ moles.

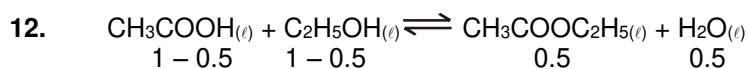**7.** As in the gaseous mixture only A will be present so the molecular weight of the gaseous mixture will be 'M$_A$'

∵ $PM_A = dRT$ where R, P, T are const.

so $d \propto M_A$

and hence it does not depend on 'α'

so 'd' will remain constant.

Option (D) is correct.

12. $CH_3COOH_{(\ell)} + C_2H_5OH_{(\ell)} \rightleftharpoons CH_3COOC_2H_{5(\ell)} + H_2O_{(\ell)}$

    1 – 0.5   1 – 0.5   0.5   0.5

So, $K_C = \dfrac{0.5 \times 0.5}{0.5 \times 0.5} = 1$

Now let a moles of CH_3COOH and b moles of C_2H_5OH are taken :

$a - \dfrac{a}{3}$ $b - \dfrac{a}{3}$ $\dfrac{a}{3}$ $\dfrac{a}{3}$

So, $K_C = \dfrac{(a/3) \times (a/3)}{2a/3 \times \left(b - \dfrac{a}{3}\right)}$ or $2\left(b - \dfrac{a}{3}\right) = \dfrac{a}{3}$ or $2b = a$ or $\dfrac{a}{b} = \dfrac{2}{1}$

13. $NH_2COONH_4(s) \rightleftharpoons 2NH_3(g) + CO_2(g)$.
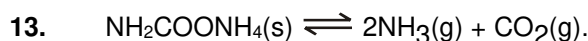
At eq. $P_{NH_3} = 4$ atm

$P_{CO_2} = 2$ atm

$K_p = P_{NH_3}^2 \times P_{CO_2} = 32$ atm^3.

Therefore x = 32 & y = 6 $\Rightarrow$ x + y = 38.

14. $2NH_3 \rightleftharpoons N_2 + 3H_2$

t =0   a   a   0
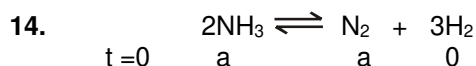
t$_{eq}$ $a(1 - \alpha)$ $\dfrac{a\alpha}{2} + a$ $\dfrac{3a\alpha}{2}$

$n_T = 2a + a\alpha = a(2 + \alpha) = 2a + \dfrac{3a\alpha}{2} \times 2a$

$2 + \alpha = 2.4$ $\Rightarrow$ $\alpha = 0.4$ **Ans.** 40%

15. $A_2B(g) \rightleftharpoons 2A(g) + B(g)$

at t = 0   1   0   0

at eq.   (1–x)   2α   α
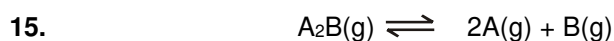
(partial pressure)

Hence, $(1 - \alpha) \simeq 1$

$\dfrac{(2x)^2 \times (\alpha)}{(1)} = 81 \times 10^{-6}$

$\alpha = 3 \times 10^{-2}$

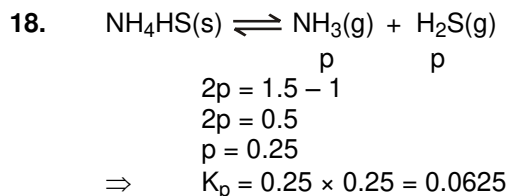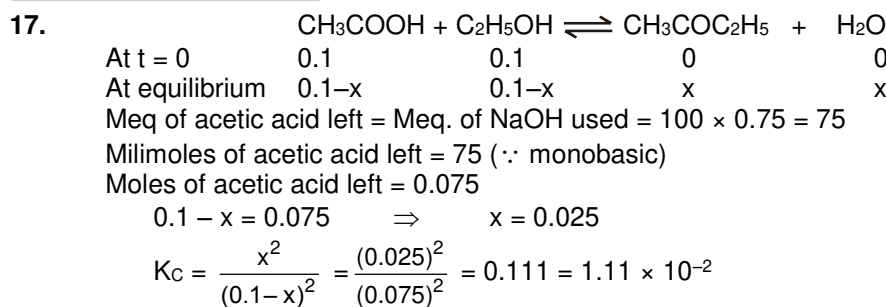percentage of dissociation = $3 \times 10^{-2} \times 100 = 3\%$

