CHEMICAL EQUILIBRIUM

1. *TYPES OF CHEMICAL REACTION :*

The chemical reactions are classified on the basis of the extent to which they proceed, into the following two classes ;

I. Reversible reactions : Reaction in which entire amount of the reactants is not converted into products is termed as reversible reaction.

(i) Characteristics of reversible reactions :

(a) These reactions can be started from either side.

(b) These reactions are never complete.

(c) This sign ($\rightleftharpoons$) represents the reversibility of the reaction.

$$\text{Reactant} \underset{\text{backward reaction}}{\overset{\text{forward reaction}}{\rightleftharpoons}} \text{Product}$$

(d) These reactions attain equilibrium and all the times, reaction mixture contains both reactant and product molecules. When reaction attains equilibrium the concentrations of reactants and product become constant (not same necessarily).

(ii) Examples of reversible reactions :

(a) Neutralisation between an acid and a base either one or both are weak.

$$CH_3COOH + NaOH \rightleftharpoons CH_3COONa + H_2O$$

(b) Salt hydrolysis

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

(c) Thermal decomposition

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

(d) Esterification

$$CH_3COOH + C_2H_5OH \rightleftharpoons CH_3COOC_2H_5 + H_2O$$

(e) Evaporation of water in a closed vessel

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

II. Irreversible reactions : Reaction in which entire amount of the reactants is converted into products is termed as irreversible reaction.

(i) Characteristics of irreversible reactions :

(a) These reactions proceed only in one direction (forward direction)

(b) These reactions can proceed to completion and reactant is completely converted into product.

(c) The arrow (→) is placed between reactants and products

Reactant → Product

(d) These reactions never attain equilibrium.

(ii) Examples of irreversible reactions :

(a) Neutralisation between strong acid and strong base

$$NaOH(aq) + HCl(aq) \rightarrow NaCl(aq) + H_2O(l)$$

(b) Precipitation reactions

$$AgNO_3(aq) + NaCl(aq) \rightarrow AgCl(s)\downarrow + NaNO_3(aq)$$

(c) Thermal decomposition

$$CaCO_3(s) \rightarrow CaO(s) + CO_2(g)\downarrow$$

However, if the above reaction is carried out in closed container, i.e., leaving no scope for gas to escape out, the reaction shows reversible nature.

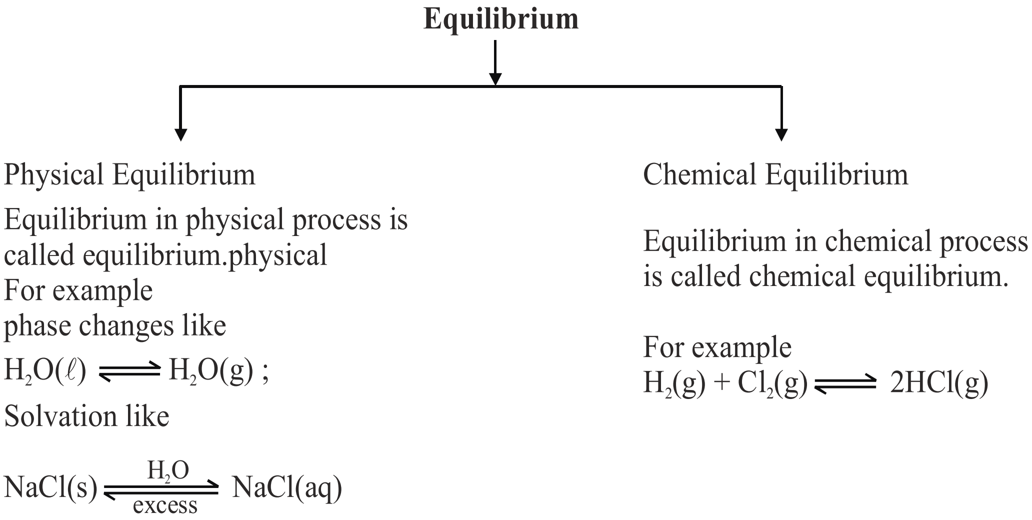
(d) Combustion reactions

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(\ell)$$

2. EQUILIBRIUM :

In the state of equilibrium, system loses its tendency for a change and all the properties associated with system like pressure, temperature, composition, etc become constant and do not vary without external stimulation. On the basis of nature of process in which state of equilibrium is attained , it may be of two types :

(A) Physical equilibrium (B) Chemical equilibrium



Equilibrium

Physical Equilibrium
Equilibrium in physical process is called equilibrium.physical
For example
phase changes like
$H_2O(\ell) \rightleftharpoons H_2O(g)$;
Solvation like
$NaCl(s) \underset{excess}{\overset{H_2O}{\rightleftharpoons}} NaCl(aq)$

Chemical Equilibrium

Equilibrium in chemical process is called chemical equilibrium.

For example
$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

2.1 Physical equilibrium :

If in a system only physical state (phase) is changed and equilibrium is established, (i.e. there is no chemical change), the equilibrium is called ***physical equilibrium.*** Ex : Fusion of ice, evaporation of water, dissolution of salts , absorption of gases in liquid, etc.

Following are the types of common physical equilibria :

(i) **Liquid-Vapour equilibria :** In a closed vessel, the vapours above the liquid are in equilibrium at given temperature.

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

(ii) **Solid-Liquid equilibria :** This equilibrium can be established only at melting point of solid. At this stage solid and liquid phases exist simultaneously in equilibrium.

Ex. $H_2O(s) \rightleftharpoons H_2O(\ell)$ at melting point

(iii) **Solid-Vapour equilibria :** Let us now consider the systems where solids sublime to vapour phase. If we place solid iodine in a closed vessel, after sometime the vessel gets filled up with violet vapour and the intensity of colour increases with time. After certain time the intensity of colour becomes constant and at this stage equilibrium is attained. Hence solid iodine sublimes to give iodine vapour and the iodine vapour condenses to give solid iodine. The equilibrium can be represented as,

$$I_2(\text{solid}) \rightleftharpoons I_2(\text{vapour})$$

Other examples showing this kind of equilibrium are,

$$\text{Camphor (solid)} \rightleftharpoons \text{Camphor (vapour)}$$

$$NH_4Cl\ (\text{solid}) \rightleftharpoons NH_4Cl\ (\text{vapour})$$

(iv) **(Solute-Solvent) Saturated solution equilibria :** If the rate of dissolution of solids in liquid is equal to the rate of crystallization of solid from solution i.e. solution is saturated with respect to solid then saturated solution equilibria established, provided temperature is constant.

Ex. $NaI(s) \xrightleftharpoons{H_2O} Na^+(aq.) + I^-(aq.)$

(v) **(Gas + Solvent) Saturated solution equilibria :** In such equilibriums, solvents is saturated with respect to gas i.e. rate of entering of gas molecules in solvent is equal to rate of escaping of gas molecules from solvents. Above phenomenon can be observed in closed container at definite temperature. Ex : Dissolved CO_2 in cold drinks, dissolved O_2 in water, etc.

Note: (i) The solubilities of gases in liquid is a function of pressure of gas over liquid.

(ii) **Henry's law** can be applied on such system, that states, the mass of gas dissolved in a given mass of solvent at any temperature is proportional to the pressure of the gas above the solvent.

(iii) One should not compare it with liquid vapour equilibria.

2.2 Chemical equilibrium :

Analogous to the physical systems, chemical reactions also attain a state of equilibrium. These reactions can occur both in forward and backward directions. When the rates of the forward and reverse reactions become equal, the concentrations of the reactants and the products become constant. This is the stage of chemical equilibrium. This equilibrium consists of a forward reaction in which the reactants give product(s) and reverse reaction in which product(s) gives the original reactants.

2.2.1 Characteristics of Chemical equilibrium :

(i) It is attained in reversible chemical reactions only.

(ii) Equilibrium is possible only in closed system.

(iii) In this state, all the measurable properties of the system like temperature, concentration, colour, density etc. don't undergo any change with time, i.e. constant.

(iv) Equilibrium is dynamic in nature i.e., at microscopic level reaction is not stopped. It appears that no change is occurring but both the opposing reactions are proceeding at the same rate. So there is no net change. Thus equilibrium is not static in nature.

(v) Chemical equilibrium can be approached from both sides

$$2\,HI \rightleftharpoons H_2 + I_2$$

or

$$H_2 + I_2 \rightleftharpoons 2HI$$

At equilibrium, reactants and products have fixed composition and this is independent of the fact whether the reaction start with the reactant or with the product.

(vi) Equilibrium is not affected by the presence of catalyst. The catalyst only helps in attaining equilibrium rapidly.

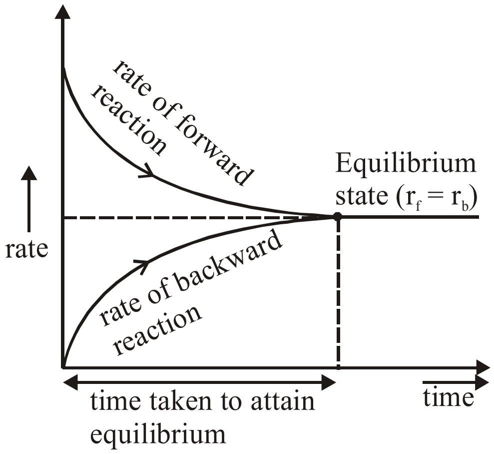
(vii) At equilibrium, opposing reactions (i.e., forward and backward) proceeds with equal rates.

i.e., rate of forward reaction = rate of backward reaction.

Note: (i) Whenever question doesn't ask about direction, then we take forward direction only.

(ii) In a reversible reaction if forward reaction is exothermic then the backward reaction will be endothermic and vice versa.

2.2.2 Variation of Rate v/s Time :



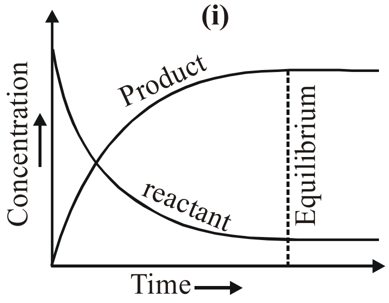
From above graph, initially rate of forward reaction decreases and the rate of backward reaction increases. At certain stage, rate of forward reaction becomes equal to rate of backward reaction called ***equilibrium state.***

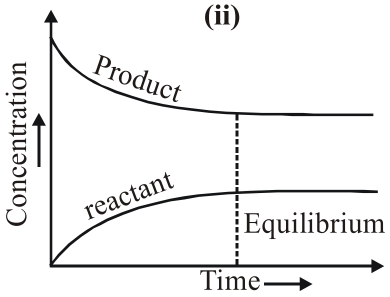
2.2.3 Variation of Concentration v/s Time :

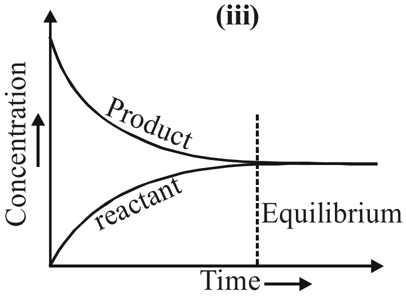
Let us consider a reversible reaction,

$$A + B \underset{\text{reverse}}{\overset{\text{forward}}{\rightleftharpoons}} C + D$$

	A	B	C	D
initial conc. (t = 0)	1M	1M	0	0
eq. conc. (t = t)	(1–x)	(1–x)	x	x







In the begining (at time t = 0), the container has only the reacting molecules A and B while the products C and D are nil. With the passage of time, the reactants A and B will be used up or consumed to form the products , C and D. It means that the concentration or molar concentration of the reactants will decrease while those of the products will increase. A stage will be ultimately reached when their concentration becomes constant i.e., their will be no further change in concentration of either of the reactants A and B or of the products C and D. This represents a state of equilibrium.

Note: At equilibrium, the concentration of reactant and product will be constant. It means, it may be different as above graph (i) & (ii) or same as above graph (iii) but the rate of forward reaction and the backward reaction will be always same.

Ex.1 Chemical equilibrium is a condition :

(A) where all species have same concentration

(B) where all species have constant concentration with respect to time.

(C) where all species have unit concentration

(D) all of above

Sol. (B)

Ex.2 Example of physical equilibria, is :

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

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

(C) $H_2O(s) \rightleftharpoons H_2O(\ell)$

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

Sol. (C)

Physical equilibria does not include any chemical change.

3. *TYPES OF CHEMICAL EQUILIBRIUM :*

I. Homogeneous equilibrium II. Heterogeneous equilibrium

I. Homogeneous equilibrium :

It is the equilibrium when all reactants and products are in same phase.

Ex. $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$

$SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$

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

II. Heterogeneous equilibrium :

It is the equilibrium the reactants and the products are present in different phases. All physical equilibria are heterogeneous.

Ex. $3Fe(s) + 4H_2O(g) \rightleftharpoons Fe_3O_4(s) + 4H_2(g)$

$2Na_2O_2(s) + 2H_2O(\ell) \rightleftharpoons 4NaOH + O_2(g)$

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

$H_3O(\ell) \rightleftharpoons H_2O(g)$

4. *ACTIVE MASS :*

The mass of a substance which effect the rate of reaction i.e. mass of substance which take a part actively in a reaction. Active mass depends on state of substance.

(i) Solution state : In this state, active mass of a substance is represented by concentration (molarity). Active mass is usually expressed in concentration by enclosing the symbol of the reactant in square bracket [ ].

$$\text{Active mass} = \frac{\text{moles}}{\text{Volume in litres}} = \frac{\text{grams(w)}}{\text{mol.wt.}(M_w) \times \text{Volume in litres(V)}} = \frac{w \times 1000}{M_w \times V(\text{mL})}$$

(ii) Gaseous state : In this state, active mass of a substance may be represented as concentration (molarity) or partial pressure.

(iii) Pure solid & pure liquid : In this state, active mass of solids , pure liquids and solvents in large excess is a constant quantity because there is no change in activity with the change in quantity or volume of system.

$$\text{Molar concentration (M)} = \frac{w}{M \times V} = \frac{d}{M} = \frac{\text{density of the substance}}{\text{molar mass of the substance}} = \text{constant}$$

as density of pure solids and liquids is constant and molar mass is also constant.

5. *LAW OF MASS ACTION AND LAW OF EQUILIBRIUM CONSTANT :*

The law of mass action is given by ***Guldberg*** and ***Waage***. According to it, "the rate of a chemical reaction at a particular temperature is proportional to the product of active masses of reactants raised to the powers equal to their stoichiometric coefficients".

Consider a reversible reaction : $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

According to law of mass action

rate of forward reaction $(r_f) \propto (a_A)^{m_1} (a_B)^{m_2}$

$$r_f = k_f(a_A)^{m_1} (a_B)^{m_2}$$

rate of backward reaction $(r_b) \propto (a_C)^{n_1} (a_D)^{n_2}$

$$r_b = k_b(a_C)^{n_1} (a_D)^{n_2}$$

At equilibrium $r_f = r_b$

$$k_f(a_A)^{m_1} (a_B)^{m_2} = k_b(a_C)^{n_1} (a_D)^{n_2}$$

$$K_{eq} = \frac{k_f}{k_b} = \frac{(a_C)^{n_1}(a_D)^{n_2}}{(a_A)^{m_1}(a_B)^{m_2}}$$

where, K_{eq} = equilibrium constant

k_f = forward rate (velocity) constant

k_b = backward rate (velocity) constant

a_A , a_B = active mass of reactant A & B

a_C , a_D = active mass of product C & D

m_1 , m_2 = stoichiometry coefficient of reactant A & B

n_1 , n_2 = stoichiometry coefficient of product C & D

At a given temperature, the product of molar concentrations of the reaction products raised to the respective stoichiometric coefficient in the balanced chemical equation divided by the product of molar concentrations of the reactants raised to their individual stoichiometric coefficients has a constant value. This is known as the ***Equilibrium Law or Law of Chemical Equilibrium***.

5.1 Types of equilibrium constant ($K_{eq.}$) :

(i) Equilibrium constant in terms of concentration (K_C) : K_C is defined for reactions in gas phase & solution phase. Molar concentrations are used to express amounts.

(ii) Equilibrium constant in terms of partial pressure (K_P) : K_P is defined for reactions in gas phase. Parial pressures are used to express amounts.

Ex. Consider a reversible reaction in gas phase : $m_1A + m_2B \rightleftharpoons n_1C + n_2D$

$$K_C = \frac{[C]^{n_1}[D]^{n_2}}{[A]^{m_1}[B]^{m_2}}$$

$$K_P = \frac{(P_C)^{n_1}(P_D)^{n_2}}{(P_A)^{m_1}(P_B)^{m_2}}$$

here,

[A], [B], [C], [D] = Molar concentration of A, B, C, D respectively at equilibrium .

(P_A), (P_B), (P_C), (P_D) = partial pressure of A, B, C, D respectively at equilibrium .

5.2 Units of equilibrium constant :

5.2.1 The value of equilibrium constant K_c can be calculated by substituting the concentration terms in mol/L or M and for K_p partial pressure is substituted in Pa, kPa, bar or atm. This results in units of equilibrium constant based on molarity or pressure, unless the exponents of both the numerator and denominator are same. For general reactions,

$$aA \rightleftharpoons bB$$

(i) $K_C = \dfrac{[B]^b}{[A]^a}$

unit of $K_C = \left(\dfrac{mol}{L}\right)^{b-a} = [M]^{b-a} = M^{\Delta n_g}$

here, $\Delta n_g = b - a$ = moles of (Product – Reactant)

(ii) $K_P = \dfrac{(P_B)^b}{(P_A)^a}$

unit of $K_p = (atm)^{b-a} = (atm)^{\Delta n_g}$ or $(Pa)^{\Delta n_g}$ or $(bar)^{\Delta n_g}$

here, $\Delta n_g = b - a$ = moles of (Product – Reactant)

Ex.3 Write down the expression and unit for following reaction :

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

$K_C = \dfrac{[HI]^2}{[H_2][I_2]}$ $\quad \left(\dfrac{mol}{L}\right)^0$

$K_p = \dfrac{P_{HI}^2}{P_{H_2}P_{I_2}}$ $\quad (atm)^0$

∴ K_C and K_p have no unit.

