CHEMICAL EQUILIBRIUM

Table of Contents

₿	Theory	2
₽	Solved Examples	7
₽	Exercise - 1 : Basic Objective Questions	13
₽	Exercise - 2 : Previous Year JEE MAINS Questions	21
₽	Exercise - 3 : Advanced Objective Questions	24
₽	Exercise - 4 : Previous Year JEE Advanced Questions	36
Ø	Answer Key	39

THEORY

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1. INTRODUCTION

Equilibrium represents the state of a process in which the proprties like temperature, pressure, concentration of the system do not show any change with the passage of time.

If the opposing processes involve only physical changes, the equilibrium is called physical equilibrium. If the opposing processes involve chemical changes, i.e., the opposing processes are chemical reactions, the equilibrium is called chemical equilibrium.

2. EQUILIBRIA IN CHEMICAL PROCESSES

2.1 Reversible Reactions

A reaction in which not only the reactants react to form the products under certain conditions but also the products react to form reactants under the same conditions is called a reversible reaction. In other words a reaction which takes place not only in the forward direction but also in the backward direction under the same conditions is called a reversible reaction.

A reversible reaction between A and B to form C and D is represented as :

$$A+B \implies C+D$$

2.2 Irreversible Reactions

If a reaction cannot take place in the reverse direction, i.e., the products formed do not react to give back the reactants under the same conditions, it is called an irreversible reaction.

$$A + B \longrightarrow C + D$$



- It is the state of minimum Gibb's energy
- dG = 0 and $\Delta G = 0$ at this state
- Rate of forward reaction = Rate of backward reaction
 - This equilibrium is dynamic and stable in nature

Dynamic Nature of Chemical Equilibrium

In the Haber's process, starting with definite amounts of N_2 and H_2 and carrying out the reaction at a particular temperature, when equilibrium is attained, the concentrations of N_2 , H_2 and NH_3 become constant. If the experiment is repeated by taking deuterium (D_2) in place of H_2 but with the same amounts and exactly similar conditions as before, equilibrium is attained containing D_2 and ND_3 in place of H_2 and NH_3 but in the same amounts. Now, if the two reaction mixtures are mixed, then after some time, it is found that the concentrations of ammonia and hydrogen are same except that now all forms of ammonia (i.e., NH_3 , NH_2D , NHD_2 , ND_3) and all forms of hydrogen (i.e., H_2 , HD, D_2) are present. This shows that at equilibrium, the reaction is still going on, i.e., equilibrium is dynamic in nature.



Representing the attainment of equilibrium for the reaction $N_2(g) + 3H_2(g) \rightleftharpoons NH_3(g)$

2.4 Characteristics of Chemical Equilibrium

- At equilibrium, the concentration of each of the reactants (i) and the products becomes constant.
- At equilibrium, the rate of forward reaction becomes equal (ii) to the rate of backward reaction and hence the equilibrium is dynamic in nature.
- A chemical equilibrium can be established only if none of (iii) the products is allowed to escape out or separate out as a solid.

e.g. if CO₂ gas escapes out in case of decomposition of CaCO₃, the reaction will no longer remain reversible.

Similarly, the reaction is irreversible if one of the products separates out as solid,

 $AgNO_{2} + KCl \longrightarrow AgCl \downarrow + KNO_{2}$

(iv) Chemical equilibrium can be attained from either direction, i.e., from the direction of the reactants as well as from the direction of the products.

3. RATE OF A REACTION

Average Rate = Change in concentration/Time taken $=\Delta c/\Delta t$

 $\Delta c = Final Concentration - Initial concentration$

Lim $\Delta c/\Delta t = dc/dt$

 $\Delta t \rightarrow 0$

Units of rate : conc/time or mol/Ls

3.2 Overall rate of a reaction

$aA + bB \leftrightarrow cC + dD$

Overall Rate =

 $-(1/a)\Delta A/\Delta t = -(1/b)\Delta B/\Delta t = +(1/c)\Delta C/\Delta t = +(1/d)\Delta D/\Delta t$

Overall rate :

Rate of forward reaction - Rate of backward reaction

"At equilibrium the overall rate of a reversible reaction becomes zero".

4. EQUILIBRIUM CONSTANT (K)

4.1 Law of Mass Action

The rate of a reaction is proportional to the product of the active masses of the reactants, each raised to the power equal to its stoichiometric coefficient as represented by the balanced chemical equation.

 $aA + bB + cC + \dots$ Products

Rate of reaction $\propto [A]^{a} [B]^{b} [C]^{c} \dots$

Law of Chemical Equilibrium is a result obtained by applying the Law of Mass Action to a reversible reaction in equilibrium.

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

Rate of the forward reaction \propto [A] [B] = k_f[A] [B]

Rate of the backward reaction \propto [C] [D] = k_{h} [C] [D]

At equilibrium,

Rate of forward reaction = Rate of backward reaction

$$k_{f}[A][B] = k_{b}[C][D] \text{ or } \frac{[C][D]}{[A][B]} = \frac{k_{f}}{k_{b}} = K$$

At constant temperature, as k_f and k_h are constant, therefore,

 $\frac{\mathbf{k}_{f}}{\mathbf{k}_{f}} = \mathbf{K}$ is also constant at constant temperature and is

called 'Equilibrium constant'.