16. $P_B : P_D = 1 : 6$ Let the partial pressure of B$_{eq}$. be P$_0$

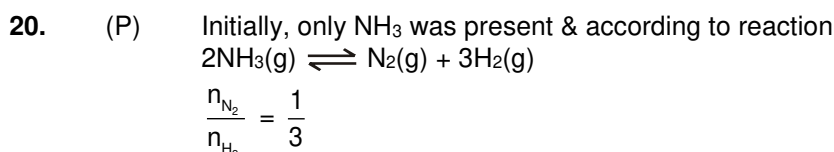$K_{P_1} = (P_0)^2 \left(\dfrac{3P_0}{2}\right)^3$

$K_{P_2} = (6P_0)^3$

$\dfrac{K_{P_2}}{K_{P_1}} = \dfrac{6^3}{\left(\dfrac{3}{2}\right)^3} = 64$

$\dfrac{K_{P_2}}{8K_{P_1}} = \dfrac{64}{8} = 8$

17.
$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COC_2H_5 + H_2O$$

| At t = 0 | 0.1 | 0.1 | 0 | 0 |
| At equilibrium | 0.1–x | 0.1–x | x | x |

Meq of acetic acid left = Meq. of NaOH used = $100 \times 0.75 = 75$

Milimoles of acetic acid left = 75 ($\because$ monobasic)

Moles of acetic acid left = 0.075

$$0.1 - x = 0.075 \qquad \Rightarrow \qquad x = 0.025$$

$$K_C = \frac{x^2}{(0.1-x)^2} = \frac{(0.025)^2}{(0.075)^2} = 0.111 = 1.11 \times 10^{-2}$$

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

$$\qquad\qquad\qquad\qquad p \qquad\quad p$$

$2p = 1.5 - 1$

$2p = 0.5$

$p = 0.25$

$\Rightarrow \qquad K_p = 0.25 \times 0.25 = 0.0625$

19. $n = \dfrac{PV}{RT} = \dfrac{3000 \times 10^{-3}}{\dfrac{25}{3} \times 300} = 1.2 \times 10^{-3}$ moles.

20. (P) Initially, only NH_3 was present & according to reaction

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

$$\frac{n_{N_2}}{n_{H_2}} = \frac{1}{3}$$

Same volume for both gases $\Rightarrow \dfrac{p_{N_2}}{p_{H_2}} = \dfrac{1}{3} \Rightarrow \dfrac{p_{H_2}}{p_{N_2}} = 3$

(Q) When B is closed, only H_2 diffuses through filter until partial pressure of H_2 becomes equal.

$$\frac{n_{H_{2total}}}{n_{N_2}} = 3 \qquad\qquad\qquad\qquad ...(1)$$

$$p_{H_2}^{I} = p_{H_2}^{II} \qquad \& \qquad V_I = 2V_{II} \qquad \Rightarrow \qquad n_{H_2}^{I} = 2\,n_{H_2}^{II}$$

$$n_{H_2}^{I} + n_{H_2}^{II} = n_{H_{2total}} \quad \Rightarrow \quad n_{H_{2total}}/n_{H_2}^{I} = \frac{3}{2} \qquad ...(2)$$

from eq.(1) & (2)

$$\frac{n_{H_2}^{I}}{n_{N_2}} = \frac{n_{H_2}^{I}}{n_{H_{2total}}} \times \frac{n_{H_{2total}}}{n_{N_2}} = \frac{2}{3} \times 3 = 2$$

(R) Again same volume for N_2 & H_2

$$n_{N_{2total}} / n_{H_{2total}} = \frac{1}{3} \qquad\qquad\qquad\qquad ...(1)$$

$$p_{N_2}^{I} = p_{N_2}^{II} \quad \& \quad V_I = 2V_{II} \quad \Rightarrow \quad n_{N_2}^{I} = 2\,n_{N_2}^{II} \quad \& \quad n_{H_2}^{I} = 2\,n_{H_2}^{II}$$

$$n_{N_{2total}} = n_{N_2}^{I} + n_{N_2}^{II} = 3\,n_{N_2}^{II} = \frac{3}{2}\,n_{N_2}^{I}$$

$$n_{H_{2total}} = n_{H_2}^{I} + n_{H_2}^{II} = 3\,n_{H_2}^{II}$$

from eq.(1) $\qquad \dfrac{3}{2}\,n_{N_2}^{I} / 3\,n_{H_2}^{II} = \dfrac{1}{3} \qquad \Rightarrow \qquad \dfrac{n_{N_2}^{I}}{n_{H_2}^{II}} = \dfrac{2}{3}$

(S) $(n_{N_2}^{I} + n_{N_2}^{II})/(n_{H_2}^{I} + n_{H_2}^{II}) = \dfrac{1}{3}$

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