(b) $N_2O_4(g) \rightleftharpoons 2NO_2\,(g)$

$K_C = \dfrac{[NO_2]^2}{[N_2O_4]}$ $\quad \left(\dfrac{mol}{L}\right)^1$

$K_p = \dfrac{P_{NO_2}^2}{P_{N_2O_4}}$ $\quad (atm)^1$

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

$K_C = [CO_2]$ $\quad \left(\dfrac{mol}{L}\right)^1$

$K_p = P_{CO_2}$ $\quad (atm)^1$

5.2.2 Equilibrium constants is expressed in standard state that is called standard state equilibrium constant or thermodynamic equilibrium constant, which is dimensionless quantity. It is denoted by K_c^0 and K_p^0. For a pure gas, the standard state is 1 bar. Therefore a pressure of 4 bar in standard state can be expressed as 4 bar/1 bar = 4, which is a dimensionless number and concentration of 3 M solution in standard state can be expressed as $\frac{3M}{1M} = 3$, which is a dimensionless number. The numerical value of equilibrium constant depends on the standard state chosen. Thus, in this system both K_c^0 and K_p^0 are dimensionless quantities but have different numerical values due to different standard states. For example,

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

$K_C = [C]$ (mol/L)

but K_C^0 is a dimensionless quantity so $K_C^0 = \frac{[C]}{1M}$

$K_p = P_C$ $(\text{bar})^1$

but K_p^0 is a dimensionless quantity so $K_p^0 = \frac{P_C}{1\,\text{bar}}$

5.3 Relation between K_P & K_C :

For the reaction , $aA + bB \rightleftharpoons cC + dD$

we can write

$$K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b} \quad \text{............(i)}$$

Assuming the gaseous components to behave ideally ,

$P_iV_i = n_iRT$

$P_i = (n_i/V_i)\ RT = C_iRT = [i]\ RT$

where [i] is the molar concentration of the species 'i'.

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

$$K_P = \frac{(P_C)^c(P_D)^d}{(P_A)^a(P_B)^b} = \frac{([C]RT)^C.([D]RT)^d}{([A]RT)^a.([B]RT)^b} = \frac{[C]^C.[D]^d}{[A]^a.[B]^b} \times (RT)^{(c+d)-(a+b)}$$

from eq..(i)

$K_P = K_C(RT)^{(c+d)-(a+b)}$

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

Δn_g = (Number of moles of gaseous products) - (Number of moles of gaseous reactants).

$\Delta n_g = (c + d) - (a + b)$

The units of K_P & K_C are not fixed and depend on stoichiometry of the reaction. In case the number of moles of the reactant & that of the product are same K_P & K_C do not have any unit.

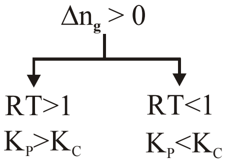
5.4 Different cases for $K_p = K_c(RT)^{\Delta ng}$:

Case-I : If $\Delta n_g = 0$ then $K_p = K_c$

Ex : $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

K_p = unit less ; K_c = unit less ;

Case-II :



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

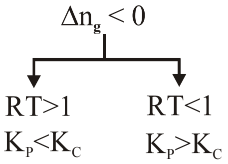
$\Delta n_g = 2 - 1 = 1$ then $K_p = K_C\,(RT)^1$

if $RT > 1$ then $K_p > K_c$

if $RT < 1$ then $K_p < K_c$

Unit: $K_p = atm^1$; $K_c = conc.^1$

Case-III :



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

$\Delta n_g = 2 - 4 = -2$ then $K_p = K_C\,(RT)^{-2}$

if $RT > 1$ then $K_p < K_c$

if $RT < 1$ then $K_p > K_c$

$K_p = atm^{-2}$; $K_c = conc.^{-2}$

Case-IV : If $T = \frac{1}{R} = \frac{1}{0.821} \approx 12.2\,K$

$[K_P = K_C$; for any value of $\Delta n_g]$

Ex.4 $C(s) + O_2(g) \rightleftharpoons CO_2(g)$

Mole of O_2 and CO_2 are 5 mole and 10 mole at equilibrium respectively, then find K_P & K_C for above reaction.

Sol. Partial pressure = Mole fraction × Total pressure

$$P_{CO_2} = X_{CO_2}.P_T = \frac{n_{CO_2}}{n_T} \times P_T = \frac{10}{15} \times P_T$$

$$P_{O_2} = X_{O_2}.P_T = \frac{n_{O_2}}{n_T} \times P_T = \frac{5}{15} \times P_T$$

$$K_P = \frac{P_{CO_2}}{P_{O_2}}$$

$$K_P = \frac{\frac{10}{15} \times P_T}{\frac{5}{15} \times P_T} = 2$$

$\because$ $K_P = K_C\,(RT)^{\Delta n_g}$

$$K_C = \frac{K_P}{(RT)^{\Delta n_g}} = \frac{2}{(RT)^0} = 2$$

Ex.5 Find the values of K_c for each of the following equilibria from the value of K_p.

(a) $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$ $K_p = 1.8 \times 10^{-2}$ atm at 600 K

(b) $CaCO_3\,(s) \rightleftharpoons CaO\,(s) + CO_2\,(g)$ $K_p = 167$ atm at 1173 K

Sol. *(a)* $2NOCl\,(g) \rightleftharpoons 2NO\,(g) + Cl_2\,(g)$

$K_p = 1.8 \times 10^{-2}$ atm and $\Delta n_g = 3 - 2 = 1$

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

$$\therefore \quad K_c = \frac{K_p}{RT} = \frac{1.8 \times 10^{-2}}{0.0821 \times 600} = 3.65 \times 10^{-4}\ M$$

(b) $K_p = 167$ atm and $\Delta n_g = 1$

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

$$\therefore \quad K_c = \frac{K_p}{RT} = \frac{167}{0.0821 \times 1173} = 1.734\ M$$

Ex.6 In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ the concentration of H_2, I_2 and HI at equilibrium are 10.0, 6.0 and 28 moles per litre respectively. What will be the equilibrium constant?

(A) 30.61 (B) 13.066 (C) 29.40 (D) 20.90

Sol.(B)

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

Applying law of mass action,

$$K_c = \frac{[HI]^2}{[H_2][I_2]}$$

Given $[H_2] = 10 \text{ mol } L^{-1}$
$[I_2] = 6.0 \text{ mol } L^{-1}$
$[HI] = 28.0 \text{ mol } L^{-1}$

So, $K_c = \frac{(28.0)^2}{(10)\times(6.0)} = 13.066$

Ex.7 For a gas phase reaction at equilibrium,

$3H_2(g) + N_2(g) \rightleftharpoons 2NH_3(g)$, the partial pressures of H_2 and N_2 are 0.4 and 0.8 atmosphere respectively. The total pressure of the entire system is 2.4 atmosphere. What will be the value of K_P if all the pressures are given in atmosphere ?

(A) 32 atm^{-2} (B) 20 atm^{-2} (C) 28.125 atm^{-2} (D) 80 atm^{-2}

Sol.(C)

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

Partial pressures at equilibrium

$0.8 \quad 0.4 \quad [2.4 - (0.8 + 0.4) = 1.2]$

Applying law of mass action,

$$K_P = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{1.2\times1.2}{0.8\times0.4\times0.4\times0.4} \Rightarrow K_P = 28.125 \text{ atm}^{-2}$$

Ex.8. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; Correct option for reaction is/are :

(a) $K_p = K_c$
(b) $K_p > K_c$
(c) $K_p < K_c$
(d) *any of these, depending on temperature.*

Sol.(D)

If (d) option is not given, then the answer is (b) because $\frac{1}{R} \approx 12.2\text{K}$ *which is very low relative to room temperature.*

Ex.9. For which of the following reactions, $K_p > K_c$ at 25°C (298K)

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

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

(c) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_2(g)$

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

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

Sol. (b, d, e)

Ex.10. For a gaseous reaction $K_p = 0.4$ atm^3 at 27°C. Calculate K_c.

Sol. $K_p = K_c\,(RT)^{(3)}$

$0.4 = K_C(0.0821 \times 300)^3$

$K_C = 2.6 \times 7 \times 10^{-8}\ M^3$

---

6. Characteristics of equilibrium constant :

(i) The expression for equilibrium constant K is applicable only when concentrations of the reactants and products have attained their equilibrium values and do not change with time.

(ii) The value of equilibrium constant is independent of initial concentration of the reactants and product.

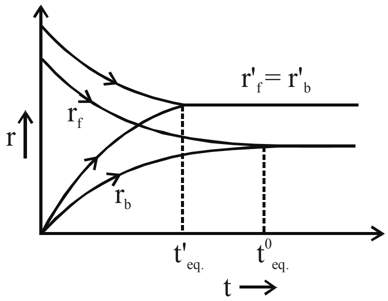
(iii) Equilibrium constant has one unique value for a particular reaction represented by a balanced equation at a given temperature.

(iv) Value of equilibrium constant is not affected by catalyst. Catalyst simply helps in attaining equilibrium earlier.

The relative increase in the rate of forward as well as backward reaction remaine same on using the catalyst.

$$K_{eq.}\ \text{uncatalyst} = \frac{K_f}{K_b}$$

$$K_{eq.}\ \text{catalyst} = \frac{K_f \times x}{K_b \times x} = \frac{K_f}{K_b} = K_{eq.}\ \text{(uncatalyst)}$$



6.1 Factor affecting the equilibrium constant :

(A) Mode of representation of the reaction :

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

The equilibrium constant for the reaction

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

If the reaction is reversed

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

then, $K_c' = \dfrac{[A][B]}{[C][D]}$

The two equilibrium constant related as ; $K_c = \dfrac{1}{K_c'}$

If the reaction is reversed, the value of the equilibrium constant is inversed.

(B) Stoichiometry of the reaction :

When a reversible reaction can be written with the help of two or more stoichiometric equation, the value of equilibrium constant will be numerically different.

(i) For reaction, $2NO_2 \rightleftharpoons N_2 + 2O_2$

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

For reaction $NO_2 \rightleftharpoons \frac{1}{2}N_2 + O_2$

$$K_c' = \frac{[N_2]^{\frac{1}{2}}[O_2]}{[NO_2]}$$

The two constants are related as $K_c' = \sqrt{K_C}$

(ii) For reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

$$K_p = \frac{P_{HI}^2}{P_{H_2}.P_{I_2}}$$

For reaction $2H_2(g) + 2I_2(g) \rightleftharpoons 4HI(g)$

$$K_P' = \frac{P_{HI}^4}{P_{H_2}^2.P_{I_2}^2}$$

The two constants are related as $K_p' = K_p^2$.

In general, $nH_2(g) + nI_2(g) \rightleftharpoons 2nHI(g)$

$K' = K^n$

When the coefficient of a balanced equation are multiplied by a common factor 'n', the equilibrium constant must be raised to the respective factor, K_{eq}^n.

(C) Addition the reaction :

$N_2 + O_2 \rightleftharpoons 2NO$ ....(i)

$2NO + O_2 \rightleftharpoons 2NO_2$ ....(ii)

For the 1st step, $K_1 = \frac{[NO]^2}{[N_2][O_2]}$

For the 2nd step, $K_2 = \frac{[NO_2]^2}{[NO]^2[O_2]}$

from eq. (i) + (ii)

$N_2 + 2O_2 \rightleftharpoons 2NO_2$

For this reaction, $K = \frac{[NO_2]^2}{[N_2][O_2]^2}$

the above reaction is related as

$$\therefore \quad K_1 \times K_2 = \frac{[NO]^2}{[N_2][O_2]} \times \frac{[NO_2]^2}{[NO]^2[O_2]} = \frac{[NO_2]^2}{[N_2][O_2]^2} = K$$

If there is addition of two reaction then the equilibrium constant is multiplied.

(D) Subtract the reaction :

$$A_{(g)} \rightleftharpoons B_{(g)} \qquad ....(i)$$
$$C_{(g)} \rightleftharpoons D_{(g)} \qquad ....(ii)$$

For the (i) step, $K_1 = \frac{[B]}{[A]}$

For the (ii) step, $K_2 = \frac{[D]}{[C]}$

from eq. (i) – (ii)

$A + D \rightleftharpoons B + C$

For this reaction, $K = \frac{[B][C]}{[A][D]}$

the above reaction is related as , $K = \frac{K_1}{K_2} = \frac{[B]}{[A]} \times \frac{[C]}{[D]} = K$

If we subtract of two reaction, then the equilibrium constant will be divided.

Ex.11 What should be the equilibrium constant for the reaction HI $\rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$ if the equilibrium constant for the reaction $H_2 + I_2 \rightleftharpoons 2HI$ at 444° C is 64 ?

(A) 64 ***(B) 8*** ***(C) 0.12*** ***(D) 0.81***

Sol. $H_2 + I_2 \rightleftharpoons 2HI \qquad HI \rightleftharpoons \frac{1}{2}H_2 + \frac{1}{2}I_2$

$$K_1 = \frac{[HI]^2}{[H_2][I_2]} \qquad K_2 = \frac{[H_2]^{1/2}[I_2]^{1/2}}{[HI]}$$

Therefore, $K_2 = \frac{1}{\sqrt{K_1}} = \frac{1}{\sqrt{64}} = \frac{1}{8} = 0.12$

(E) Equilibrium constant depends upon the temperature.

The equilibrium constant of a particularly balanced reaction depends only on temperature. It is independent from all other factor like amount of components, concentration, pressure, volume etc.

$$K_{eq.} = \frac{K_f}{K_b}$$

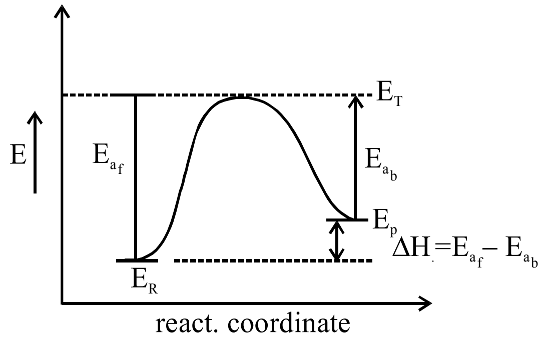
And rate constant, $K = A \cdot e^{-E_a/RT}$

Now, $$K_{eq.} = \frac{K_f}{K_b} = \frac{A_f.e^{-E_{a_f}/RT}}{A_b.e^{-E_{a_b}/RT}} = \frac{A_f}{A_b} \cdot e^{-(Ea_f - Ea_b)/RT}$$

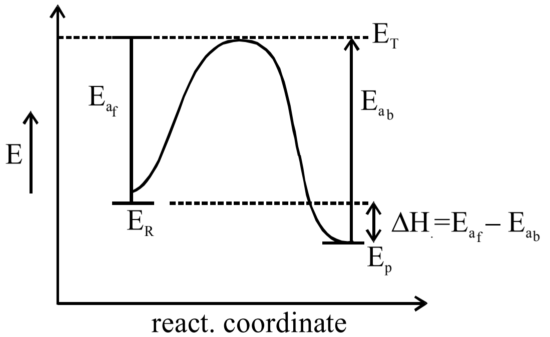
$$K_{eq.} = A \cdot e^{-\Delta H/RT} \text{ (Van't Hoff's equation)}$$

where $A = \frac{A_f}{A_b}$ = constant

and $\Delta H = E_{a_f} - E_{a_b}$



react. coordinate
(Endothermic reaction)



react. coordinate
(Exothermic reaction)

If K_1 and K_2 be the equilibrium constants of a reaction at absolute temperatures T_1 and T_2, then

$$\ell n\frac{K_2}{K_1} = \frac{\Delta H}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

On increasing the temperature the rate constant of reaction increases. But the reaction with higher activation energy is more sensitive towards temperature change. For the reaction of higher activation energy the value of rate contact increases largely on increasing temperature as well as the rate constant decreases largely as decrease in temperature.

For endothermic reaction

$\Delta H = E_{a_f} - E_{a_b} = +ve$

$\Rightarrow \quad T\uparrow ;\ K_{eq.} = \dfrac{K_f \uparrow}{K_b \uparrow}$ (K_f larger increasing and hence $K_{eq.}$ increase)

For exothermic reaction

$\Delta H = E_{a_f} - E_{a_f} = -ve$

$\Rightarrow \quad T\uparrow ;\ K_{eq.} = \dfrac{K_f \uparrow}{K_b \uparrow}$ (K_b larger increasing and hence $K_{eq.}$ decreases)

Ex.12 The equilibrium constant for the reaction $H_2(g) + S(s) \rightleftharpoons H_2S(g)$; is 18.5 at 925 K and 9.25 at 1000 K respectively. The enthalpy of the reaction will be :

(A) – 68000.05 J mol^{-1} ***(B) –71080.57 J mol^{-1}***

(C) – 80071.75 J mol^{-1} ***(D) 57080.75 J mol^{-1}***

Sol.(B)

Using the relation,

$$log\ \frac{K_2}{K_1} = \frac{\Delta H}{2.303R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$log\ \frac{9.25}{18.5} = \frac{\Delta H}{2.303 \times 8.314} \times \frac{75}{925 \times 1000}$$

$$-0.301 = \frac{\Delta H \times 75}{2.303 \times 8.314 \times 925 \times 1000} \Rightarrow \Delta H = -71080.57\ J\ mol^{-1}.$$

Ex.13. The equilibrium $2A + B_2 \rightleftharpoons 2AB$ involves the two component equilibria,

$A + B_2 \rightleftharpoons AB + B$ and $A + B \rightleftharpoons AB$ with respective equilibrium constants K_1 and K_2. How is the equilibrium constant, K, for the overall equilibrium related to K_1 and K_2?