The product of the molar concentrations of the products, each raised to the power equal to its stoichiometric coefficient divided by the product of the molar concentrations of the reactants, each raised to the power equal to its stoichiometric coefficient is constant at constant temperature and is called Equilibrium constant.

4.2 Characteristics of Equilibrium Constant

- (i) The value of the equilibrium constant for a particular reaction is always constant depending only upon the temperature of the reaction and is independent of the concentrations of the reactants with which we start or the direction from which the equilibrium is approached.
- (ii) If the reaction is reversed, the value of the equilibrium constant in inversed.
- (iii) If the equation (having equilibrium constant K) is divided by 2, the equilibrium constant for the new equation is the square root of K (i.e., \sqrt{K}).
- (iv) If the equation (having equilibrium constant K) is multiplied by 2, the equilibrium constant for the new equation is the square of K (i.e., K^2)
- (v) If the equation (having equilibrium constant K) is written in two steps (having equilibrium constant K_1 and K_2) then $K_1 \times K_2 = K$.
- (vi) The value of the equilibrium constant is not affected by the addition of a catalyst to the reaction.

This is because the catalyst increases the speed of the forward reaction and the backward reaction to the same extent.

4.3 Extent of Reaction

High value of Kc ($K_c > 10^3$) \rightarrow At equilibrium reaction is forward dominant

Low value of Kc ($K_c < 10^{-3}$) \rightarrow At equilibrium reaction is backward dominant

Moderate value of K_c (between 10³ and 10⁻³) \rightarrow At equilibrium neither direction dominates



4.4 Reaction Quotient (Q)

$aA + bB \leftrightarrow cC + dD$

 $Q = [C]^{c} [D]^{d} / [A]^{a} [B]^{b}$

- $Q > K_{c}$: Reaction will tend towards backward direction
- $Q > K_c$: Reaction will tend towards forward direction
- $Q > K_c$: Reaction will be at equilibrium

Note :

Q is a variable which always approaches K_{eq} which is a constant.

4.5 Calculating Equilibrium Concentrations

Suppose we are given the following data :

- 1. The balanced reaction and value of K_c
- 2. The initial concentration of the reactants, or the initial moles
- 3. Volume of the container

And we need to find the final equilibrium concentration of the reactants and products. Then we can follow the following steps :

Step-1

Write down the balanced chemical equation for the reaction

Step-2

Under every reactant and product, write down the initial moles/concentration

Step-3

Subtract the amount reacting and add the amount produced in terms of a variable x and note down the equilibrium concentration in terms of x. If we are dealing in moles then we will need to divide the moles by volume to obtain concentrations.

Step-4

Substitute the equilibrium concentration in the expression of K_c and equate it to the value of K_c .

Step-5

Solve the above equation and calculate the value of x and in case of multiple solutions select the value which is sensible from reaction point of view. Then back substitute the value of x in the equilibrium concentration expression and obtain the actual value of the same.

4.6 Equilibrium constant K

$aA + bB \leftrightarrow cC + dD$

 $K_{p} = (P_{C}^{c} \times P_{D}^{d}) / (PAa \times P_{B}^{b})$

where P_C , P_D , P_A , P_B are partial pressures of A, B, C and D respectively.

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

R = 0.0821 L atm/mol-K

4.7 Relationship of K_{eq} and ΔG

For any reaction :

 $\Delta G = \Delta G^{\circ} + RT InQ$ Where Q is the reaction quotient.

At equilibrium $\Delta G = 0$

 $\Delta G^{\circ} = -RT \ln K_{eq} = -2.303RT \log_{10} K_{eq}$

where K_{eq} is generally taken as K_p . It depends on the definition of standard values to define ΔG° .

If the standard active masses are taken as 1 M each then we will take $K_{eq} = K_{C}$ and if they are taken as 1 atm each then we will take $K_{eq} = K_{p}$.

4.8 Dependence of $\mathbf{K}_{_{eq}}$ on temperature

Van't Hoff Equation :

ln (K₂/K₁) = (Δ H/R) (1/T₁-1/T₂) or log10 (K₂/K₁) = (Δ H/2.303R) (1/T₁-1/T₂)

Exothermic Reactions

 $\Delta H = negative$

On increasing the temperature the equilibrium constant will decrease i.e. The reaction will become more backward dominant.

Endothermic Reaction

 $\Delta H = possitive$

On increasing the temperature the equilibrium constant will increase. The reaction will become more forward dominant.

POINTS TO REMEBER

Whether the reaction is exothermic or endothermic on increasing the temperature, it will tend towards endothermic direction.

5. HOMOGENOUS EQUILIBRIA

Reactions in which all reactants and products are in the same phase Homogenous Reactions can further be divided into three sub-categoreis :

5.1 Those reactions where gaseous moles increase $(\Delta n = +ve)$

$$PCl_{5}(g) \leftrightarrow PCl_{3}(g) + Cl_{2}(g)$$

5.2 Those reactions where gaseous moles remain the same $(\Delta n = 0)$

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

5.3 Those reactions where gaseous moles decrease $(\Delta n = -ve)$

 $2NO_2(g) \leftrightarrow N_2O_4(g)$

6. DEGREE OF DISSOCIATION, α

It is defined as the fraction of molecules dissociating. For example, if 100 molecules are present and only 40 dissociate then the degree of dissociation is 0.4 or 40%.

7. HETEROGENEOUS EQUILIBRIA

Category of reactions where various phases/states exist in the same reaction.