(A) $K = K_1 + K_2$ (B) $K = K_1K_2$ (C) $K = K_1/K_2$ (D) $K/_2 = K_1K_2$

Sol. *(B)*

Ex.14. For the reactions :

$2NO \rightleftharpoons N_2 + O_2$ $\quad KC_1 = 2.4 \times 10^{30}$

$NO + \frac{1}{2}Br \rightleftharpoons NOBr$ $\quad KC_2 = 1.4$

$\frac{1}{2}N_2 + \frac{1}{2}O_2 + \frac{1}{2}Br_2 \rightleftharpoons NOBr$ $\quad K_{C_3} = x$ ***Find the value of x.***

Sol. *9.04×10^{-16}*

Ex.15. From the following data :

(i) $H_2(g) + CO_2(g) \rightleftharpoons H_2O(g) + CO(g)$ $\quad K_{2000K} = 4.4$

(ii) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$ $\quad K_{2000K} = 5.31 \times 10^{-10}$

(iii) $2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)$ $\quad K_{1000K} = 2.24 \times 10^{22}$

State whether the reaction (iii) is exothermic or endothermic?

Sol. *Equation (iii) = – [2 × (i) + (ii)]*

$$\therefore \quad K_{2000(iii)} = \frac{1}{K_1^2K_2} = \frac{1}{(4.4)^2 \times 5.31 \times 10^{-10}} = 9.7 \times 10^7$$

$\therefore \quad T \uparrow K \downarrow \quad \Rightarrow$ *reaction is exothermic.*

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7. APPLICATION OF EQUILIBRIUM CONSTANT :

(I) Predicting the extent of a reaction
(II) Predicting the direction of the reaction and
(III) Calculating equilibrium composition.

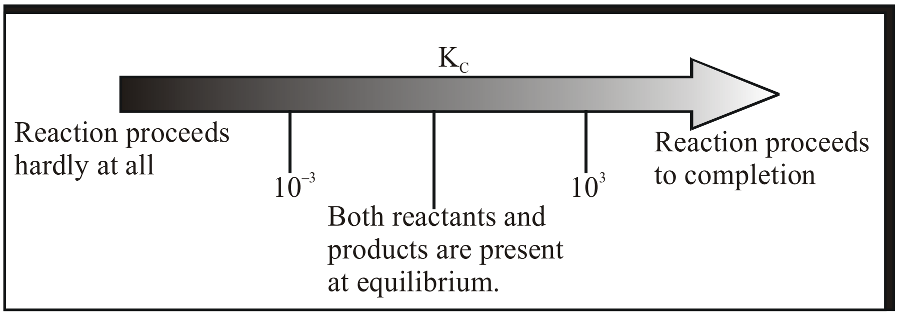
7.1 Predicting the extent of reaction :

The numerical value of the equilibrium constant for a reaction indicates the extent of the reaction. But it is important to note that an equilibrium does not give any information about the rate at which the equilibrium is reached. The magnitude of K_c or K_p is directly proportional to the concentrations of products (as these appear in the numerator of equilibrium constant expression) and inversely proportional to the concentrations of the reactants (these appear in the denominator). This implies that a high value of K is suggestive of a high concentration of products and vice-versa. We can make the following generalisations concerning the composition of equilibrium mixtures:

(i) If $K_c > 10^3$, products predominate over reactants. If K_c is very large, the reaction proceeds almost all the way to completion.

(ii) If $K_c < 10^{-3}$, reactants predominate over products. If K_c is very small, the reaction proceeds hardly at all.

(iii) If K_c is in the range 10^{-3} to 10^3, appreciable concentration of both reactants and products are present.



Ex.16 In the following cases which is predominant (reactant or product) for the given value of K_c.

(a) $H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$***, at 300K has*** $K_c = 4.0 \times 10^{31}$.

(b) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$***, at 298 K has*** $K_c = 4.8 \times 10^{-31}$.

(c) $N_2O_4 \rightleftharpoons 2NO_2$ ***, at 298 K has*** $K_c = 4.64 \times 10^{-3}$.

Sol. (a) If $K_c > 10^3$, products predominate over reactants. If K_c is very large, the reaction proceeds almost all the way to completion.

(b) If $K_c < 10^{-3}$, reactants predominate over products. If K_c is very small, the reaction proceeds hardly at all.

(c) Also, gas phase decomposition of N_2O_4 to NO_2 is another reaction with a value of $K_c = 4.64 \times 10^{-3}$ at 25°C which is neither too small nor too large. Hence, equilibrium mixtures contain appreciable concentrations of both N_2O_4 and NO_2.

7.2 Predicting the direction of the Reaction :

The equilibrium constant is also used to find in which direction, the reaction mixture of reactants and products will proceed. For this purpose, we calculate the reaction quotient, Q. The reaction quotient is defined in the same way as the equilibrium constant (with molar concentrations to give Q_C, or with partial pressure to give Q_P) at any stage of reaction. For a general reaction:

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

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

Then, if $Q_C > K_c$, the reaction will proceed in the direction of reactants (reverse reaction).

if $Q_C < K_c$, the reaction will move in the direction of the products

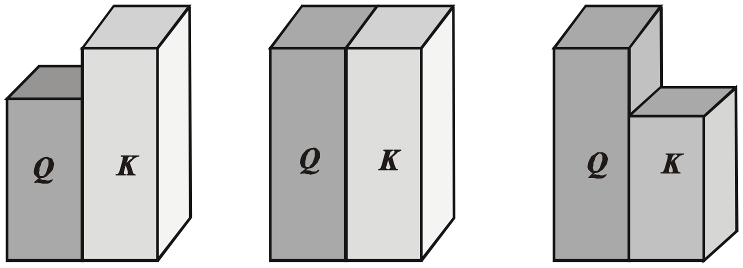
if $Q_C = K_c$, the reaction mixture is already at equilibrium.

In the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$, if the molar concentrations of H_2 , I_2 and HI are 0.1 M, 0.2 M and 0.4 M, respectively at 783 K, then reaction quotient at this stage of the reaction is

$$Q_C = \frac{[HI]^2}{[H_2][I_2]} = \frac{(0.4)^2}{(0.1)(0.2)} = 8$$

K_C for this reaction at 783 K is 46 and we find that $Q_C < K_C$. The reaction, therefore, will move to right i.e. more $H_2(g)$ and $I_2(g)$ will react to form more HI (g) and their concentration will decrease till $Q_C = K_C$.

Thus, a reaction has a tendency to form products if Q < K and to form reactants if Q > K.



Reactants → Products
Q < K
(Forward reaction)

Equilibrium
Q = K
(At equilibrium)

Reactants ← Products
Q > K
(Reverse reaction)

Ex.17. For the reaction $NOBr\ (g) \rightleftharpoons NO(g) + \frac{1}{2} Br_2\ (g)$

$K_P = 0.15$ atm at 90°C. If NOBr, NO and Br_2 are mixed at this temperature having partial pressures 0.5 atm, 0.4 atm and 2.0 atm respectively, will Br_2 be consumed or formed ?

Sol. $$Q_P = \frac{[P_{Br_2}]^{1/2}[P_{NO}]}{[P_{NOBr}]} = \frac{[0.20]^{1/2}[0.4]}{[0.50]} = 0.36$$

$\therefore\ K_P = 0.15$

Hence, reaction will shift in backward direction

$\therefore$ Br_2 will be consumed

Ex.18. Predict weather 1% CO_2 in air be sufficient to prevent any loss in weight of $MgCO_3$ or not.

Sol. $MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g) \qquad K_P = 0.095$ atm

$$Q = \frac{P_{CO_2}}{1} = P_{CO_2} = X_{CO_2} \cdot 1_{total}$$

$$\frac{1}{100} \times 1\,atm = 0.01\,atm. < K_P$$

It will go in forward direction

0.1% CO_2 is not sufficient

Ex.19. Predict weather $CuSO_4.5H_2O(s)$ be efflorescent or $CuSO_4.3H_2O(s)$ be hydroscopic and vapour pressure of H_2O at 25°C = 0.04 atm.

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

Partical pressure of H_2O at eq. $= P_{H_2O}$

$$K_p = P^2_{H_2O}$$

$$P_{H_2O} = \sqrt{4\times10^{-4}} = 2\times10^{-2}\text{atm}$$

$Q = 4 \times 10^{-2}$ atm

So, $CuSO_4.3H_2O$ be hydroscopic in this condition.

Ex.20. In above problem what maximum humidity for which $CuSO_4.5H_2O(s)$ work as efflorescent.

Sol. $$\left(0.04\times\frac{x}{100}\right)^2 < 4\times10^{-4}$$

$$0.16\times1.0^{-4}\times\frac{x^2}{10000} < 4\times10^{-4}$$

$x^2 < 50$

$x < 50\%$

Max. R.H. = 50% Ans.

Ex.21. Study the following reaction

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

B. $3H_2O(s) \rightleftharpoons B(s) + 3H_2O(g)$ $K_P = 2.7 \times 10^{-5}$ atm^3

C. $4H_2O(s) \rightleftharpoons C(s) + 4H_2O(g)$ $K_P = 2.56 \times 10^{-6}$ atm^4

(i) Which of the following is best dehydrating drying agent.

(A) $A.2H_2O(g)$	(D) A(s)
(B) $B.3H_2O(g)$	(E) B(s)
(C) $C.4H_2O(g)$	(F) C(s)

$A \to K_P = P^2_{H_2O} \Rightarrow P_{H_2O} = 0.02\,\text{atm}$

$B \to K_P = P^3_{H_2O} \Rightarrow P_{H_2O} = 0.03\,\text{atm}$

$C \to K_P = P^4_{H_2O} \Rightarrow P_{H_2O} = 0.04\,\text{atm}$

For the best dehydrating agent the moisture remained must be minimum.

(ii) If A(s), B(s) and C(s) are placed in a room where $P_{H_2O}(g) = 0.025\,\text{atm}$, which will act as dehy drating agent.

(A) A(s) (B) B(s) & C (s) (C) B(s) (D) All

(iii) Which of the following will be efflorescent at 7.5% R.H. if aqueous terim = 0.04 atm.

(a) Only A. $2H_2O$ (s)	(b) Only B. $3H_2O(s)$
(c) Only C. $4H_2O$ (s)	(d) Only A. $2H_2O(s)$ & B. $3H_2O(s)$
(e) Only B. $3H_2O(s)$ & C. $4H_2O(s)$	

Sol. (i) D (ii) A (iii) C

7.3 Calculating equilibrium concentrations :

In case of a problem in which we know the initial concentrations but do not know any of the equilibrium concentrations, the following three steps shall be followed :

Step 1. Write the balanced equation for the reaction.

Step 2. Under the balanced equation, make a table that lists for each substance involved in the reaction :

(a) the initial concentration,

(b) the change in concentration on going to equilibrium, and

(c) the equilibrium concentration.

In constructing the table, define x as the concentration (mol/L) of one of the substances that reacts on going to equilibrium, then use the stoichiometry of the reaction to determine the concentrations of the other substances in terms of x.

Step 3. Substitute the equilibrium concentrations into the equilibrium equation for the reaction and solve for x. If you are to solve a quadratic equation choose the mathematical solution that makes chemical sense.

Step 4. Calculate the equilibrium concentrations from the calculated value of x.

Step 5. Check your results by substituting them into the equilibrium equation.

7.3.1 Some General Equilibrium Expressions :

(a)

	H_2 (g)	+ I_2 (g)	$\rightleftharpoons$ 2HI (g)
Initially mol	a	b	0
At equilibrium	(a–x)	(b–x)	2x

$$K_c = \frac{[HI]^2}{[H_2][I_2]} = \frac{\left(\frac{2x}{V}\right)^2}{\left(\frac{a-x}{V}\right)\left(\frac{b-x}{V}\right)} = \frac{4x^2}{(a-x)(b-x)}$$

$$K_p = \frac{(p_{HI})^2}{p_{H_2} \times p_{I_2}} = \frac{\frac{(2x)^2}{(a+b)^2}P^2}{\left(\frac{a-x}{a+b}.P\right)\left(\frac{b-x}{a+b}.P\right)} = \frac{4x^2}{(a-x)(b-x)}$$

So $K_c = K_p$ $(\Delta n_g = 0)$

(b) $2NO\,(g) \rightleftharpoons N_2\,(g) + O_2\,(g)$

	$2NO\,(g)$	$N_2\,(g)$	$O_2\,(g)$
Initially mol	a	0	0
At equilibrium	(a–x)	x/2	x/2

$$K_c = \frac{[N_2][O_2]}{[NO]^2} = \frac{x/2 \times x/2}{(a-x)^2} = \frac{x^2}{4(a-x)^2} = K_P \qquad (\Delta n_g = 0)$$

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

	$CH_3COOH(\ell)$	$C_2H_5OH(\ell)$	$CH_3COOC_2H_5(\ell)$	$H_2O(\ell)$
Initially mol	a	b	0	0
At equilibrium	(a–x)	(b–x)	x	x

$$K_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]} = \frac{x^2}{(a-x)(b-x)}$$

K_p should not be given for this reaction ,

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

	$PCl_5\,(g)$	$PCl_3\,(g)$	$Cl_2\,(g)$
Initially mol	a	0	0
At equilibrium	(a–x)	x	x
Active mass	$\frac{(a-x)}{v}$	$\frac{x}{v}$	$\frac{x}{v}$

$$K_c = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{\frac{x}{v}\times\frac{x}{v}}{\frac{(a-x)}{v}} = \frac{x^2}{(a-x)v}$$

$$K_p = \frac{p_{PCl_3}\times p_{Cl_2}}{p_{PCl_5}} = \frac{\left(\frac{x}{a+x}.P\right)\times\left(\frac{x}{a+x}.P\right)}{\left(\frac{a-x}{a+x}\right)P} = \frac{x^2P}{(a+x)(a-x)} = \frac{x^2P}{a^2-x^2}$$

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

	$N_2\,(g)$	$3H_2\,(g)$	$2NH_3\,(g)$
Initially mol	a	b	0
At equilibrium	(a–x)	(b–3x)	2x
Active mass	$\frac{(a-x)}{v}$	$\left(\frac{b-3x}{v}\right)$	$\left(\frac{2x}{v}\right)$

$$K_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{\left(\frac{2x}{v}\right)^2}{\left(\frac{a-x}{v}\right)\left(\frac{b-3x}{v}\right)^3} = \frac{4x^2V^2}{(a-x)(b-3x)^3}$$

$$K_p = \frac{(p_{NH_3})^2}{p_{N_2}\times(p_{H_2})^3} = \frac{\left[\frac{2xP}{a+b-2x}\right]^2}{\left[\frac{(a-x)P}{(a+b-2x)}\right]\left[\frac{(b-3x)P}{(a+b-2x)}\right]^3} = \frac{4x^2(a+b-2x)^2}{(a-x)(b-3x)^3P^2}$$

(g) Equilibrium constant expressions in term of 'α'

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

	$PCl_5(g)$	$PCl_3(g)$	$Cl_2(g)$
Initial moles	1	–	–
At. Eq.	1–α	α	α

$$K_C = \frac{\alpha^2}{1-\alpha}\left(\frac{1}{V}\right) \quad \text{and} \quad K_P = \frac{\alpha^2}{1-\alpha^2}P_T$$

(h) Degree of dissociation in terms of molar mass and vapour density

(i) $A(g) \rightleftharpoons nB(g)$

$$\alpha = \frac{M_T - M_O}{M_O(n-1)} \quad \text{or} \quad \alpha = \frac{D_T - D_O}{D_O(n-1)}$$

M_T = Theoretical molar mass of reactant

M_O = Observed molar mass of mixture

$$D_T = \frac{M_T}{2} \quad \text{and} \quad D_O = \frac{M_O}{2}$$

(ii) $nA(g) \rightleftharpoons A_n(g)$

$$\alpha = \frac{M_T - M_O}{M_O\left(\frac{1}{n} - 1\right)}$$

Ex.22 5 moles H_2 gas and 5 moles iodine-vapours are taken in vessel of 10 L capacity. Determine the moles of each at equilibrium.

Sol $H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K = 49$

$$49 = \frac{(2x)^2 v^2}{(5-x)(5-x)v^2}$$

$$49 = \frac{(2x)^2}{(5-x)^2}$$

$$7 = \frac{2x}{5-x}$$

$35 - 7x = 2x$

$35 = 9x$

$$x = \frac{35}{9}$$

Moles at equilbrium = $\frac{10}{9}, \frac{10}{9}, \frac{70}{9}$

Ex.23 How many moles of H_2 (g) should be mixed with each mole I_2 vapours in order to convert 90% of it into HI.

Sol. $H_2(g) + I_2(g) \rightleftharpoons 2HI(g) \qquad K = 50$

$x \qquad 1$

$x - a \qquad 0.1 \qquad 1.8$

$$50 = \frac{3.24}{(x-0.9)(0.1)} \Rightarrow x = 1.548$$

Ex.24 2 moles of $PCl_5(g)$ is taken in 10 ℓ vessel. Calculate its concentration at equilibrium.