In presence of gases the activity of solids and excess liquids is constant. Therefore we can assume the active masses of solids and excess liquids as constant.

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

 $K_c = [CO_2]$
 $Kp = P_{CO_2}$

8. LE CHATELIER'S PRINCIPLE

If a distrubance is introduced in an equilibrium mixture it will behave so as to undo the distrubance and re-establish equilibrium.

8.1 Effect of Change of Concentration

If in a reaction in equilibrium, the concentration of any reactant is increased, the equilibrium shifts in the forward direction. On the other hand, if the concentration of any product is increased, the equilibrium shifts in the backward direction. The reverse happens if the concentrations are decreased.

8.2 Effect of change of temperature

Exothermic reactions are favoured by low temperature whereas endothermic reations are favoured by high temperature.

8.3 Effect of change of pressure

Low pressure favours those reactions which are accompanied by increase in total number of moles and high pressure favours those reactions which take place with decrease in total number of moles. However, pressure has no effect on an equilibrium reaction which proceeds with no change in total number of moles.

8.4 Effect of change in volume

The effect of decrease of volume is equivalent to the effect of increase of pressure.

hence the effect of decrease in volume will be to shift the equilibrium in the direction in which the number of moles decreases.

8.5 Effect of a Catalyst

A catalyst increases the rate of the chemical reaction by making available a new low energy pathway for the conversion of reactants to products. It increases the rate of forward and reverse reactions that pass through the same transition state and does not affect equilibrium. Catalyst lowers the activation energy for the forward and reverse reactions by exactly the same amount. Catalyst does not affect the equilibrium composition of a reaction mixture. It does not appear in the balanced chemical equation or in the equilibrium constant expression.

eg contact process,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); K_c = 1.7 \times 10^{26}$$

Practically the oxidation of SO_2 to SO_3 is very slow. Thus, platinum or divanadium penta-oxide (V₂ O₅) is used as catalyst to increase the rate of the reaction.

8.6 Effect of adding an inert gas to a reaction mixture in equilibrium.

- (a) If the reaction takes place at constant volume addition of an inert gas will not change the molar concentrations of the reactants and products. Hence, the state of equilibrium will remain unaffected.
- (b) If the reaction takes place at constant pressure, addition of inert gas must accompany in increase in the total volume to keep pressure constant. Thus, reaction shifts towards larger number of moles.

SOLVED EXAMPLES

Example - 1

The following reaction has attained equilibrium

$$CO(g) + 2H_2(g) \Longrightarrow CH_3OH(g), \Delta H^\circ = -92.0 \text{kJ mol}^{-1}$$

What will happen if (i) volume of the reaction vessel is suddenly reduced to half? (ii) the partial pressure of hydrogen is suddenly doubled? (iii) an inert gas is added to the system?

Sol.
$$K_{c} = \frac{[CH_{3}OH]}{[CO][H_{2}]^{2}}, K_{p} = \frac{P_{CH_{3}OH}}{P_{CO} \times p_{H_{2}}^{2}}$$

(i) When volume of the vessel is reduced to half, the concentration of each reactant or product becomes double.

Thus, $Q_c = \frac{2[CH_3OH]}{2[CO] \times (2[H_2])^2} = \frac{1}{4}K_c$ As $Q_c < K_c$, equilibrium

will shift in the forward direction, producing more of CH_3OH to make $Q_c = K_c$.

(ii)
$$Q_{p} = \frac{P_{CH_{3}OH}}{p_{CO}} \times (2 p_{H_{2}})^{2} = \frac{1}{4} K_{p}.$$

Again $Q_p < K_p$, equilibrium will shift in the forward direction to make $Q_p = K_p$.

(iii) As volume remains constant, molar concentration will not change. Hence there is no effect on the state of equilibrium.

Example - 2

A sample of HI (g) is placed in a flask at a pressure of 0.2 atm. At equilibrium, the partial pressure of HI (g) is 0.04 atm. What is K_p for the given equilibrium?

Sol.

.

$$2\mathrm{HI}(\mathrm{g}) \iff \mathrm{H}_2(\mathrm{g}) + \mathrm{I}_2(\mathrm{g})$$

0

0

Initial pressure 0.2 atm

At eqm.

0.04 atm
$$\frac{0.16}{2}$$
 atm $\frac{0.16}{2}$ atm

 $= 0.08 \, \text{atm}$

(Decrease in the pressure of HI = 0.2-0.04=0.16 atm.)

.
$$K_{p} = \frac{p_{H_{2}} \times p_{I_{2}}}{p_{H_{1}}^{2}} = \frac{0.08atm \times 0.08atm}{(0.04atm)^{2}} = 4.0.$$

Example - 3

One mole of H_2O and one mole of CO are taken in a 10 litre vessel and heated at 725 K. At equilibrium 40% of water (by mass) reacts with CO according to the equation:

$$H_2O(g) + CO(g) \Longrightarrow H_2O(g) + CO_2(g)$$

Calculate the equilibrium constant for the reaction.