Sol. $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad K = 0.2\ M$

$2 - x \qquad x \qquad x$

$\frac{2-x}{v} \qquad \frac{x}{v} \qquad \frac{x}{v}$

$$0.2 = \frac{\left(\frac{x}{v}\right)^2}{\left(\frac{2-x}{v}\right)} \Rightarrow x = 1.24$$

$[PCl_5] = 0.076\ M$

$[PCl_3] = 0.124\ M$

$[Cl_2] = 0.124\ M$

Ex.25 1 : 3 molar ratio mixture of N_2 and H_2 yields 20% by mole NH_3 at 30 atm; calculate K_P for the equilibrium represented by

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

$0 \quad a \quad 3a \quad 0$

$t \quad (a-x) \quad 3(a-x) \quad 2x$

Total moles $= 4a - 2x$

$$X_{NH_3} = 0.2 = \frac{2x}{4a-2x} \Rightarrow 2x = 0.8a - 0.4x \Rightarrow x = a/3$$

$P_{NH_3} = 0.2 \times 30 = 6$ atm

$$P_{NH_3} = X_{N_2} \times P_T = \frac{a-x}{4a-2x} \times 30 = 0.2 \times 30 = 6\,\text{atm}$$

$$P_{H_2} = \frac{3(a-x)}{4a-2x} = 0.6 \times 30 = 18\,\text{atm}$$

$$\therefore \quad K_P = \frac{[P_{NH_3}]^2}{[P_{N_2}][P_{H_2}]^3} = \frac{6}{6 \times (18)^2} = 1.03 \times 10^{-3}\ \text{atm}^{-2}$$

Ex.27 An air sample containing 21:79 (mole ratio) of O_2 ***& N_2 is heated to 2400^{0}C. If the mole percent of NO at equilibrium is 1.8%, calculate K_P for the reaction $N_2 + O_2 \rightleftharpoons 2NO$.***

Sol. *At t = t*

$$\begin{array}{cccc} N_2 & + & O_2 & \rightleftharpoons & 2NO \\ 0.79 - P & & 0.21 - P & \rightleftharpoons & 2P \end{array}$$

$$X_{NO} = 0.018$$

$$P_{NO} = 0.018 \times P_T$$

$$2P = 0.018 \times P_T \qquad [\because \Delta n = 0 \Rightarrow P_T = 1atm]$$

$$P = \frac{0.018 \times 1}{2} = 0.009$$

$$K_P = \frac{[P_{NO}]^2}{P_{N_2} \times P_{O_2}} = \frac{(0.018)^2}{(0.781)(0.201)} = 2.06 \times 10^{-3}$$

Ex.28 Calculate the degree of dissociation of $PCl_5(g)$ at 20 atm.

Sol.

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad K = 0.8 \text{ atm.}$$

$$\begin{array}{ccc} x & 0 & 0 \\ x - a & a & a \end{array}$$

Total mole = x + a

$$\frac{x-a}{x+a}(20) \qquad \frac{a}{x+a}20 \qquad \frac{a}{x+a}20$$

$$0.8 = \frac{\left(\frac{a}{x+a}\right)^2 (20)^2}{\left(\frac{x-a}{x+a}\right)20} \Rightarrow 0.04 = \frac{a^2}{x^2 - a^2}$$

$$\frac{x}{a} = \frac{1}{\sqrt{26}} = 0.2$$

$$\alpha = 0.2$$

Ex.28 The vapour density a sample of N_2O_4 (g) is 40 at 10 atm. Calculate K_P for the reaction.

Sol.

$$\begin{array}{lcc} & N_2O_4 & \rightleftharpoons 2NO_2(g) \\ \text{Initial} & a & 0 \\ a - x & 2x & \end{array}$$

Total mole = (a – x) + 2x = a + x

$$\frac{a-x}{a+x}P \qquad \frac{2x}{a+x}P$$

$$V.D. = \frac{M_{avg}}{2}$$

$$M_{avg} = 2 \times 40 = 80$$

$$M_{avg} = \frac{\text{Total mass}}{\text{Total moles}} = \frac{92a}{a+x} = 80$$

$$x = \frac{12}{80}a = 0.15a$$

$$K_P = \frac{4x^2}{a^2 - x^2} = 9.2 \times 10^{-2}$$

Ex.29 At what pressure an equimolar mixture of PCl_5 *(g)* ***and*** $Cl_2(g)$ ***should be taken in order to convert 75% of*** PCl_3 ***into*** PCl_5.

Sol.

	$PCl_3(g)$	+	$Cl_2(g) \rightleftharpoons$	$PCl_5(g)$	$K_P = 0.4$ atm
Initial	a		0		
Final	a – 0.75 a = 0.25a		a – 0.75a = 0.25a	0.75a	

Total mole = 1.25a

Equ. par. pr.	$\frac{0.25a\times P}{1.25a}$	$\frac{0.25a\times P}{1.25a}$	$\frac{0.75a\times P}{1.25}$
	$\frac{P}{5}$	$\frac{P}{5}$	$\frac{3P}{5}$

$$K_P = \frac{P_{PCl_5}}{P_{PCl_3}P_{Cl_2}} \Rightarrow 0.4 = \frac{\frac{3P}{5}}{\frac{P}{5}\times\frac{P}{5}} \Rightarrow P = 37.5$$

But this is pressure at equilibrium but we have to find initial pressure
Now, from PV = nRT

$$\frac{P_1}{P_2} = \frac{n_1}{n_2} \Rightarrow \frac{P_1}{37.5} = \frac{2}{1.25} \Rightarrow P = 60 \text{ atm}$$

Alternate method :

	$PCl_3(g)$	+	$Cl_2(g) \rightleftharpoons$	$PCl_5(g)$
Initial partial pressure	P_0		P_0	0
E.P.P.	$P_0 - 0.75\ P_0$ $= 0.25P_0$		$P_0 - 0.75P_0$ $= 0.25P_0$	$0.75P_0$

$$0.4 = \frac{0.75P_0}{0.25P_0\times 0.25P_0} \Rightarrow P_0 = 30 \text{ atm}$$

$\therefore$ Initial total pressure of mixture = $P_0 + P_0 = 60$ atm

Note : In any problem related with relative extent of reaction, initial mole may be taken as 1 but the intial pressure or concentration should not be taken as 1.

Ex.30 100 gm $CaCO_3$ is taken in 30 ℓ empty vessel and the vessel is sealed and the sample is heated to 627°C. Calculate the mass % of $CaCO_3$ decomposed.

$$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g) \qquad K_P = 0.821 \text{ atm}$$

Sol.

	$CaCO_3(s) \rightleftharpoons$	$CaO(s)$ +	$CO_2(g)$
Initial1 mole	0	0	
Final	1 – x	x	x

Total mole = 1 + x

$$K_P = \frac{P_{CO_2}}{1} = P_{CO_2} \Rightarrow P_{CO_2} = \frac{n.RT}{V}$$

$$0.821 = \frac{x\times 0.0821\times 900}{30} \Rightarrow x = \frac{1}{3}$$

% of $CaCO_3$ decomposed = $\frac{1}{3}\times 100 = \frac{100}{3}\%$

Ex.31 ***Some solid ammonium carbomate NH_4COONH_4 is take in a evacuated vessel and the vessel is sealed after a very long time a constant pressure of 0.6 atm is observed due to dissociation of the solid into NH_3 and CO_2 gas. Calculate the dissociation constant of solid.***

Sol

NH_2COONH_4 $\rightleftharpoons$	$2NH_3(g)$	+	$CO_2(g)$
E.P.P.	2P		P
	= 0.4 atm		= 0.2 atm

$$K_P = \frac{[0.4]^2[0.2]}{1} = 0.032\ atm^3$$

Ex.32 ***Some solid ammonium hydrogen sulphide NH_4HS is a vessel containing ammonium gas at 0.5 atm. Calculate the equilibrium partial pressure of gas.***

Sol.:

$NH_4HS(s)$ $\rightleftharpoons$	$NH_3(g)$	+	$H_2S(g)$	$K_P = 0.24\ atm^2$
Initial	0.5 atm		0	
E.P.P.	0.5 + x		x	

$$K_P = \frac{P_{NH_3}}{1}\cdot P_{H_2S} \Rightarrow 0.24 = (0.5+x)x \quad \Rightarrow \quad x = 0.3\ atm.$$

Ex.33 ***0.6 moles of $H_2(g)$ and 0.4 moles of Br_2 vapour are allowed to reactant. Calculate the moles of each gas at equilibrium.***

Sol.

	$H_2(g)$	+	$Br_2(g)$ $\rightleftharpoons$	$2HBr(g)$	$K_P = 5 \times 10^8$
Initial	0.6 moles		0.4 moles	0	
Final	0.6 – x		0.4 – x	2x	

Total = 1 mole

$$K = \frac{(2x)^2}{(0.6-x)(0.4-x)} = \frac{4x^2}{x^2 - x + 0.24}$$

$(5 \times 10^8 - 4)x^2 - 5 \times 10^8x + 1.2 \times 10^8 = 0$

$5 \times 10^8x^2 - 5 \times 10^8x + 1.2 \times 10^8 = 0$

$8x^2 - x + 0.24 = 0$

x = 0.4, 0.6(Not acceptable)

As K_P is much larger than 1000 the reaction almost completes.

Final moles of HBr = 0.8

Final moles of H_2 = 0.2

But Final moles of $Br_2 \neq 0$

Note :

The final moles of Br_2 may be calculated by first completing the reaction in forwards direction and then achieving equilibrium from backward direction.

	$H_2(g)$	+	$Br_2(g)$ $\rightleftharpoons$	$2HBr(g)$
Initial	0.6		0.4	0
Final	0.2		0	0.8

	$2HBr$ $\rightleftharpoons$	H_2	+	$Br_2(g)$	$K' = \frac{1}{K} = 2\times10^{-9} << 10^{-3}$
	0.8	0.2		0	
Final	0.8 – y	$0.2 + \frac{y}{2}$		$\frac{y}{2}$	

$$K' = \frac{[H_2][Br_2]}{[HBr]^2} = 2\times10^{-9} = \frac{\left(0.2+\frac{y}{2}\right)\frac{y}{2}}{(0.8-y)^2}$$

As K' is very small we may assume that $0.8 - y \simeq 0.8$

and, $0.2 + \frac{y}{2} \simeq 0.2$

$$\therefore \quad 2\times10^{-9} = \frac{0.2\times\frac{y}{2}}{0.64}$$

$y = 1.28 \times 10^{-8}$

Final moles $HBr = 0.8 - y \simeq 0.8$

$$H_2 = 0.2 + \frac{y}{2} \simeq 0.2$$

$$Br_2 = \frac{y}{2} = 6.4 \times 10^{-9}$$

Ex.34 Calculate concentration of A at equilibrium for a reaction, $A(g) \rightleftharpoons B(g)$; $K_C = 10^{50}$, if the initial concentration of A is 2 M.

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

initial conc.	2	0
Change in conc.	– x	x
equib. conc.	2–x	0+x

K_C is very-very high so maximum reactant converted into product.

$$\because \quad \frac{K_C}{\text{initial conc.}} \geq 10^3 \ \textbf{then}\ \frac{10^{50}}{2} \geq 10^3 .$$

So $2–x \simeq 0 \Rightarrow x \simeq 2$ but reactant never zero.

equib. conc. $\quad 2–x \simeq y \qquad x \simeq 2$

$$K_C = \frac{[B]}{[C]}$$

$$10^{50} = \frac{x}{2-x}$$

$$10^{50} = \frac{2}{y} \Rightarrow y = 2 \times 10^{-50}\ M$$

$[A] = 2 \times 10^{-50}$ M

8. LE CHATELIER'S PRINCIPLE :

Le Chatelier's principle is applicable for any system in equilibrium which states as :

When a system in equilibrium is disturbed by external agency, the system tends to attain again an equilibrium by adjusting itself. These are these some factors by which a system in equilibrium can be disturbed.

(i) Changing the concentration of reactant and product.

(ii) Changing the pressure (or volume) of the system.

(iii) Changing the temperature.

For a chemical reaction in equilibrium, Le Chatelier's principle can be stated as,

If we change concentration, pressure or temperature of a chemical reaction in equilibrium, the equilibrium will shift to the right or the left so as to minimise the change.

8.1 Effect of a change in concentration :

(a) If more reactant is added or some product is removed from an equilibrium mixture having equilibrium constant K then the reaction moves in the forward direction (as $Q_c < K_C$) to give a new equilibrium and more products are produced.

(b) If more product are added to or some reactant are removed from an equilibrium mixture, the reaction moves in the reverse direction (as $Q_C > K_C$) to give a new equilibrium and more reactant are produced.

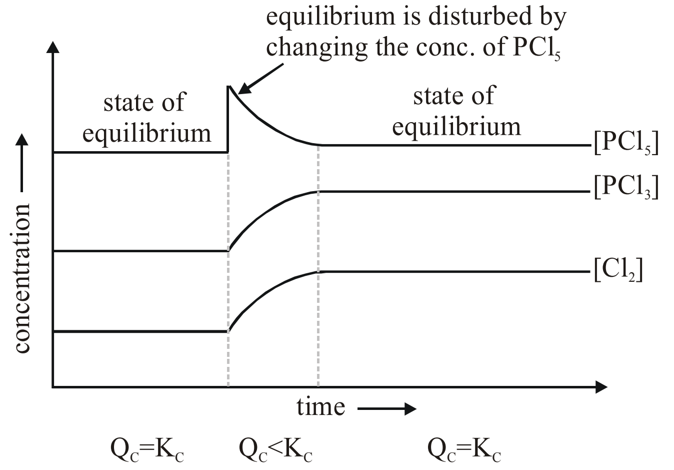
Ex. The decomposition of gaseous PCl_5 is a reversible reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$. Let the equilibrium concentrations of PCl_5, PCl_3 and Cl_2 are respectively $[PCl_5]$, $[PCl_3]$ and $[Cl_2]$. The K_C for this reaction can be written as :

$$K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]}$$ Also we know that at equilibrium $K_C = Q_C$.

Case-I : Let the concentration of PCl_5 is doubled to disturb the equilibrium. This will change the reaction quotient, Q_C to :

$$Q_C = \frac{[PCl_3][Cl_2]}{[2PCl_5]} = \frac{1}{2}\frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{K_C}{2}$$

After disturbing the equilibrium, the value of Q_C becomes less than K_C. In order to restore the Q_C value to K_C, the concentration of PCl_5 must be decreased while the concentrations of PCl_3 and Cl_2 are to be increased. This is achieved by favoring the forward reaction.

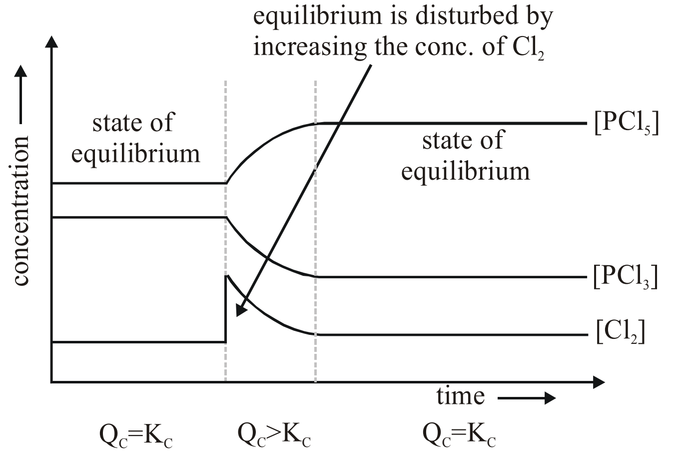


The forward reaction is also favored by removing the products from the reaction mixture (decrease in the concentration of products). Upon removal of products, the rate of forward reaction becomes greater than that of backward reaction momentarily. This will also decrease the reaction quotient. Hence the system tries to reestablish the equilibrium by converting more reactants to products so as to make the rates of both forward and backward reactions become equal again.

Case-II : For example, in case of the decomposition of PCl_5, if the concentration of Cl_2 is increased by two times at equilibrium, the Q_C value becomes greater than the K_C value.

$$Q_C = \frac{[PCl_3][2Cl_2]}{[PCl_5]} = 2x\frac{[PCl_3][Cl_2]}{[PCl_5]} = 2K_C$$

Hence the system tries to restore the value of Q_C to K_C again. The backward reaction is favored to decrease the concentration of Cl_2. However the concentration of PCl_3 also decreases automatically while the concentration of PCl_5 increases while doing so.



8.2 Effect of a change in pressure :

We know that, if we increase the volume of container then the pressure of the container decreases and if we decrease the volume of container then the pressure of the container increases.

i.e., Pressure (P) $\propto \frac{1}{\text{Volume (V)}}$

Hence, if the pressure is decreased by increasing the volume of a reaction mixture, the reaction shifts in the direction of more moles of gas while if the pressure is increased by decreasing the volume of a reaction mixture, the reaction shifts in the direction of fewer moles of gas.

Here moles of reactant or product means co-efficients of reactant or product.

(a) Suppose a general equation

	$A_3(g)$ +	$B_3(g)$	$\rightleftharpoons$	$3AB(g)$
at equi :	a M	b M		c M

For this reaction, moles of product > moles of reactant i.e., $[\Delta n = (3-2) > 0]$

$$K_C = \frac{(c)^3}{a \times b}$$

If we increase the pressure of the system from 0.5 atm pressure to 1 atm pressure by decreasing the volume of container from 5 litre to 2.5 litre. Hence, concentration of all the reactant and product will change and it will be greater than the initial value. Hence we can say that,

If pressure becomes double then volume becomes half and hence concentration becomes double as (Concentration $\propto \frac{\text{Moles}}{\text{Volume}}$)

∴ Concentration $\propto$ Pressure

$$Q_C = 2 \times \frac{c^3}{a \times b} > K_C$$

Hence reaction will move from right to left i.e., in the backward direction.

Hence,	$A_3(g)$ +	$B_3(g)$	$\rightleftharpoons$	$3AB(g)$
Moles at equi.	2a+x	2b+x		2c–3x

It can be simply said that, reaction will move from right to left by increasing the pressure of the system as moles of product > moles of reactant i.e., move in the direction of fewer moles.

(b) If pressure decreases from 1 atm to 0.5 atm. Volume will increase by factor 2 concentration will decrease by factor 1/2

Hence,	$A_3(g)$ +	$B_3(g)$	$\rightleftharpoons$	$3AB(g)$
changed conc.	a/2	b/2		c/2
at equi. conc.	a/2–x	b/2 – x		c/2 + 3x

$$Q_C = \frac{(c/2)^3}{a/2 \times b/2} = \frac{1}{2}\frac{c^3}{a \times b} < K_C$$

i.e., $Q_C < K_C$

Therefore, reaction will move from left to right and as moles of product > moles of reactants, therefore reaction will move from left to right by decreasing the pressure of the system i.e. move in the direction of greater moles.

(c) If moles of reactant = moles of product i.e., $\Delta n = 0$ then change in pressure of equilibrium mixture has no effect i.e. at this position $Q_C = K_C$ will always exist.