Sol. At equilibrium $[H_2O] = \frac{1-0.40}{10} \text{ mol } L^{-1} = 0.06 \text{ mol } L^{-1}$, [CO]=0.06 mol L⁻¹.

$$[H_2] = \frac{0.4}{10} \operatorname{mol} L^{-1} = 0.04 \operatorname{mol} L^{-1},$$

$$[CO_2] = 0.04 \text{ mol } L^{-1},$$

$$K = \frac{[H_2][CO_2]}{[H_2O][CO]} = \frac{0.04 \times 0.04}{0.06 \times 0.06} = 0.444$$

Example - 4

At 700 K, equilibrium constant for the reaction $H_2(g) + I_2(g) \Longrightarrow 2HI(g)$ is 54.8. If 0.5 mol L⁻¹ of HI (g) is present at equilibrium at 700K, what are the concentrations of $H_2(g)$ and $I_2(g)$ assuming that we initially started with HI (g) and allowed it to reach equilibrium at 700 K.

Sol.
$$2\text{HI}(g) \Longrightarrow H_2(g) + I_2(g), K = \frac{1}{54.8}$$

At equilibrium [HI]= $0.5 \text{ mol } L^{-1}$,

$$[H_2] = [I_2] = x \mod L^{-1} \therefore K = \frac{x \times x}{(0.5)^2} = \frac{1}{54.8}$$

This gives
$$x = 0.068. i.e., [H_2] = [I_2] = 0.068 \text{ mol } L^{-1}$$

Example - 5

What is the equilibrium concentration of each of substances in the equilibrium when the initial concentration of ICI was 0.78 M?

 $2ICl(g) \Longrightarrow I_2(g)+Cl_2(g), K_c=0.14$

Sol. Suppose at equilibrium, $[I_2] = [CI_2] = x \mod L^1$. Then

$$2ICl \Longrightarrow I_2(g) + Cl_2(g)$$

х

х

Initial conc. 0.78M 0 0

At eqm. 0.78-2x

$$K_{c} = \frac{[I_{2}][Cl_{2}]}{[ICl]^{2}} \quad \therefore \quad 0.14 = \frac{x \times x}{(0.78 - 2x)^{2}}$$

or
$$x^2 = 0.14(0.78 - 2x)^2$$
 or $\frac{x}{0.78 - 2x} = \sqrt{0.14} = 0.374$

or x = 0.292 - 0.748x or 1.748x = 0.292 or x = 0.167

Hence, at equilibrium,

$$[I_2] = [CI_2] = 0.167M, [ICI] = 0.78-2 \times 0.167M = 0.446M$$

Example - 6

Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium represented as:

 $CH_3COOH(l) + C_2H_5OH(l) \Longrightarrow CH_3COOC_2H_5(l) + H_2O(l)$

- (i) Write the concentration ratio (reaction quotient), Q_c for this reaction (Note: water is not in excess and is not a solvent in this reaction)
- (ii) At 293 K, if one starts with 1.00 mol of acetic acid and 0.18 mol of ethanol, there is 0.171 mol of ethyl acetate in the final equilibrium mixture. Calculate the equilibrium constant.
- (iii) Starting with 0.5 mol of ethanol and 1.0 mol of acetic acid and maintaining it at 293 K, 0.214 mol of ethyl acetate is found after some time. Has equilibrium been reached?

Sol. (i) $Q_c = \frac{[CH_3COOC_2H_5][H_2O]}{[CH_3COOH][C_2H_5OH]}$

(ii)
$$CH_3COOH + C_2H_5OH \Longrightarrow CH_3COOC_2H_5 + H_2O$$

Initial 1.00 mol 0.180 mol

= 0.829 mol = 0.009 mol

Molar

$$K_{c} = \frac{[CH_{3}COOC_{2}H_{5}][H_{2}O]}{[CH_{3}COOH][C_{2}H_{5}OH]} = \frac{(0.171/V)(0.171/V)}{(0.829/V)(0.009/V)} = 3.92$$

(iii) $CH_3COOH + C_2H_5OH \Longrightarrow CH_3COOC_2H_5 + H_2O$

Initial 1.000 mol 0.500 mol

After time t 1-0.214 0.500-0.214 0.214 mol 0.214 mol

 $= 0.786 \,\mathrm{mol} = 0.286 \,\mathrm{mol}$

Reaction quotient (Q_c) = $\frac{(0.214/V)(0.214/V)}{(0.786/V)(0.286/V)} = 0.204$

As $Q_c \neq K_c$, equilibrium has not been attained

Example - 7

A sample of pure PCl₅ was introduced into an evacuated vessel at 473 K. After equilibrium was attained, concentration of PCl₅ was found to be 0.5×10^{-1} mol L⁻¹. If value of K_c is 8.3×10^{-3} , what are the concentrations of PCl₃ and Cl₂ at equilibrium?

Sol.
$$PCl_5(g) \implies PCl_3(g) + Cl_2(g)$$

At eqm 0.5×10^{-1} mol L⁻¹ x mol L⁻¹ x mol L⁻¹ (suppose)

:
$$K_c = \frac{x^2}{0.5 \times 10^{-1}} = 8.3 \times 10^{-3}$$
 (Given)

or
$$x^2 = (8.3 \times 10^{-3})(0.5 \times 10^{-1}) = 4.15 \times 10^{-4}$$
 or

$$x = \sqrt{4.15 \times 10^{-4}} = 2.04 \times 10^{-2} M = 0.02 M$$

Hence,
$$[PCl_3]_{eq} = [Cl_2]_{eq} = 0.02M$$

Example - 8

Equilibrium constant, K_c for the reaction, $N_2(g) + 3H_2(g) \implies 2NH_3(g)$ at 500 K is 0.061. At a particular time, the analysis shows that composition of the reaction mixture is 3.0 mol L⁻¹ N₂, 2.0 mol L⁻¹ H₂ and 0.5 mol L⁻¹ NH₃. I_s the reaction at equilibrium? If not, in which direction does the reaction tend to proceed to reach equilibrium?