8.3 Effect of a change in temperature :

On increasing the temperature equilibrium shifts in the direction of absorption of heat (endothermic direction)

8.4 EFFECT OF INERT GAS AT THE EQUILIBRIUM :

(i) Effect of inert gas at constant volume :

When the addition of inert gas (non-reacting gas) is carried out at constant volume (V), the equilibrium remains unaffected for reactions whether they have $\Delta n = 0$ or $\Delta n \neq 0$.

Let us consider a general equation at temperature T K, and a, b, c and d are the moles of A, B, C and D respectively,

$$\begin{array}{lcccccc} & A & + & B & \rightleftharpoons & C & + & D \\ \text{conc.} & \frac{a}{V} & & \frac{b}{V} & & \frac{c}{V} & & \frac{d}{V} \end{array}$$

Since, V = constant, so addition of inert gas has no effect on equilibrium

$$\therefore \quad \frac{a}{V}, \frac{b}{V}, \frac{c}{V} \text{ and } \frac{d}{V} \text{ will not change}$$

$$Q_C = K_C \quad \text{or} \quad Q_P = K_p$$

(ii) Effect of inert gas at constant pressure :

(a) The addition of an inert gas at constant pressure to an equilibrium, the equilibrium shifts in the direction of greater number of moles.

At constant pressure, addition of inert gas or non-reacting gas means increase in volume of the system.

Suppose a reaction having $\Delta n > 0$ and a, b, c and d are the moles of A, B, C and D respectively and V be the volume before addition of inert gas.

$$\begin{array}{ccccc} A_3(g) & + & B_3(g) & \rightleftharpoons & 3AB(g) \\ \frac{a}{V} & & \frac{b}{V} & & \frac{c}{V} \end{array} \quad \text{[equilibrium conc. before addition of inert gas]}$$

Let us consider V' be the total volume of the system after addition of inert gas So, V' > V

$$\begin{array}{lccccc} & A_3(g) & + & B_3(g) & \rightleftharpoons & 3AB(g) \\ \text{conc. after addition of inert gas} & \frac{a}{V'} & & \frac{b}{V'} & & \frac{c}{V'} \end{array}$$

$$\therefore \quad \frac{a}{V'} < \frac{a}{V}, \frac{b}{V'} < \frac{b}{V} \text{ and } \frac{c}{V'} < \frac{c}{V}$$

$$\text{Now,} \quad K_c = \frac{\left(\frac{c}{V}\right)^3}{\left(\frac{a}{V}\right)\left(\frac{b}{V}\right)} = \frac{1}{V} \times \frac{c^3}{a \times b} \quad \text{and} \quad Q_c = \frac{\left(\frac{c}{V'}\right)^3}{\left(\frac{a}{V'}\right)\left(\frac{b}{V'}\right)} = \frac{1}{V'} \times \frac{c^3}{a \times b}$$

$K_c > Q_c$, hence reaction will move from left to right (forward direction) as $\Delta n > 0$ and similarly we can prove that for a reaction having $\Delta n < 0$

i.e., $3AB(g) \rightleftharpoons A_3(g) + B_3(g)$

For this reaction $K_c < Q_c$, after addition of inert gas. Hence, reaction will move from right to left (reverse direction) as $\Delta n < 0$.

8.5 APPLICATION OF LE-CHATELIER'S PRINCIPLE :

The principle is applicable not only to chemical equilibria but also to physical equilibria in similar way.

(a) Dissolution of ammonium chloride in water

$$\text{Heat} + NH_4Cl(s) + H_2O(\ell) \rightleftharpoons NH_4^+(aq) + Cl^-(aq)\ ;\ \Delta H = +ve$$

With rise in temperature, equilibrium will shift in direction which will lower the temperature counteract the effect. So, equilibrium shifts in forward direction which is endotherm reaction. Hence, solubility of NH_4Cl increases with rise in temperature.

(b) Dissolution of sodium hydroxide in water

$$NaOH(s) + H_2O(\ell) \rightleftharpoons Na^+(aq) + OH^-(aq) + \text{Heat}\ ;\ \Delta H = -ve$$

Sodium hydroxide dissolve in water with evolution of heat. Therefore, a rise in temperature will decrease its solubility. On the other hand, a decrease in temperature will increase the solubility of sodium hydroxide and reaction will shift in forward direction.

(c) Effect of pressure on boiling point :

$$\text{Water} \rightleftharpoons \text{Vapour}$$

An increase in pressure will favour backward reaction i.e., the reaction in which volume decreases ($V_{vap.} > V_w$). thus more water will exist at equilibrium (B.pt of solvent increase with increase in pressure). So decrease in pressure will shift the reaction forward.

(d) Effect of pressure on melting point :

$$\text{Ice} \rightleftharpoons \text{Water}$$

increase in pressure will favour forward reaction because $V_{ice} > V_{water}$. Thus more ice melt or the m.pt of ice is lowered with pressure.

For, $\text{Solid} \rightleftharpoons \text{Liquid}$

An increase in pressure will favour backward reaction because volume of liquid is more than solid thus more solid will exist at equilibrium (m.pt of solid increases with pressure).

(e) Effect of pressure on solubility of gases :

$$\text{gas} + H_2O \rightleftharpoons \text{solution}$$

increase in pressure favour forward reaction. [Henry's law]

(f) In solid reactants equilibrium will not shift to the right side even if the more reactants an added.

$$CaCO_{3(s)} \rightleftharpoons CaO_{(s)} + CO_{2(g)}$$

$$K_P = P_{CO_2}$$

Equilibrium will not be affected by adding CaO or $CaCO_3$ at that temperature. But if volume is increased the equilibrium will shift to the right side to keep the pressure of CO_2 constant.

(g) Effect of temperature on solubility

$$\text{Solute} + \text{solvent} \rightleftharpoons \text{solution} + \text{Heat}\ ;\quad \Delta H = +ve$$

An increase in temperataure favour endothermic or forward reaction i.e., solubility increases (urea, glucose).

$$\text{Solute} + \text{solvent} \rightleftharpoons \text{solution}\ ;\ \Delta H = -ve$$

In exothermic dissolution solubility decreases with temperature i.e., reaction will be in backward direction.

9. SIMULTANEOUS EQUILIBRIUM

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

$$\begin{array}{lllll}
\text{e.g.} & A(s) & \rightleftharpoons X(g) & + & Y(g) \\
t=0 & a & 0 & & 0 \\
t=\text{teq} & a-t & t & & t+u \\
 & B(s) & \rightleftharpoons Z(g) & + & Y(g) \\
 & b & 0 & & 0 \\
 & b-u & u & & u+t
\end{array}$$

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

$$K_{C_2} = (u+t)\,u$$

Ex.35 Two solid compounds A and B dissociate into gaseous products at 20°C as

(i) $A(s) \rightleftharpoons A'(g) + H_2S(g)$

(ii) $B(s) \rightleftharpoons B'(g) + H_2S(g)$

At 20°C, pressure over excess solid A is 50 mm and that over excess solid B is 68 mm find

(a) The dissociation constant of A and B

(b) Relative no. of moles of A and B in the vapour phase over a mixture of solid A and B.

(c) Show that the total pressure of the gas over the solid mixture would be 84.4 mm

Sol. $A(s) \rightleftharpoons A'(g) + H_2S(g)$ $\qquad$ $B(s) \rightleftharpoons B'(g) + H_2S(g)$

$A(s) \rightleftharpoons A'(g) + H_2S(g)$ $\quad P = 50\text{ mm} \quad \Rightarrow \quad P_{H_2S} = P_{A'} = \frac{P}{2} = 25\text{mm}$

$B(s) \rightleftharpoons B'(g) + H_2S(g)$ $\quad P = 68\text{ mm} \quad \Rightarrow \quad P_{H_2S} = P_{B'} = \frac{P}{2} = 34\text{mm}$

(i) $K_{P_1} = (25)^2 = 625\,\text{mm}^2$

$K_{P_2} = (34)^2 = 1156\,\text{mm}^2$

(ii) Ratio of moles is same as that of partial pressure so,

$$\begin{array}{ll}
A(s) & \rightleftharpoons A'(g) + H_2S(g) \\
P_1 & \qquad P_1 + P_2
\end{array}$$

$$\begin{array}{ll}
B(s) & \rightleftharpoons B'(g) + H_2S(g) \\
P_2 & \quad P_2 + P_1
\end{array}$$

$K_{P_1} = P_{A'} \times P_{H_2S} = P_1(P_1 + P_2)$ $\qquad$ *...(i)*

$K_{P_2} = P_{B'} \times P_{H_2S} = P_2(P_1 + P_2)$ $\qquad$ *...(ii)*

$$\frac{K_{P_1}}{K_{P_2}} = \frac{P_1}{P_2} = \frac{625}{1156}$$

(iii) total pressure = $P_1 + P_2 + (P_1 + P_2) = 2(P_1 + P_2)$

$(i) + (ii) = (P_1 + P_2)^2$

$\sqrt{K_{P_1} + K_{P_2}} = P_1 + P_2 \quad \Rightarrow \quad P_T = 2\sqrt{KP_1 + KP_2} = 84.4\,\text{mm}$

10. SEQUENTIAL EQUILIBRIUM

$$\begin{array}{lll} A(s) \longrightarrow B(g) + C(g) & & K_{C_1} = (x)(x-y) \\ a-x \qquad x \qquad x-y & & \end{array}$$

$$\begin{array}{lll} C(g) \longrightarrow D(g) & & K_{C_2} = \dfrac{y}{x-y} \\ x-y \qquad y & & \end{array}$$

Ex36. 102 g of solid NH4HS is taken in the 2L evacuated flask at 57°C. Following two equilibrium exist simultaneously

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

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

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 $NH_4HS = \frac{102}{51} = 2$

$$\begin{array}{llll} NH_4HS(s) \rightleftharpoons & NH_3(g) + & H_2S(g) & K_{C_1} \\ 2 & 1 & 0 & \\ 1-x & 0 & 1 & \end{array}$$

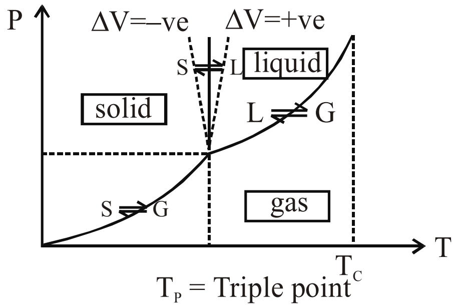
$$\begin{array}{llll} NH_3(g) \rightleftharpoons & \frac{1}{2}N_2(g) + & \frac{3}{2}H_2(g) & K_{C_2} \\ 1-x & \frac{x}{2} & \frac{3x}{3} & \end{array}$$

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

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

$$K_{C_3} = \frac{\left(\frac{3x}{4}\right)^{3/2}\left(\frac{x}{4}\right)^{1/2}}{\left(\frac{1-x}{2}\right)} = \frac{\left(\frac{3}{8}\right)^{3/2}\left(\frac{1}{4}\right)^{1/2}}{\left(\frac{1}{4}\right)} = (3)^{3/2}\frac{1}{64}\times\frac{4}{1} = \frac{(3)^{3/2}}{16}$$

11. PHYSICAL EQUILIBRIUM



T_P = Triple point

(i) The combination of temperature and pressure at which all the three physical state of matter co-exist is called triple point of that matter.

(ii) The vapour pressure solid is minimum (0) at absolute zero and maximum at triple point.

(iii) The vapour pressure of liquid is minimum at triple point and maximum at critical temperature.

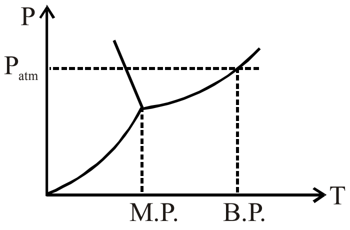
(iv) On each line in the graph, the matter exist in two physical states is equilibrium.

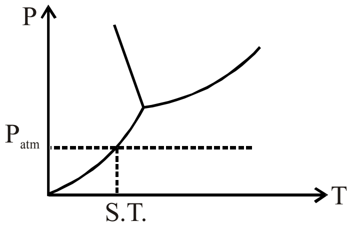
(v) In between two lines, the matter exist in only one physical state.

(vi) The melting point of solid and the triple point of matter differs slightly.

(vii) Any solid may be directly converted into gasous state or through liquid state by adjusting the external pressure relative to triple point pressure.

(viii)





MISSLENIOUS PREVIOUS YEARS QUESTION

1. For the reaction $CO_{(g)} + 2H_{2(g)} \rightleftharpoons CH_3OH(g)$; H_2 is introduced into a five litre flask at 327°C, containing 0.2 mole of $CO_{(g)}$ and a catalyst till the pressure is 4.92 atmosphere. At this point 0.1 mole of $CH_3OH_{(g)}$ is formed. Calculate K_c and K_p. **[JEE 1990]**

1. **K_c = 279.64 litre^2 mole^{-2} ; K_p = 0.115 atm^{-2}**

2. At temperature T, a compound $AB_{2(g)}$ dissociates according to the reaction $2AB_{2(g)} \rightleftharpoons 2AB_{(g)} + B_{2(g)}$; with a degree of dissociation 'x', which is small compared to unity. Deduce the expression for 'x' in terms of the equilibrium constant K_p and the total pressure P. **[JEE 1994]**

2. $\mathbf{x} = \sqrt[3]{\dfrac{2K_p}{P}}$

3. A sample of air consisting of N_2 and O_2 was heated to 2500 K until the equilibrium

$$N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$$

was established with an equilibrium constant $K_c = 2.1 \times 10^{-3}$. At equilibrium, the mole% of NO was 1.8. Estimate the initial composition of air in mole fraction of N_2 and O_2. **[JEE 1997]**

3. **79%, 21%**

4. The degree of dissociation is 0.4 at 400K & 1.0 atm for the gasoeus reaction $PCl_5 \rightleftharpoons PCl_3 + Cl_2(g)$. Assuming ideal behaviour of all gases. Calculate the density of equilibrium mixture at 400K & 1.0 atm pressure. **[JEE 1999]**

4. **Ans. 4.54 g dm^{-3}**

Sol.
$$\begin{array}{lll} PCl_5 = & PCl_3 & + \; Cl_2 \\ 1 & - & - \\ 1-0.4 & 0.4 & 0.4 \end{array}$$

$$M_{av} = \frac{208.5}{1.4}$$

PM = dRT

$$1 \times \frac{208.5}{1.4} = d \times 0.0821 \times 400$$

5. For the reversible reaction : **[JEE 2000]**

$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ 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 mol L^{-1} is :

(A) $1.44 \times 10^{-5} / (0.082 \times 500)^2$

(B) $1.44 \times 10^{-5} / (8.314 \times 773)^2$

(C) $1.44 \times 10^{-5} / (0.082 \times 500)^2$

(D) $1.44 \times 10^{-5} / (0.082 \times 773)^{-2}$

5. **Ans.(D)**

Sol. $K_P = K_C (RT)^{-2}$

6. When two reactants A and B are mixed to give products C and D, the reaction quotient Q, at the initial stages of the reaction : **[JEE 2000]**

(A) is zero
(B) decrease with time
(C) independent of time
(D) increases with time

6. Ans.(D)

Sol. Q increases at initial steps

7. When 3.06g of solid NH_4HS is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide. **[JEE 2000]**

(i) Calculate K_C & K_P for the reaction at 27°C.

(ii) What would happen to the equilibrium when more solid NH_4HS is introduced into the flask?

7. (i) $K_c = 8.1 \times 10^{-5}$ mol² L² ; $K_p = 4.91 \times 10^{-2}$ atm² (ii) No effect;

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

$$\frac{0.06}{2}\text{ mole} \qquad - \qquad -$$

$$\frac{0.042}{2}\text{ mole} \qquad \frac{0.018}{2} \qquad \frac{0.018}{2}$$

$$K_C = \frac{0.018}{2} \times \frac{0.018}{2}$$

$K_C = 8.1 \times 10^{-5}$

$K_P = (8.1 \times 10^{-5}) \times (RT)^2$

(ii) When more of $NH_4H_5(s)$ is added then no-effect will occur on equilibrium

8. At constant temperature, the equilibrium constant (K_P) for the decomposition reaction. $N_2O_4 \rightleftharpoons 2NO_2$ is expressed by $K_P = 4x^2P/(1 - x^2)$ where P is pressure, x is extent of decomposition. Which of the following statement is true ? **[JEE 2001]**

(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 or x

8. Ans.(D)

Sol. K_P depends only on temperature.

9. Consider the following equilibrium in a closed container : $N_2O_4(g) \rightleftharpoons 2NO_2(g)$.

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) : **[JEE 2002]**

(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

9. Ans.(D)

Sol. K_P is independent of volume of container

EXERCISE # S-I

1. Which of the following reactions goes almost all the way to completion, and which proceeds hardly at all?

(a) $N_2(g) + O_2(g) \rightleftharpoons 2NO\ (g)$; $K_c = 2.7 \times 10^{-18}$

(b) $2NO(g) + O_2(g) \rightleftharpoons 2NO_2\ (g)$; $K_c = 6.0 \times 10^{13}$

CE0001

2. Write down the expression for equilibrium constant K_C and K_P for the following reactions :

(a) $SO_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons SO_3(g)$

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

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

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

(e) $NH_3(aq) + \underset{\text{(excess)}}{H_2O(\ell)} \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

(f) $Zn(s) + 2H^+(aq) \rightleftharpoons Zn^{2+}(aq) + H_2(g)$

CE0002

3. Write the relationship between K_p and K_c for the following reactions :

(a) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ (b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (d) $2H_2O(g) \rightleftharpoons 2H_2(g) + O_2(g)$

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

CE0003

4. Find stability of reactants for the given equilibrium reaction :

$2XO\ (g) \rightleftharpoons X_2(g) + O_2(g)$; $K_1 = 1 \times 10^{24}$

$2XO_2\ (g) \rightleftharpoons X_2(g) + 2O_2(g)$; $K_2 = 2.5 \times 10^{10}$

CE0004

5. The value of K_c for the reaction $2A \rightleftharpoons B + C$ is 2×10^{-3}. At a given time, the composition of reaction mixture is $[A] = [B] = [C] = 3 \times 10^{-4}$ M. In which direction the reaction will proceed?

CE0005

6. The ester or ethyl acetate is formed by the reaction between ethanol and acetic acid and equilibrium is represented as :

$$CH_3COOH_{(l)} + C_2H_5OH_{(l)} \rightleftharpoons CH_3COOC_2H_{5(\ell)} + H_2O_{(l)}.$$

(a) Write the concentration ratio (reaction quotient), Q_C for this reaction. (Note that water is not in excess and is not a solvent in this reaction).

(b) At 293 K, if starts with 1.00 mole of acetic acid and 0.180 moles of ethanol, there is 0.171 moles of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.

(c) Starting with 0.500 moles of ethanol and 1.000 mole of acetic acid and maintaining it at 293 K, 0.214 moles of ethyl acetate is found after some time. Has equilibrium been reached ?

CE0006

7. If $K_c = 0.5 \times 10^{-9}$ at 1000 K for the reaction $N_2\ (g) + O_2\ (g) \rightleftharpoons 2NO\ (g)$, what is K_c at 1000 K for the reaction $2NO\ (g) \rightleftharpoons N_2\ (g) + O_2\ (g)$?

CE0007

8. An equilibrium mixture of PCl_5, PCl_3 and Cl_2 at a certain temperature contains 0.5×10^{-3} M PCl_5, 1.5×10^{-2} M PCl_3, and 3×10^{-2} M Cl_2. Calculate the equilibrium constant K_c for the reaction $PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$.

CE0008

9. A sample of HI (9.6×10^{-3} mol) was placed in an empty 2.00 L container at 1000 K. After equilibrium was reached, the concentration of I_2 was 4×10^{-4} M. Calculate the value of K_c at 1000 K for the reaction $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$.

CE0009

10. The vapour pressure of water at 27°C is 0.2463 atm. Calculate the values of K_p and K_c at 27°C for the equilibrium $H_2O\ (l) \rightleftharpoons H_2O\ (g)$.

CE0010

11. The value of K_c for the reaction $3O_2\ (g) \rightleftharpoons 2O_3\ (g)$ is 8×10^{-55} at 25°C. Do you expect pure air at 25°C to contain much O_3 (ozone) when O_2 and O_3 are in equilibrium? If the equilibrium concentration of O_2 in air at 25°C is 8×10^{-3} M, what is the equilibrium concentration of O_3?

CE0011

12. One mole of H_2O and one mole of CO are taken in a 10 L vessel and heated to 725 K. At equilibrium 40 percent of water (by mass) reacts with carbon monoxide according to the equation.

$$H_2O_{(g)} + CO_{(g)} \rightleftharpoons H_{2(g)} + CO_{2(g)}$$

Calculate the equilibrium constant for the reaction.

CE0012

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

CE0013

14. Calculate the equilibrium concentration of H_2, I_2 and HI at 300 K if initially 2 mol of H_2 and I_2 are taken in a closed container of having volume 10 lit. **[Given : $H_2 + I_2 \rightleftharpoons 2HI$; K = 100 at 300 K]**

CE0014

15. A mixture of SO_3, SO_2 and O_2 gases is maintained at equilibrium in 10 litre flask at a particular temperature in 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 number of mole of SO_3 and SO_2 in flask are same, how many mole of O_2 are present ?

(b) If number of mole of SO_3 in flask are twice the number of mole of SO_2, how many mole of O_2 are present ?

CE0015

16. For the given reaction,

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

the number of moles at equilibrium was found to be 4, 4 , 2 & 8 respectively in 1 L container. Find the new equilibrium concentration if 18 moles of D are added to above 1 L container.

CE0016

17. For the given reaction,

$PCl_5 \rightleftharpoons PCl_3 + Cl_2$

the number of moles at equilibrium was found to be 2, 6 & 4 respectively at 10 atm pressure. Find the new equilibrium moles & partial pressure, if it is restablished at an equilibrium pressure 50 atm.

CE0017

18. For the dissociation reaction $N_2O_4\ (g) \rightleftharpoons 2NO_2\ (g)$ derive the expression for the degree of dissociation in terms of K_p and total pressure P.

CE0018

19. For the reaction $2SO_{3(g)} \rightleftharpoons 2SO_{2(g)} + O_{2(g)}$

Initially 5 moles of SO_3 is taken and at equillibrium 4 moles of SO_3 is dissociated then find out α and the value of K_C (Volume = 2litre)

CE0019

20. 1.1 mole of A mixed with 2.2 mole of B and the mixture is kept in a 1 litre flask at the equillibrium, $A + 2B \rightleftharpoons 2C + D$ is reached. At equillibrium 0.2 mole of C is formed then the value of K_C will be.

CE0020

21. The air pollutant NO is produced in automobile engines from the high temperature reaction $N_2(g) + O_2(g) \rightleftharpoons 2NO\ (g)$; $K_c = 16$ at 2300 K. If the initial concentrations of N_2 and O_2 at 2300 K are both 1.5 M, what are the concentrations of NO, N_2, and O_2 when the reaction mixture reaches equilibrium?

CE0021

22. At 700 K, $K_p = 0.2$ for the reaction $ClF_3\ (g) \rightleftharpoons ClF\ (g) + F_2(g)$. Calculate the equilibrium partial pressure of ClF_3, ClF, and F_2 if only ClF_3 is present initially, at a partial pressure of 0.150 atm.

CE0022

23. The degree of dissociation of N_2O_4 into NO_2 at 1.5 atmosphere and 40°C is 0.25. Calculate its K_p at 40°C.Also report degree of dissociation at 10 atmospheric pressure at same temperature.

CE0023

24. At 46°C, K_p for the reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 0.667 atm . Compute the percent dissociation of N_2O_4 at 46° C at a total pressure of 380 Torr .

CE0024

25. $2\ NOBr\ (g) \rightleftharpoons 2\ NO\ (g) + Br_2\ (g)$. If nitrosyl bromide (NOBr) is 33.33% dissociated at 25° C & a total pressure of 0.28 atm . Calculate K_p for the dissociation at this temperature.

CE0025

26. The system $N_2O_4 \rightleftharpoons 2\,NO_2$ maintained in a closed vessel at 60° C & a pressure of 5 atm has an average (i.e. observed) molecular weight of 69, calculate K_p. At what pressure at the same temperature would the observed molecular weight be (230/3) ?

CE0026

27. In the esterfication $C_2H_5OH\ (l) + CH_3COOH\ (l) \rightleftharpoons CH_3COOC_2H_5\ (l) + H_2O\ (l)$ an equimolar mixture of alcohol and acid taken initially yields under equilibrium, the water with mole fraction = 0.333. Calculate the equilibrium constant.

CE0027

28. The equilibrium constant for the reaction is 9 at 900°C $S_2(g) + C(s) \rightleftharpoons CS_2(g)$. Calculate the pressure of two gases at equilibrium, when 2 atm of S_2 and excess of C(s) come to equilibrium.

CE0028

29. A sample of $CaCO_3(s)$ is introduced into a sealed container of volume 0.821 litre & heated to 1000K until equilibrium is reached. The equilibrium constant for the reaction $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ is 4×10^{-2} atm at this temperature. Calculate the mass of CaO present at equilibrium.

CE0029

30. Anhydrous calcium chloride is often used as a dessicant. In the presence of excess of $CaCl_2$, the amount of the water taken up is governed by $K_p = 6.4 \times 10^{85}$ for the following reaction at room temperature, $CaCl_2(s) + 6H_2O(g) \rightleftharpoons CaCl_2\,.6H_2O(s)$. What is the equilibrium vapour pressure of water in a closed vessel that contains $CaCl_2(s)$?

CE0030

31. 20.0 grams of $CaCO_3(s)$ were placed in a closed vessel, heated & maintained at 727° C under equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ and it is found that 75 % of $CaCO_3$ was decomposed. What is the value of K_p ? The volume of the container was 15 litres.

CE0031

32. **(a)** Methanol, a liquid fuel that could possibly replace gasoline, can be prepared from water gas and additional hydrogen at high temperature and pressure in the presence of a suitable catalyst. Write the expression for the equilibrium constant for the reversible reaction.

$2H_2\,(g) + CO\,(g) \rightleftharpoons CH_3OH\,(g) \qquad \Delta H = -\,90.2\text{ kJ}$

(b) Assume that equilibrium has been established and predict how the concentration of H_2, CO and CH_3OH will differ at a new equilibrium if (1) more H_2 is added. (2) CO is removed. (3) CH_3OH is added. (4) the pressure on the system is increased. (5) the temperature of the system is increased. (6) more catalyst is added.

CE0032

33. Ammonia is a weak base that reacts with water according to the equation

$NH_3\,(aq) + H_2O\,(l) \rightleftharpoons NH_4^+ + OH^-\,(aq)$

Will any of the following increase the percent of ammonia that is converted to the ammonium ion in water?

(a) Addition of NaOH. (b) Addition of HCl. (c) Addition of NH_4Cl.

CE0033

34. Consider the gas-phase hydration of hexafluoroacetone, $(CF_3)_2CO$:

$$(CF_3)_2CO\,(g) + H_2O\,(g) \underset{k_r}{\overset{k_f}{\rightleftharpoons}} (CF_3)_2C(OH)_2\,(g)$$

At 76°C, the forward and reverse rate constants are $k_f = 0.15\ M^{-1}s^{-1}$ and $k_r = 6 \times 10^{-4}s^{-1}$. What is the value of the equilibrium constant K_c?

CE0034

35. Listed in the table are forward and reverse rate constants for the reaction $2NO\,(g) \rightleftharpoons N_2(g) + O_2(g)$

Temperature (K)	**k_f ($M^{-1}s^{-1}$)**	**k_r ($M^{-1}s^{-1}$)**
1400	0.29	1.1×10^{-6}
1500	1.3	1.4×10^{-5}

Is the reaction endothermic or exothermic? Explain in terms of kinetics.

CE0035

EXERCISE # S-II

1. One mole of N_2O_4 (g) at 300 K is left in a closed container under one atm . It is heated to 600 K when 20 % by mass of N_2O_4 (g) decomposes to NO_2 (g) . Calculate resultant pressure.

CE0036

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

CE0037

3. A definite amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. NH_4HS decomposes to give NH_3 and H_2S and at equilibrium total pressure in flask is 0.84 atm. Calculate equilibrium constant for the reaction :

CE0038

4. For the reaction $A(g) + 2B(g) \rightleftharpoons C(g) + D(g)$; $K_c = 10^{12}$.
If the initial moles of A,B,C and D are 0.5, 1, 0.5 and 3.5 moles respectively in a one litre vessel. What is the equilibrium concentration of B?

CE0039

5. Calculate the equilibrium concentration of PCl_3 and Cl_2 at 300 K if initially 1 mol of PCl_5 is taken in a closed container of having volume 10 lit.

[Given : $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$; $K_C = 10^{-2}$ at 300 K, $\sqrt{41} = 6.4$]

CE0040

6. When 36.8g N_2O_4 (g) is introduced into a 1.0-litre flask at 27°C . The following equilibrium reaction occurs : $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; $K_p = 0.1642$ atm.

(a) Calculate K_c of the equilibrium reaction.

(b) What are the number of moles of N_2O_4 and NO_2 at equilibrium?

(c) What is the total gas pressure in the flask at equilibrium?

(d) What is the percent dissociation of N_2O_4?

CE0041

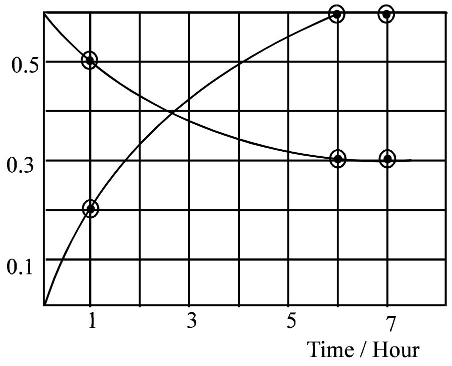
7. The progress of the reaction

$A \rightleftharpoons nB$ with time, is presented in figure. Determine

(i) the value of n.

(ii) the equilibrium constant K.

(iii) the initial rate of conversion of A.



CE0042

8. A mixture of hydrogen & iodine in the mole ratio 1.5 : 1 is maintained at 450° C. After the attainment of equilibrium $H_2(g) + I_2(g) \rightleftharpoons 2\,HI(g)$, it is found on analysis that the mole ratio of I_2 to HI is 1 : 18. Calculate the equilibrium constant and the number of moles of each species present under equilibrium, if initially, 127 grams of iodine were taken.

CE0043

9. At certain temperature (T) for the gas phase reaction

$$2H_2O(g) + 2Cl_2\,(g) \rightleftharpoons 4HCl(g) + O_2(g) \qquad K_p = 12 \times 10^8 \text{ atm}$$

If Cl_2, HCl & O_2 are mixed in such a manner that the partial pressure of each is 2 atm and the mixture is brough into contact with excess of liquid water. What would be approximate partial pressure of Cl_2 when equilibrium is attained at temperature (T)?

[Given : Vapour pressure of water is 380 mm Hg at temperature (T)]

CE0044

10. Two solids X and Y disssociate into gaseous products at a certain temperature as follows: $X(s) \rightleftharpoons A(g) + C(g)$, and $Y(s) \rightleftharpoons B(g) + C(g)$. At a given temperature, pressure over excess solid X is 40 mm and total pressure over solid Y is 60 mm. When they are preset in separate containers. Calculate

(a) the values of K_p for two reactions (in mm^2)

(b) the ratio of moles of A and B in the vapour state over a mixture of X and Y.

(c) the total pressure of gases over a mixture of X and Y.

CE0045

11. When 1 mole of A(g) is introduced in a closed rigid 1 litre vessel maintained at constant temperature the following equilibria are established.

$$A\,(g) \rightleftharpoons B(g) + C(g) \ :\ K_{C_1}$$

$$C\,(g) \rightleftharpoons D(g) + B(g) \ :\ K_{C_2}$$

The pressure at equilibrium is twice the initial pressure. Calculate the value of $\dfrac{K_{C_2}}{K_{C_1}}$ if $\dfrac{[C]_{eq}}{[B]_{eq}} = \dfrac{1}{5}$

CE0046

12. Equilibrium constants are given (in atm) for the following reactions at 0° C:

$SrCl_2{\cdot}6H_2O(s) \rightleftharpoons SrCl_2 \cdot 2H_2O\,(s) + 4H_2O(g) \qquad K_p = 5 \times 10^{-12}$

$Na_2HPO_4{\cdot}12\,H_2O(s) \rightleftharpoons Na_2HPO_4 \cdot 7\,H_2O\,(s) + 5H_2\,O(g) \qquad K_p = 2.43 \times 10^{-13}$

$Na_2SO_4{\cdot}10\,H_2O(s) \rightleftharpoons Na_2SO_4\,(s) + 10\,H_2O\,(g) \qquad K_p = 1.024 \times 10^{-27}$

$$\left(\%\text{ Relative humidity} = \frac{P_{H_2O}}{\text{Vapour pressure of } H_2O} \times 100\right)$$

The vapor pressure of water at 0°C is 4.56 torr.

Out of $SrCl_2 \cdot 2H_2O$ (s), $Na_2HPO_4 \cdot 7\,H_2O$ (s) and Na_2SO_4 (s),
Which is the most effective drying agent at 0°C?

CE0047

13. At certain temperature , $K_C = 1.0$ for reaction :

$NO_2(g) + NO(g) \rightleftharpoons N_2O(g) + O_2(g)$

equal moles of NO and NO_2 are to be placed in 5 litre container until N_2O concentration at equilibrium is 0.5M. How many mole of $(NO + NO_2)$ must be placed in the container.

CE0048

14. In a vessel, two equilibrium are simultaneously established at same temperature as follows,

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

$N_2(g) + 2H_2(g) \rightleftharpoons N_2H_4(g)$ ....(ii)

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.

CE0049

15. If vapour density of equilibrium mixture NO_2 and N_2O_4 is found to be 42 for the reaction,

$N_2O_4 \rightleftharpoons 2NO_2$. Find :

(a) Abnormal molecular weight

(b) Degree of dissociation

(c) Percentage of NO_2 in the mixture

CE0050

EXERCISE # O-I

Only one is correct

1. x $\rightleftharpoons$ y reaction is said to be in equilibrium, when :-

(A) Only 10% conversion of x to y takes place

(B) Complete conversion of x to y has taken place

(C) Conversion of x to y is only 50% complete

(D) The rate of change of x to y is just equal to the rate of change of y to x in the system

CE0051

2. For which reaction is $K_p = K_c$:-

(A) $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ (B) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

(C) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ (D) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

CE0052

3. For the reaction

$CuSO_4.5H_2O(s) \rightleftharpoons CuSO_4.3H_2O_{(s)} + 2H_2O_{(g)}$

Which one is correct representation :–

(A) $K_p = (P_{(H_2O)})^2$ (B) $K_c = [H_2O]^2$ (C) $K_p = K_c(RT)^2$ (D) All

CE0053

4. $\log \frac{K_p}{K_c} + \log RT = 0$ is true relationship for the following reaction:-

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

(C) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (D) (B) and (C) both

CE0054

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

(a) Initial concentration of the reactants (b) Pressure

(c) Temperature (d) Catalyst

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

CE0055

6. If some He gas is introduced into the equilibrium $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$ at constant pressure and temperature then equilibrium constant of reaction:

(A) Increase (B) Decrease (C) Unchange (D) Nothing can be said

CE0056

7. The equilibrium constant for the given reaction :

$$SO_3(g) \rightleftharpoons SO_2(g) + \frac{1}{2}O_2(g) \ ; K_c = 5 \times 10^{-2}$$

The value of K_c for the reaction :

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

(A) 400 (B) 2.40×10^{-3} (C) 9.8×10^{-2} (D) 4.9×10^{-2}

CE0057

8. For the following three reactions, 1, 2 and 3 equilibrium, constants are given :

(1) $CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g) \quad ; K_1$

(2) $CH_4(g) + H_2O(g) \rightleftharpoons CO(g) + 3H_2(g) \quad ; K_2$

(3) $CH_4(g) + 2H_2O(g) \rightleftharpoons CO_2(g) + 4H_2(g) \ ; K_3$

Which of the following relations is correct ?