Sol.
$$Q_c = \frac{[NH_3]^2}{[N_2][H_2]^3} = \frac{(0.5)^2}{(3.0)(2.0)^3} = 0.0104$$

As $Q_c \neq K_c$, reaction is **not in equilibrium**

As $Q_c < K_c$, reaction will proceed in the forward direction.

Example - 9

The equilibrium constant for the reaction $H_2(g) + Br_2(g) \longrightarrow 2HBr(g)$ at 1024 K is 1.6×10⁵. Find the equilibrium pressure of all gases if 10.0 bar of HBr is introduced into a sealed container at 1024 K.

p/2

Sol.
$$2\text{HBr}(g) \Longrightarrow H_2(g) + \text{Br}_2(g). \text{ K} = \frac{1}{(1.6 \times 10^5)}$$

Initial 10 bar

At eqm. 10-p

$$K_{p} = \frac{(p/2)(p/2)}{(10-p)^{2}} = \frac{1}{1.6 \times 10^{5}} \frac{p^{2}}{4(10-p)^{2}} = \frac{1}{1.6 \times 10^{5}}$$

p/2

Taking square root of both sides, we get

$$\frac{p}{2(10-p)} = \frac{1}{4 \times 10^2}$$
 or $4 \times 10^2 p = 2(10-p)$ or

$$402p = 20 \text{ or } p = \frac{20}{402} = 4.98 \times 10^{-2} \text{ bar}$$

Hence, at equilibrium $p_{H_2} = p_{Br_2}$

$$= p/2 = 2.5 \times 10^{-2}$$
 bar, $p_{HBr} = 10 - p \approx 10$ bar

Example - 10

Dihydrogen gas used in Haber's process is produced by reacting methane from natural gas with high temperature steam. The first stage of two stage reaction involves the formation of CO and H₂. In second stage, CO formed in first state is reacted with more steam in water gas shift reaction, $CO(g) + H_2O(g) \implies CO_2(g) + H_2(g)$. If a reaction vessel at 400°C is charged with an equimolar mixture of CO and steam such that $P_{CO} = P_{H_2O} = 4.0$ bar, what will be the partial pressure of H₂ at equilibrium? $K_p = 0.1$ at 400°C.

Sol. Suppose the partial pressure of H_2 at equilibrium= p bar

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

p

Initial pressure 4.0 bar 4.0 bar

At eqm (4–p) (4–p) p

$$K_p = \frac{p^2}{(4-p)^2} = 0.1$$
(given) $\therefore \frac{p}{4-p} = \sqrt{0.1} = 0.316$

p=1.264-0.316p or 1.316p=1.264 or p=0.96 bar. Hence,

 $(p_{H_2})_{eq} = 0.96 \text{ bar}$

Example - 11

Predict which of the following reaction will have appreciable concentration of reactants and products:

(a)
$$Cl_2(g) \Longrightarrow 2Cl(g), K_c = 5 \times 10^{-39}$$

(b)
$$Cl_2(g) + 2NO(g) \Longrightarrow 2NOCl(g), K_c = 3.7 \times 10^8$$

(c)
$$Cl_2(g) + 2NO_2(g) \Longrightarrow 2NO_2Cl(g), K_c = 1.8$$

Sol. For reaction (c), as K_c is neither high nor very low, reactants and products will be present in comparable amounts.

Example - 12

The value of K_c for reaction, $3O_2(g) = 2O_3(g)$, is 2.0×10^{-50} at 25°C. If the equilibrium concentration of O_2 in air at 25°C is 1.6×10^{-2} , what is the concentration of O_3 ?

Sol.
$$K_{c} = \frac{[O_{3}]^{2}}{[O_{2}]^{3}} \therefore 2.0 \times 10^{-50} = \frac{[O_{3}]^{2}}{(1.6 \times 10^{-2})^{3}}$$

or
$$[O_3]^2 = (2.0 \times 10^{-50}) (1.6 \times 10^{-2})^3 = 8.192 \times 10^{-56} \text{ or}$$

 $[O_3] = 2.86 \times 10^{-28} \text{ M}$

Example - 13

The reaction, CO(g)+3H₂(g) \longrightarrow CH₄(g) + H₂O (g), is at equilibrium at 1300 K in a 1 L flask. It also contains 0.30 mol of CO, 0.10 mol of H₂ and 0.02 mol of H₂O and an unknown amount of CH₄ in the flask. Determine the concentration of CH₄ in the mixture. The equilibrium constant, K_c, for the reaction at the given temperature is 3.90.

Sol.
$$K_{c} = \frac{[CH_{4}][H_{2}O]}{[CO][H_{2}]^{3}}$$

: $3.90 = \frac{[CH_4](0.02)}{(0.30)(0.10)^3}$ (molar conc= No. of moles

because volume of flask = 1L)

or [CH₄]=
$$0.0585 \text{ M}=5.85 \times 10^{-2} \text{ M}$$

Example - 14

At emperature T, a compound $AB_2(g)$ dissociates according to the reaction

 $2AB_2 \implies 2AB(g) + B_2(g)$

with a degree of dissociation, x, which is small compared with unity. Deduce the expression for x in terms of the equilibrium constant K_p and the total pressure, P.

х

Sol.

Initial

 $2AB_2 \Longrightarrow 2AB(g) + B_2(g)$ 1 mole 0 0

At equilibrium 1 - x 2x

Total number of moles at equilibrium = 1-x+2x+x=1+2x

$$p_{AB_2} = \frac{1-x}{1+2x} \times P, \ p_{AB} = \frac{2x}{1+2x} \times P, \ p_{B_2} = \frac{x}{1+2x} \times P$$
$$\therefore \ K_p = \frac{p_{AB}^2 \times p_{B_2}}{p_{AB_2}^2} = \left(\frac{2x \times P}{1+2x}\right)^2 \times \left(\frac{x \times P}{1+2x}\right) \left(\frac{1-x}{1+2x} \times P\right)^2$$

or
$$K_p = \frac{4x^3 P}{(1-x)(1+2x)}$$

Neglection x in comparison to unity,

$$\mathbf{K}_{\mathrm{p}} = 4\mathrm{x}^{3}\mathrm{P}\,\mathrm{or}\,\mathrm{x} = \left(\frac{\mathrm{K}_{\mathrm{p}}}{4\mathrm{P}}\right)^{1/3}$$

Example - 15

Prove that the pressure necessary to obtain 50% dissociation of PCl_s at 500 K is numerically equal to three times the value of the equilibrium constant, K_s .

0

Sol.

Initial moles 1 0

Moles at eqm. 1–0.5=0.5 0.5 0.5 Total=1.5 moles

 $PCl_5 \implies PCl_3 + Cl_2$

If P is the total required pressure, then

$$p_{PCl_5} = \frac{0.5}{1.5} \times P = \frac{P}{3}, P_{PCl_3} = \frac{0.5}{1.5} \times P = \frac{P}{3}$$
$$p_{Cl_2} = \frac{0.5}{1.5} \times P = \frac{P}{3}$$

:.
$$K_p = \frac{p_{PCl_3} \times p_{Cl_2}}{p_{PCl_5}} = \frac{(P/3)(p/3)}{(p/3)} = \frac{P}{3} \text{ or } P = 3K_p$$

Example - 16

What is the effect of reducing the volume on the system described below?

$$2C(s) + O_2(g) \Longrightarrow 2CO(g)$$

Sol. On reducing the volume, the pressure will increase. By Le Chatelier's principle, equilibrium will shift to the side accompanied by decrease of pressure, i.e., decrease in the number of gaseous moles, i.e., backward direction.

Example - 17

The degree of dissociation is 0.4 at 400 K and 1.0 atm for the gaseous reaction

$$PCl_5 \implies PCl_3 + Cl_2$$
.

Assuming ideal behaviour of all the gases, calculate the density of the equilibrium mixture at 400 K and 1.0 atmosphere. (Atomic mass of P = 31.0 and Cl = 35.5)

Sol.

Initial 1 mole 0 0 At eqm. 0.6 0.4 0.4 moles Average molecular mass of mixture

 $PCl_5 \implies PCl_3 + Cl_2$

$$=\frac{0.6(31+5\times35.5)+0.4(31+3\times35.5)+0.4(2\times35.5)}{0.6+0.4+0.4}$$

$$=\frac{125.1+55+42.6}{1.4}=148.92$$

For ideal gases,

Initial 0.1 mol

$$PV = nRT = \frac{W}{M}RT$$
 or $PM = \frac{W}{V}RT = dRT$

$$\therefore d = \frac{PM}{RT} = \frac{1 \times 148.92}{0.08205 \times 400} = 4.5374 \text{ g } \text{L}^{-1}$$

Example - 18

At 540 K, 0.10 mol of PCl₅ are heated in a 8.0 L flask. The pressure of the equilibrium mixture is found to be 1.0 atm. Calculate K_p and K_c for the reaction.

Sol.

 $PCl_5 \implies PCl_3 + Cl_2$

At eqm. 0.1 - x x x Total no. of moles at eqm. = 0.1 + x

$$PV = nRT$$
, i.e., $n = \frac{PV}{RT} = \frac{1 \times 8}{0.0821 \times 540} = 0.18$

$$\therefore 0.1 + x = 0.18$$
 or $x = 0.08$

$$\therefore \mathrm{K}_{\mathrm{c}} = \frac{(0.08/8)(0.08/8)}{(0.02/8)} = 0.04$$

$$K_n = K_c (RT)^{\Delta n} = 0.04 (0.0821 \times 540)^1 = 1.77$$

Example - 19

An equilibrium mixture,

 $CO(g) + H_2O(g) \implies CO_2(g) + H_2(g)$, present in a vessel of one litre capacity at 1000 K was found to contain 0.4 mole of CO, 0.3 mole of H₂O, 0.2 mole of CO₂ and 0.6 mole of H₂. If it is desired to increase the concentration of Co to 0.6 mole by adding CO₂ into the vessel, how many moles of it must be added into equilibrium mixture at constant temperature in order to get this change.