(A) $K_1\sqrt{K_2} = K_3$ (B) $K_2K_3 = K_1$ (C) $K_3 = K_1K_2$ (D) $K_3 = K_2^3K_1^2$

CE0058

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

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

CE0059

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

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

CE0060

11. 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 concentrations of N_2 and O_2 will respectively be

(A) 0.75 mole/lit., 0.55 mole/lit. (B) 0.50 mole/lit., 0.75 mole/lit.

(C) 0.25 mole/lit., 0.50 mole/lit (D) 0.25 mole/lit., 1.0 mole/lit.

CE0061

12. How many moles per litre of PCl_5 has to be taken to obtain 0.1 mole Cl_2, if the value of equilibrium constant K_c is 0.04 ?

(A) 0.15 (B) 0.25 (C) 0.35 (D) 0.05

CE0062

13. In the beginning of the reaction, $A \rightleftharpoons B + C$, 2 moles of A are taken, out of which 0.5 mole gets dissociated. What is the degree of dissociation of A ?

(A) 0.5 (B) 1 (C) 0.25 (D) 4.2

CE0063

14. In the reaction, $PCl_5 \rightleftharpoons PCl_3 + Cl_2$, the amount of each PCl_5, PCl_3 and Cl_2 is 2 mole at equilibrium and total pressure is 3 atmosphere. The value of K_p will be

(A) 1.0 atm. (B) 3.0 atm. (C) 2.9 atm. (D) 6.0 atm.

CE0064

15. 4 moles of PCl_5 are heated at constant temperature in closed container. If degree of dissociation for PCl_5 is 0.5 calculate total number of moles at equilibrium :-

(A) 4.5 (B) 6 (C) 3 (D) 4

CE0065

16. For the reaction $A + 2B \rightleftharpoons 2C + D$, initial concentration of A is a and that of B is 1.5 times that of A. Concentration of A and D are same at equilibrium. What should be the concentration of B at equilibrium ?

(A) $\frac{a}{4}$ (B) $\frac{a}{2}$ (C) $\frac{3a}{4}$ (D) All of the above.

CE0066

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

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

CE0067

18. 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 temperature is

(A) 0°C (B) 273 K (C) 1 K (D) 12.19 K

CE0068

19. The degree of dissociation of SO_3 is α at equilibrium pressure p^0.

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

(A) $\frac{p^0\alpha^3}{2(1-\alpha)^3}$ (B) $\frac{p^0\alpha^3}{(2+\alpha)(1-\alpha)^2}$ (C) $\frac{p^0\alpha^2}{2(1-\alpha)^2}$ (D) None of these

CE0069

20. For the reaction : $2HI\,(g) \rightleftharpoons H_2(g) + I_2(g)$, the degree of dissociated (α) of HI(g) is related to equilibrium constant K_P by the expression

(A) $\frac{1+2\sqrt{K_P}}{2}$ (B) $\sqrt{\frac{1+2K_P}{2}}$ (C) $\sqrt{\frac{2K_P}{1+2K_P}}$ (D) $\frac{2\sqrt{K_P}}{1+2\sqrt{K_P}}$

CE0070

21. The equilibrium constant for the reaction

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

is 0.25 $dm^6 mol^{-2}$. In a volume of 5 dm^3, what amount of A must be mixed with 4 mol of B to yield 1 mol of C at equilibrium.

(A) 3 moles (B) 24 moles (C) 26 moles (D) None of these

CE0071

22. A 20.0 litre vessel initially contains 0.50 mole each of H_2 and I_2 gases. These substances react and finally reach an equilibrium condition. Calculate the equilibrium concentration of HI if $K_{eq} = 49$ for the reaction $H_2 + I_2 \rightleftharpoons 2HI$.

(A) 0.78 M (B) 0.039 M (C) 0.033 M (D) 0.021 M

CE0072

23. At 675 K, $H_2(g)$ and CO_2 (g) react to form CO(g) and H_2O (g), K_p for the reaction is 0.16. If a mixture of 0.25 mole of $H_2(g)$ and 0.25 mol of CO_2 is heated at 675 K, mole % of CO(g) in equilibrium mixture is :

(A) 7.14 (B) 14.28 (C) 28.57 (D) 33.33

CE0073

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

(A) 53.3% (B) 106.6% (C) 26.7% (D) None

CE0074

25. The equilibrium constant K_P (in atm) for the reaction is 9 at 7 atm and 300 K.

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

Calculate the average molar mass (in gm/mol) of an equilibrium mixture.

Given : Molar mass of A_2, B_2 and C_2 are 70, 49 & 21 gm/mol respectively.

(A) 50 (B) 45 (C) 40 (D) 37.5

CE0075

26. Vapour density of the equilibrium mixture of the reaction

$2NH_3\ (g) \rightleftharpoons N_2\ (g) + 3H_2\ (g)$ is 6.0

Percent dissociation of ammonia gas is:

(A) 13.88 (B) 58.82 (C) 41.66 (D) None of these

CE0076

27. The equilibrium concentration of B $[(B)_e]$ for the reversible reaction $A \rightleftharpoons B$ can be evaluated by the expression:-

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

CE0077

28. The equilibrium $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$ shifts forward if :-

(A) A catalyst is used.

(B) An adsorbent is used to remove SO_3 as soon as it is formed.

(C) Small amounts of reactants are removed.

(D) None of these

CE0078

29. In manufacture of NO, the reaction $N_{2(g)} + O_{2(g)} \rightleftharpoons 2NO_{(g)}$, ΔH +ve is favourable if :-

(A) Pressure is increased (B) Pressure is decreased

(C) Temperature is increased (D) Temperature is decreased

CE0079

30. In which of the following reactions, increase in the pressure at constant temperature does not affect the moles at equliibrium :

(A) $2NH_3(g) \rightleftharpoons N_2(g) + 3H_2(g)$ (B) $C(g) + \frac{1}{2}O_2(g) \rightleftharpoons CO(g)$

(C) $H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g)$ (D) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

CE0080

31. Change in volume of the system does not alter the number of moles in which of the following equilibrium

(A) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ (B) $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

(C) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (D) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

CE0081

32. The conditions favourable for the reaction :

$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$; $\Delta H° = -198$ kJ

are :

(A) low temperature, high pressure (B) any value of T and P

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

CE0082

33. Densities of diamond and graphite are 3.5 and 2.3 gm/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

CE0083

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

(A) concentrations of SO_2, Cl_2 and SO_2Cl_2 do not change

(B) more chlorine is formed

(C) concentration of SO_2 is reduced

(D) more SO_2Cl_2 is formed

CE0084

35. The yield of product in the reaction

$$2A(g) + B(g) \rightleftharpoons 2C(g) + Q\ \text{kJ}$$

would be lower at :

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

(C) low temperature and to high pressure (D) high temperature & low pressure

CE0085

EXERCISE # O-II

More than one may be correct

1. Following two equilibrium is simultaneously established in a container

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$$
$$CO(g) + Cl_2(g) \rightleftharpoons COCl_2(g)$$

If some Ni(s) is introduced in the container forming Ni $(CO)_4$ (g) then at new equilibrium

(A) PCl_3 concentration will increase
(B) PCl_3 concentration will decrease
(C) Cl_2 concentration will remain same
(D) CO concentration will remain same

CE0086

2. For the reaction $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$, the forward reaction at constant temperature is favoured by

(A) introducing an inert gas at constant volume
(B) introducing chlorine gas at constant volume
(C) introducing an inert gas at constant pressure
(D) introducing PCl_5 at constant volume.

CE0087

3. When $NaNO_3$ is heated in a closed vessel, oxygen is liberated and $NaNO_2$ is left. At equilibrium

(A) addition of $NaNO_2$ favours reverse reaction
(B) addition of $NaNO_3$ favours forward reaction
(C) increasing temperature favours forward reaction
(D) increasing pressure favours reverse reaction

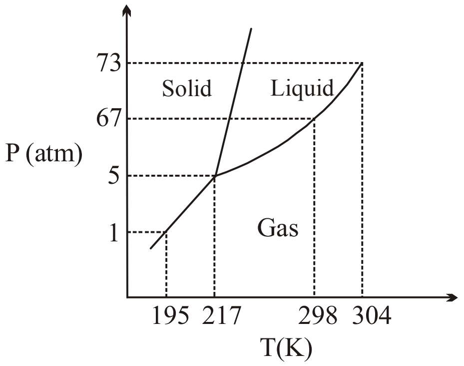
CE0088

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

(A) increasing the temperature
(B) decreasing the pressure
(C) removing some H_2
(D) adding some C_2H_6

CE0089

5. Phase diagram of CO_2 is shown as following



Based on above find the correct statement(s)

(A) 298K is the normal boiling point of liquid CO_2

(B) At 1 atm & 190 K CO_2 will exist as gas.

(C) CO_2(s) will sublime above 195K under normal atmospheric pressure

(D) Melting point & boiling point of CO_2 will increase on increasing pressure

CE0090

6. The equilibrium between, gaseous isomers A, B and C can be represented as

Reaction		**Equilibrium constant**
$A(g) \rightleftharpoons B(g)$	:	$K_1 = ?$
$B(g) \rightleftharpoons C(g)$	:	$K_2 = 0.4$
$C(g) \rightleftharpoons A(g)$	:	$K_3 = 0.6$

If one mole of A is taken in a closed vessel of volume 1 litre, then

(A) [A] + [B] + [C] = 1 M at any time of the reactions

(B) Concentration of C is 4.1 M at the attainment equilibrium in all the reactions

(C) The value of K_1 is $\frac{1}{0.24}$

(D) Isomer [A] is least stable as per thermodynamics.

CE0091

7. For the gas phase exothermic reaction, $A_2 + B_2 \rightleftharpoons C_2$, carried out in a closed vessel, the equilibrium moles of A_2 can be increased by

(A) increasing the temperature (B) decreasing the pressure

(C) adding inert gas at constant pressure (D) removing some C_2

CE0092

8. Consider the equilibrium $HgO(s) + 4I^-(aq) + H_2O(l) \rightleftharpoons HgI_4^{2-}(aq) + 2OH^-(aq)$, which changes will decrease the equilibrium concentration of HgI_4^{2-}

(A) Addition of 0.1 M HI (aq) (B) Addition of HgO (s)

(C) Addition of H_2O (l) (D) Addition of KOH (aq)

CE0093

9. Decrease in the pressure for the following equilibria : $H_2O\ (s) \rightleftharpoons H_2O(l)$ result in the :

(A) formation of more H_2O (s) (B) formation of more $H_2O(l)$

(C) increase in melting point of H_2O(s) (D) decrease in melting point of H_2O(s)

CE0094

Assertion Reason

10. **Statement -1 :** Total number of moles in a closed system at new equilibrium is less than the old equilibrium if some amount of a substance is removed from a system (consider a reaction $\mathbf{A(g) \rightleftharpoons B(g)}$) at equilibrium.

Statement -2 : The number of moles of the substance which is removed, is partially compensated as the system reached to new equilibrium.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is false, statement-2 is true.

(D) Statement-1 is true, statement-2 is false.

CE0095

11. **Statement-1** : Ammonia at a pressure of 10 atm and CO_2 at a pressure of 20 atm are introduced into an evacuated chamber. If K_p for the reaction $NH_2COONH_4\ (s) \rightleftharpoons 2NH_3\ (g) + CO_2\ (g)$ is 2020 atm^3, the total pressure after a long time is less than 30 atm.

Statement-2 : Equilibrium can be attained from both directions.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

CE0096

12. **Statement-1** : Catalyst does not alter the equilibrium constant

Statement-2 : Because for the catalysed reaction and uncatalysed reaction ΔH remain same an equilibrium constant depend on ΔH.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

CE0097

13. **Statement-1** : Equilibrium constant may show higher or lower values with increase in temperature

Statement-2 : The change depend on heat of reaction.

(A) Statement-1 is true, statement-2 is true and statement-2 is correct explanation for statement-1.

(B) Statement-1 is true, statement-2 is true and statement-2 is NOT the correct explanation for statement-1.

(C) Statement-1 is true, statement-2 is false.

(D) Statement-1 is false, statement-2 is true.

CE0098

Comprehension :

Paragraph for Question Nos. 12 to 15

In a 7.0 L evacuated chamber, 0.50 mol H_2 and 0.50 mol I_2 react at 427°C .
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$. At the given temperature, $K_C = 49$ for the reaction.

14. What is the value of K_p ?

(A) 7 (B) 49 (C) 24.5 (D) None

CE0099

15. What is the total pressure (atm) in the chamber?

(A) 83.14 (B) 831.4 (C) 8.21 (D) None

CE0099

16. How many moles of the iodine remain unreacted at equilibrium?

(A) 0.388 (B) 0.112 (C) 0.25 (D) 0.125

CE0099

17. What is the partial pressure (atm) of HI in the equilibrium mixture?

(A) 6.385 (B) 12.77 (C) 40.768 (D) 646.58

CE0099

Paragraph for Question Nos. 16 to 18

Influence of pressure, temperature, concentration and addition of inert gas on a reversible chemical reaction in equilibrium can be explained by formulating the expression for equilibrium constant K_c or K_p for the equilibrium. On the other hand Le Chatelier principle can be theoretically used to explain the effect of P, T or concentration on the physical or chemical equilibrium both.

18. For the reaction : $PCl_5 \rightleftharpoons PCl_3 + Cl_2$ increase of pressure shows :

(A) An increase in degree of dissociation and a decrease in K_c
(B) A decrease in degree of dissociation and a decrease in K_c
(C) An increase in degree of dissociation but K_c remains constant
(D) A decrease in degree of dissociation but K_c remains constant

CE0100

19. For the reaction : $2SO_2 + O_2 \rightleftharpoons 2SO_3$; $\Delta H = -ve$, An increase in temperature shows :

(A) More dissociation of SO_3 and a decrease in K_c
(B) Less dissociation of SO_3 and an increase in K_c
(C) More dissociation of SO_3 and an increase in K_c
(D) Less dissociation of SO_3 and an decrease in K_c

CE0101

20. For the reaction : $\underset{\text{Yellow}}{Fe^{3+}(aq.)} + SCN^-(aq.) \rightleftharpoons \underset{\text{Red}}{[Fe(NCS)]^{2+}(aq.)}$; in equilibrium if little more aqueous solution of $FeCl_3$ is added, than :

(A) Forward reaction becomes more and red colours is deepened
(B) Backward reaction becomes more and red colour faintens
(C) Solution becomes colourless
(D) None of these

CE0102

Match the column :

21.

	Column I		**Column II**
(A)	$K_P < K_C$	(P)	$N_2 + 3H_2 \rightleftharpoons 2NH_3$
(B)	Introduction of inert gas at constant pressure will decrease the concentration of reactants	(Q)	$PCl_5\ (g) \rightleftharpoons PCl_3\ (g) + Cl_2\ (g)$
(C)	K_P^o is dimensionless	(R)	$2NO_2\ (g) \rightleftharpoons N_2O_4\ (g)$
(D)	Temperature increase will shift the reaction on product side.	(S)	$NH_3\ (g) + HI\ (g) \rightleftharpoons NH_4I\ (s)$

CE0103

22.

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

CE0104

Matching list type :

Answer Q.No. 23, 24 and 25 by appropriately matching the information given in the three columns of the following table.

Column-I (Reaction)	**Column-II (If α is negligiable w.r.t. 1)**	**Column-III**
(A) $2X(g) \rightleftharpoons Y(g) + Z(g)$, $\Delta H = -ve$	(P) $\alpha = 2 \times \sqrt{K_p}$	(I) K increase with increase in temperature
(B) $X(g) \rightleftharpoons Y(g) + Z(g)$, $\Delta H = +ve$	(Q) $\alpha = 3 \times \sqrt{K_p.P}$	(II) K decrease with increase in temperature
(C) $3X(g) \rightleftharpoons Y(g) + Z(g)$, $\Delta H = +ve$	(R) $\alpha = \left(\frac{2Kp}{P}\right)^{1/3}$	(III) Pressure has no effect
(D) $2X(g) \rightleftharpoons Y(g) + 2Z(g)$, $\Delta H = +ve$	(S) $\alpha = \sqrt{K_p / P}$	(IV) Addition of inert gas at constant pressure shift equilibrium in forward direction

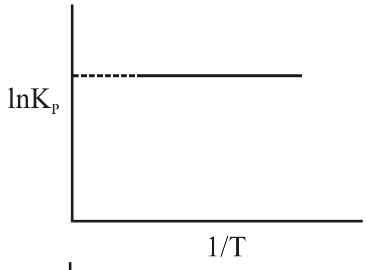
23. Which of the following option is correctly matched ?