Sol. Step 1. To calculate K_c of the reaction.

$$K_{c} = \frac{[CO(g)][H_{2}(g)]}{[CO(g)][H_{2}O(g)]} = \frac{0.2 \times 0.6}{0.4 \times 0.3} = 1$$

Step 2. To calculate extra CO_2 to be added

Suppose extra CO_2 to be added = x mole. Then writing the reverse reaction, we have

$$CO_2 + H_2 \rightleftharpoons CO + H_2O$$

initial moles after

addition0.2 + x0.60.40.3Moles (MolarConc.)at new(0.2+x-0.2)(0.6-0.2)0.6(0.3+0.2)equilibrium= x= 0.4= 0.5

$$K_{c}' = \frac{1}{K_{c}} = \frac{0.6 \times 0.5}{x \times 0.4} = 1$$
 or $x = 0.75$ moles

Example - 20

The degree of dissociation of N_2O_4 into NO_2 at one atmospheric pressure and 313 K is 0–310. Calculate K_p of the dissociation reaction at this temperature. What will be the degree of dissociation at 10 atmospheric pressure at the same temparture?

0

Sol.

For the dissociation

reaction
$$N_2O_4(g) \Longrightarrow 2NO_2(g)$$

Initial moles 1

Moles at eqm. 1-0.310=0.69 2×0.310=0.62 (α=0.310,Given)

Total = 0.69+0.62=1.31 moles

At one atmospheric

pressure,
$$p_{N_2O_4} = \frac{0.69}{1.31} \times 1 \text{ atm}, p_{NO_2} = \frac{0.62}{1.31} \times 1 \text{ atm}$$

$$K_{p} = \frac{p_{NO_{2}}^{2}}{p_{N,O_{4}}} = \frac{(0.62/1.3 \, \text{latm})^{2}}{(0.69/1.3 \, \text{latm})} = 0.425 \, \text{atm}$$

At 10 atmoshperic pressure, suppose degree of dissociation = α . Then

 $N_2O_4 \Longrightarrow 2NO_2$ Initial moles 1 0

Moles at eqn $1-\alpha$ 2α , Total = $1+\alpha$

$$\mathbf{p}_{N_{2}O_{4}} = \frac{1-\alpha}{1+\alpha} \times 10 \text{ atm}, \mathbf{p}_{NO_{2}} = \frac{2\alpha}{1+\alpha} \times 10 \text{ atm}$$

$$K_{p} = \frac{[20\alpha/(1+\alpha)]^{2}}{[10(1-\alpha)/(1+\alpha)]} = \frac{40\alpha^{2}}{1-\alpha(1+\alpha)} = \frac{40\alpha^{2}}{1-\alpha^{2}}$$

$$\therefore \quad \frac{40\alpha^2}{1-\alpha^2} = 0.425$$

Neglecting α^2 in comparison to 1, 40 $\alpha^2 = 0.425$

or
$$\alpha = 0.103 = 10.3 \%$$

Example - 21

When α - D glucose is dissolved in water, it undergoes mutarotation to form an equilibrium mixture of α - D glucose and β - D glucose containing 63.6% of the latter. Calculate K_c for the mutarotation.

 α -D glucose $\implies \beta$ - D glucose Sol.

At equilibrium 36.4% 63.6%

$$K_c = \frac{63.6}{36.4} = 1.747$$

Example - 22

At 77°C and one atmoshpheric pressure, N₂O₄ is 70% dissociated into NO₂. What will be the volume occupied by the mixture under these conditions if we start with 10g of N₂O₄?

Sol. Molar mass of
$$N_2O_4 = 28 + 64 = 92 \text{g mol}^{-1}$$

$$N_2O_4 \implies 2NO_2$$

0

10 Initial moles 92

After dissociation $\frac{10}{92} - \frac{70}{100} \times \frac{10}{92}$ 2×0.076

Example - 23

...

0.1 mole of N₂O₄ (g) was sealed in a tube under atmospheric condition at 25°C. Calculate the number of moles of NO₂(g) present if the equilibrium $N_2O_4(g)$ is reached after some time ($K_p = 0.14$).

Sol.	$N_2O_4(g) \rightleftharpoons$	$2NO_2(g)$
Initial amount	0.1 mole	0
At equilibrium	(0.1–x)	2x, Total

2x, Total=0.1+x moles

As P=1 atm,
$$p_{N_2O_4} = \frac{0.1 - x}{0.1 + x}$$
, $p_{NO_2} = \frac{2x}{0.1 + x}$ atm

$$K_{p} = \frac{p_{NO_{2}}^{2}}{p_{N_{2}O_{4}}} = \frac{(2x/(0.1+x))^{2}}{(0.1-x)/(0.1+x)}$$

$$=\frac{4x^2}{(0.1-x)(0.1+x)}=\frac{4x^2}{0.01-x^2}$$

$$\frac{4x^2}{0.01-x^2} = 0.14$$
 or $4.14x^2 = 0.0014$ or $x=0.018$

No. of moles of NO₂ at equilibrium = $2x=2\times0.018=0.036$ *.*.. mole

EXERCISE - 1 : BASIC OBJECTIVE QUESTIONS

7.

8.

9.

Equilibrium : Definition

1. In chemical reaction A \implies B, the system will be known in equilibrium when

(a) A completely changes to B

- (b) 50% of A changes to B
- (c) The rate of change of A to B and B to A on both the sides are same
- (d) Only 10% of A changes to B
- According to law of mass action rate of a chemical reaction 2. is proportional to
 - (a) Concentration of reactants
 - (b) Molar concentration of reactants
 - (c) Concentration of products
 - (d) Molar concentration of products
- The active mass of 64 gm of HI in a two litre flask would be 3.