(A) A-Q-III (B) B-S-II (C) C-Q-II (D) D-R-IV

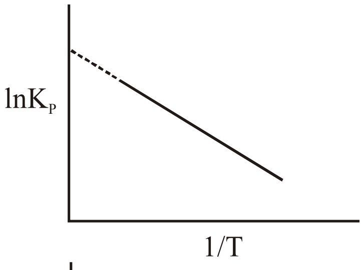
CE0105

24. Correct representation of reaction in option (A) is represented by graph

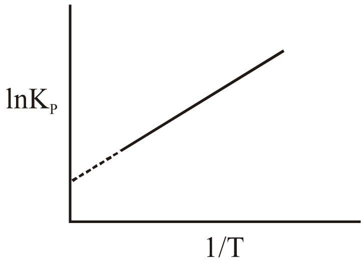
(A)



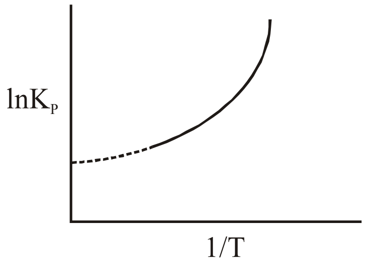
(B)



(C)



(D)



CE0106

25. For the reaction of option (B) if degree of dissociation varies inversily as square root of pressure of the system. Suppose at constant temperature volume is increased 16 times of its initial volume the degree of dissociation (α) for this reaction will become :

(A) 4 times (B) 2 times (C) 1/4 times (D) 1/2 times

CE0107

EXERCISE # J-MAIN

1. A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is :- **[AIEEE-2011]**

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

CE0108

2. The equilibrium constant (K_C) for the reaction $N_2(g) + O_2(g) \longrightarrow 2NO(g)$ at temperature T is 4×10^{-4}. The value of K_C for the reaction. $NO(g) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$ at the same temperature is :- **[AIEEE-2012]**

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

CE0109

3. 8 mol of $AB_3(g)$ are introduced into a 1.0 dm^3 vessel. If it dissociates as $2AB_3(g) \rightleftharpoons A_2(g) + 3\,B_2(g)$

At equilibrium, 2mol of A_2 are found to be present. The equilibrium constant of this reaction is :- **[JEE-MAINS(online)-12]**

(1) 36 (2) 3 (3) 27 (4) 2

CE0110

4. The value of Kp for the equilibrium reaction $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is 2. The percentage dissociation of $N_2O_4(g)$ at a pressure of 0.5 atm is **[JEE-MAINS(online)-12]**

(1) 71 (2) 50 (3) 88 (4) 25

CE0111

5. K_1, K_2 and K_3 are the equilibrium constants of the following reactions (I), (II) and (III), respectively

(I) $N_2 + 2O_2 \rightleftharpoons 2NO_2$ (II) $2NO_2 \rightleftharpoons N_2 + 2O_2$ **[JEE-MAINS(online)-12]**

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

The correct relation from the following is :

(1) $K_1 = \sqrt{K_2} = K_3$ (2) $K_1 = \frac{1}{K_2} = \frac{1}{K_3}$

(3) $K_1 = \frac{1}{K_2} = K_3$ (4) $K_1 = \frac{1}{K_2} = \frac{1}{(K_3)^2}$

CE0112

6. One mole of $O_2(g)$ and two moles of $SO_2(g)$ were heated in a closed vessel of one litre capacity at 1098 K. At equilibrium 1.6 moles of $SO_3(g)$ were found. The equilibrium constant K_C of the reaction would be :- **[JEE-MAINS(online)-12]**

(1) 60 (2) 80 (3) 30 (4) 40

CE0113

7. $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g), K_1$ (1) **[JEE-MAINS(online)-13]**

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g), K_2$ (2)

$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g), K_3$ (3)

The equation for the equilibrium constant of the reaction

$2\ NH_3(g) + \frac{5}{2}O_2(g) \rightleftharpoons 2NO(g) + 3H_2O(g), (K_4)$

in terms of K_1, K_2 and K_3 is :

(1) $\frac{K_1K_3^2}{K_2}$ (2) $\frac{K_2K_3^3}{K_1}$ (3) $\frac{K_1K_2}{K_3}$ (4) $K_1\ K_2\ K_3$

CE0114

8. In reaction $A + 2B \rightleftharpoons 2C + D$, initial concentration of B was 1.5 times of $|A|$, but at equilibrium the concentrations of A and B became equal. The equilibrium constant for the reaction is :

[JEE-MAINS(online)-13]

(1) 4 (2) 6 (3) 12 (4) 8

CE0115

9. For the decomposition of the compound, represented as **[JEE-MAINS(online)-14]**

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

the $K_P = 2.9 \times 10^{-5}$ atm^3.

If the reaction is started with 1 mol of the compound, the total pressure at equilibrium would be

(1) 38.8×10^{-2} atm (2) 1.94×10^{-2} atm

(3) 5.82×10^{-2} atm (4) 7.66×10^{-2} atm

CE0116

10. 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-MAINS-14]**

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

CE0117

11. The equilibrium constants 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-MAINS-16]

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

CE0118

12. The following reaction occurs in the Blast Furnace where iron ore is reduced to iron metal:

$Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2\,Fe(l) + 3CO_2(g)$ **[JEE-MAINS(online)-17]**

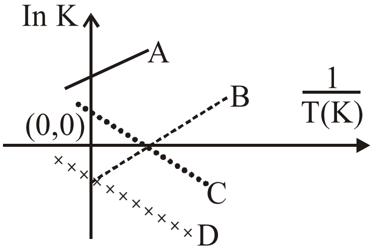
Using the Le Chatelier's principle, predict which one of the following will **not** disturb the equilibrium?

(1) Removal of CO_2 (2) Addition of Fe_2O_3

(3) Addition of CO_2 (4) Removal of CO

CE0119

13. Which of the following lines correctly show the temperature dependence of equilibrium constant, K, for an exothermic reaction ? **[JEE-MAINS(offline)-18]**



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

CE0120

14. In which of the following reactions, an increase in the volume of the container will favour the formation of products ? **[JEE-MAINS(online)-18]**

(1) $2NO_2(g) \rightleftharpoons 2NO(g)+O_2(g)$

(2) $3O_2(g) \rightleftharpoons 2O_3(g)$

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

(4) $4NH_3(g)+5O_2(g) \rightleftharpoons 4NO(g)+6H_2O(l)$

CE0121

15. 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, **[JEE-MAINS(online)-18]**

$CO + Cl_2 \rightleftharpoons CO\,Cl_2$

At equilibrium, if one mole of CO is present then equilibrium constant (K_c) for the reaction is :-

(1) 4 (2) 3 (3) 2 (4) 2.5 **[JEE-MAINS(online)-18]**

CE0122

16. 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 :

($R = 8.314\ JK^{-1}\ mol^{-1}$; $\ell n\ 2 = 0.693$; $\ell n\ 3 = 1.098$) **[JEE-MAINS(online)-18]**

(1) 4281 (2) 4763 (3) 2068 (4) 1844

CE0123

17. 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 :-

(1) Addition of an inert gas at constant volume. **[JEE-MAINS(online)-18]**

(2) Increasing the pressure.

(3) Lowering the temperature.

(4) Addition of an inert gas at constant pressure.

CE0124

18. For the following reactions, equilibrium constants are given : **[JEE-MAINS(online)-19]**

$S(s) + O_2(g) \rightleftharpoons SO_2(g); K_1 = 10^{52}$

$2S(s) + 3O_2(g) \rightleftharpoons 2SO_3(g); K_2 = 10^{129}$

The equilibrium constant for the reaction,

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

(1) 10^{181} (2) 10^{154} (3) 10^{25} (4) 10^{77}

CE0125

19. For the reaction, **[JEE-MAINS(online)-19]**

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

$\Delta H = -57.2 kJ\ mol^{-1}$ and

$K_c = 1.7 \times 10^{16}$.

Which of the following statement is INCORRECT?

(1) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required.

(2) The equilibrium will shift in forward direction as the pressure increase.

(3) The equilibrium constant decreases as the temperature increases.

(4) The addition of inert gas at constant volume will not affect the equilibrium constant.

CE0126

20. In which one of the following equilibria, $K_p \neq K_c$? **[JEE-MAINS(online)-19]**

(1) $NO_2(g) + SO_2(g) \rightleftharpoons NO(g) + SO_3(g)$ (2) $2\ HI(g) \rightleftharpoons H_2(g) + I_2(g)$

(3) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$ (4) $2C(s) + O_2(g) \rightleftharpoons 2CO(g)$

CE0127

21. Two solids dissociate as follows **[JEE-MAINS(online)-19]**

$A(s) \rightleftharpoons B(g) + C(g)\ ;\ K_{p_1} = x\ atm^2$

$D(s) \rightleftharpoons C(g) + E(g)\ ;\ K_{p_2} = y\ atm^2$

The total pressure when both the solids dissociate simultaneously is :-

(1) $(x + y)$ atm (2) $x^2 + y^2$ atm (3) $2\left(\sqrt{x+y}\right)$atm (4) $\sqrt{x+y}$ atm

CE0128

22. In a chemical reaction, $A + 2B \xrightleftharpoons{K} 2C + D$, 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-MAINS(online)-19]**

(1) 16 (2) 4 (3) 1 (4) $\frac{1}{4}$

CE0129

23. 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 $P_{NH_3} << P_{total}$ at equilibrium)

(1) $\frac{3^{\frac{3}{2}} K_P^{\frac{1}{2}} P^2}{4}$ (2) $\frac{3^{\frac{3}{2}} K_P^{\frac{1}{2}} P^2}{16}$ (3) $\frac{K_P^{\frac{1}{2}} P^2}{16}$ (4) $\frac{K_P^{\frac{1}{2}} P^2}{4}$

CE0130

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

$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

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

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

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

CE0131

25. Consider the following reversible chemical reactions : **[JEE-MAINS(online)-19]**
$A_2(g) + Br_2(g) \xrightleftharpoons{K_1} 2AB(g)$ .....(1)

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

The relation between K_1 and K_2 is :

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

CE0132

26. 5.1g 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$^{/01}$, molar mass of N = 14g mol^{-1}) **[JEE-MAINS(online)-19]**
(1) 1×10^{-4} atm^2 (2) 4.9×10^{-3} atm^2 (3) 0.242 atm^2 (4) 0.242×10^{-4} atm^2

CE0133

EXERCISE # J-ADVANCED

1. The thermal dissociation equilibrium of $CaCO_3(s)$ is studied under different conditions.

$CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ **[JEE 2013]**

For this equilibrium, the correct statement(s) is(are)

(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

CE0134

2. For the following reaction, the equilibrium constant K_c at 298 K is 1.6×10^{17}.

$Fe^{2+}(aq) + S^{2-}(aq) \rightleftharpoons FeS(s)$

When equal volumes of 0.06 M $Fe^{2+}(aq)$ and 0.2 M $S^{2-}(aq)$ solutions are mixed, the equilibrium concentration of $Fe^{2+}(aq)$ is found to be $\mathbf{Y} \times 10^{-17}$ **M**. The value of Y is (upto two decimal places.)

[JEE 2019]

CE0135

ANSWER KEY

EXERCISE # S-I

1. **(a) incomplete (b) almost complete**

2. **(a)** $K_P = \dfrac{(P_{SO_3})}{(P_{SO_2})(P_{O_2})^{\frac{1}{2}}}$; $K_C = \dfrac{[SO_3]}{[SO_2][O_2]^{\frac{1}{2}}}$

(b) $K_C = [H_2O]$ **[here $H_2O(\ell)$ is a pure liquid so its concentration is 1.]**

$K_P = P_{H_2O}$

= vapour pressure

= aqueous tension

(c) $K_C = [NH_3]^2 [CO_2]$ **($\because$ active mass of solid is 1)**

$K_P = \left(P_{NH_3}\right)^2 P_{CO_2}$

(d) $K_C = \dfrac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$ **[here H_2O is not in excess]**

K_P is not defined for liquid phase.

(e) $K_C = \dfrac{[NH_4^+][OH^-]}{[NH_3]}$ **[here $H_2O(\ell)$ is in excess (solvent) so its concentration is 1]**

(f) $K_{PC} = \dfrac{P_{H_2} \times [Zn^{2+}]}{[H^+]^2}$ **[$\because$ active mass of solid is 1]**

3. **(a)** **Here, $\Delta n_g = 1 + 1 - 1 = 1$**

$K_p = K_c (RT)^1 = K_c RT$

(b) **Here, $\Delta n_g = 2 - (3+1) = -2$**

$K_p = K_c (RT)^{-2}$

(c) **Here, $\Delta n_g = 2 - (1+1) = 0$**

$K_p = K_c (RT)^0 = K_c$

(d) **Here, $\Delta n_g = 2 + 1 - 2 = 1$**

$K_p = K_c (RT)^1 = K_c RT$

(e) **Here, $\Delta n_g = 2 - (2 + 1) = -1$**

$K_p = K_c (RT)^{-1} = K_c / RT$

4. $\because \quad K_1 > K_2$

So the stability of $XO < XO_2$

For reactants, stability increases when value of K decreases.

5. **$Q_c > K_c$ so the reaction will proceed in the reverse direction.**

6. **(a)** $Q_C = \dfrac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$ **[$\because$ Water is not a solvent here]**

(b) $K_c = \dfrac{(0.171)\times(0.171)}{(1-0.171)\times(0.180-0.171)} = 3.92$

(c) $Q_c = \dfrac{(0.214)\times(0.214)}{(0.786)\times(0.286)} = 0.204 \neq K_c$

$\therefore$ **Equilibrium has not been reached.**

7. **2×10^9**

8. **0.9**

9. **$K_C = 100$**

10. **$K_p = 0.2463$**

11. **64×10^{-32}**

12. $K_c = 0.44$

13. **$K_P = 1.2$ atm.**

14. **[HI]** $= \dfrac{1}{3}M$

$[I_2] = [H_2]$ $= \dfrac{1}{30}M$

15. **(a) 0.1** **(b) 0.4**

16. **[A] = 5 M, [B] = 5 M, [C] = 1 M, [D] = 25 M**

17.

new equilibrium	PCl_5	PCl_3	Cl_2
Mole	4	4	2
Partial pressure	20 atm	20 atm	10 atm

18. $\alpha = \sqrt{\dfrac{K_p}{4P + K_p}}$

19. **(A)** $\alpha = \dfrac{4}{5} = 0.8$ **(B)** $K_C = 16$

20. **$K_C = 0.001$**

21. **$[NO] = 2M, [N_2] = [O_2] = 0.5M$**

22. **$P_{ClF} = P_{F_2} = 0.1$ atm, $P_{ClF_3} = 05$ atm**

23. **$K_P = 0.4$, a ~ 0.1**

24. **50%**

25. **$K_p = 0.01$ atm**

26. **$K_p = 2.5$ atm, P = 15 atm**

27. **K = 4**

28. $P_{CS_2} = 1.8$ atm, $P_{S_2} = 0.2$ atm

29. 22.4 mg

30. $P_{H_2O} = 5 \times 10^{-15}$ atm

31. 0.821 atm

32. (a) $K = [CH_3OH]/[H_2]^2[CO]$,
(b) 1. [H_2] increase, [CO] decrease, [CH_3OH] increase ; 2. [H_2] increase, [CO] decrease, [CH_3OH] decrease ; 3. [H_2] increase, [CO] increase, [CH_3OH] increase ; 4. [H_2] increase, [CO] increase, [CH_3OH] increase ; 5. [H_2] increase, [CO] increase, [CH_3OH] decrease ; 6. no change

33. 2

34. 250

35. k_r increase more than k_f, this means that E_a (reverse) is greater than E_a (forward). Hence exothermic reaction.

EXERCISE # S-II

1. Ans.(2.4 atm)

2. Ans.31/27

3. Ans.(0.11)

4. Ans.(2×10^{-4})

5. $[PCl_3] = [Cl_2] = 0.027$ M

6. (a) 6.667×10^{-3} mol L^{-1}; (b) n (N_2O_4) = 0.374 mol; n (NO_2) = 0.052 mol ; (c) 10.49 atm (d) 6.44 %

7. (i) 2; (ii) 1.2 mol/L; (iii) 0.1 moles/hr

8. Ans.K_c=54, n_{HI}=0.9 mol, n_{I2}= 0.05 mol, n_{H2} = 0.3 mol

9. Ans.3.6×10^{-3} atm

10. Ans.(a) 400mm^2, 900mm^2 (b) 4: 9, (c) 72.15 mm Hg

11. Ans. (4)

12. Ans. ($SrCl_2 \cdot 2H_2O$)

13. Ans. (10)

14. $K_{p_1} = \dfrac{1}{20P_0^2}$; $K_{p_2} = \dfrac{3}{20P_0^2}$

15. (a) 84 ; (b) 0.095 ; (c) 17.35 %

EXERCISE # O-I

1.	(D)	2.	(C)	3.	(D)]	4.	(B)
5.	(C)	6.	(C)	7.	(A)	8.	(C)
9.	(A)	10.	(A)	11.	(A)	12.	(C)
13.	(C)	14.	(A)	15.	(B)	16.	(B)
17.	(A)	18.	(D)	19.	(B)	20.	(D)
21.	(C)	22.	(B)	23.	(B)	24.	(A)
25.	(C)	26.	(C)	27.	(C)	28.	(B)
29.	(C)	30.	(D)	31.	(A)	32.	(A)
33.	(C)	34.	(A)	35.	(D)		

EXERCISE # O-II

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

Match the column :

21. **(A) - P,R,S (B) - P,Q,R,S (C) - P, Q, R, S ; (D) - Q**

22 **A - (s), B - (p,q,s), C - (p,q,r), D - (r)**

23.	**(D)**	**24.**	**(C)**	**25.**	**(A)**

EXERCISE # J-MAIN

1.	**Ans.(3)**	**2.**	**Ans.(1)**	**3.**	**Ans(3)**	**4.**	**Ans(1)**
5.	**Ans(4)**	**6.**	**Ans(2)**	**7.**	**Ans(2)**	**8.**	**Ans(1)**
9.	**Ans(3)**	**10.**	**Ans.(4)**	**11.**	**Ans.(4)**	**12.**	**Ans.(2)**
13.	**Ans.(4)**	**14.**	**Ans.(1)**	**15.**	**Ans.(4)**	**16.**	**Ans.(2)**
17.	**Ans.(4)**	**18.**	**Ans.(3)**	**19.**	**Ans.(1)**	**20.**	**Ans.(4)**
21.	**Ans. (3)**	**22.**	**Ans.(2)**	**23.**	**Ans.(2)**	**24.**	**Ans.(4)**
25.	**Ans.(2)**	**26.**	**Ans.(3)**				

EXERCISE # J-ADVANCED

1. **Ans.(A,B,D)**

2. **Ans.(8.92 or 8.93)**