(a) 2	(b) 1
(c) 5	(d) 0.25

4. The rate constant for forward and backward reactions of hydrolysis of ester are 1.1×10^{-2} and 1.5×10^{-3} per minute respectively. Equilibrium constant for the reaction is

$CH_3COOC_2H_5 + H_2O =$	\geq CH ₃ COOH + C ₂ H ₅ OH
(a) 4.33	(b) 5.33
(c) 6.33	(d) 7.33

Equilibrium Constant : Expression

For the system $3A + 2B \implies C$, the expression for 5. equilibrium constant is

(a)
$$\frac{[3A][2B]}{C}$$
 (b) $\frac{[C]}{[3A][2B]}$
(c) $\frac{[A]^{3}[B]^{2}}{[C]}$ (d) $\frac{[C]}{[A]^{3}[B]^{2}}$

4 moles of A are mixed with 4 moles of B. At equilibrium for 6. the reaction $A + B \longrightarrow C + D$, 2 moles of C and D are formed. The equilibrium constant for the reaction will be

(a) $\frac{1}{4}$	(b) $\frac{1}{2}$
c) 1	(d) 4

On a given condition, the equilibrium concentration of HI, H₂ and I₂ are 0.80, 0.10 and 0.10 mole/litre. The equilibrium constant for the reaction $H_2 + I_2 \implies 2HI$ will be

(a) 64	(b) 12
(c) 8	(d) 0.8

For the system $A(g) + 2B(g) \implies C(g)$, the equilibrium concentrations are (A) 0.06 mole/litre (B) 0.12 mole/litre (C) 0.216 mole/litre. The K_{eq} for the reaction is

(a) 250	(b) 416
(c) 4×10^{-3}	(d) 125

For the reaction A + 2B \implies C, the expression for equilibrium constant is

(a)
$$\frac{[A][B]^2}{[C]}$$
 (b) $\frac{[A][B]}{[C]}$
(c) $\frac{[C]}{[A][B]^2}$ (d) $\frac{[C]}{2[B][A]}$

10. For which of the following reactions does the equilibrium constant depend on the units of concentration

(a) NO(g)
$$\xrightarrow{} \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$$

(b) Zn (s) + Cu²⁺ (aq) $\xrightarrow{} Cu (s) + Zn^{2+}$ (aq)

(c) $C_{2}H_{5}OH(l) + CH_{3}COOH \longrightarrow CH_{3}COOC_{2}H_{5}(l) + H_{2}O(l)$ (Reaction carried in an inert solvent)

(d) $\operatorname{COCl}_2(g) \xrightarrow{} \operatorname{CO}(g) + \operatorname{Cl}_2(g)$

Unit of equilibrium constant for the reversible reaction 11. $H_2 + I_2 \xrightarrow{} 2HI$ is

(a) mol^{-1} litre	(b) mol^{-2} litre
(c) mol litre ⁻¹	(d) None of these

12. In a reaction $A + B \xrightarrow{} C + D$, the concentrations of A, B, C and D (in moles/litre) are 0.5, 0.8, 0.4 and 1.0 respectively. The equilibrium constant is

(a) 0.1	(b) 1.0
(c) 10	(d) ∞

13. The suitable expression for the equilibrium constant of the reaction $2NO(g) + Cl_2(g) \implies 2NOCl(g)$ is

(a)
$$K_{c} = \frac{[2NOCl]}{[2NO][Cl_{2}]}$$
 (b) $K_{c} = \frac{[NOCl]^{2}}{[NO]^{2}[Cl_{2}]}$
(c) $K_{c} = \frac{[NOCl]^{2}}{[NO][Cl_{2}]^{2}}$ (d) $K_{c} = \frac{[NOCl]^{2}}{[NO]^{2}[Cl_{2}]^{2}}$

14. $A + B \xrightarrow{} C + D$. If finally the concentration of A and B are both equal but at equilibrium concentration of D will be twice of that of A then what will be the equilibrium constant of reaction.

(a) 4 / 9	(b) 9 / 4
(c) 1 / 9	(d) 4

15. For the reaction $2SO_2 + O_2 \rightleftharpoons 2SO_3$, the units of K_c are

(a) litre/mole	(b) mol/litre
(c) (mol litre ⁻¹) ²	(d) (litre mole ⁻¹) ²

16. The equilibrium concentration of X, Y and YX_2 are 4, 2 and 2 moles respectively for the equilibrium $2X + Y \longrightarrow YX_2$. The value of K_c is

(a) 0.625	(b) 0.0625
(c) 6.25	(d) 0.00625

17. In a 500 ml capacity vessel CO and Cl_2 are mixed to form $COCl_2$. At equilibrium, it contains 0.2 moles of $COCl_2$ and 0.1 mole of each of CO and CO_2 . The equilibrium constant K_c for the reaction $CO + Cl_2 \rightleftharpoons COCl_2$ is

(a) 5	(b) 10
(c) 15	(d) 20

18. 4.5 moles each of hydrogen and iodine heated in a sealed ten litre vessel. At equilibrium, 3 moles of HI were found. The equilibrium constant for H₂(g) + I₂(g) → 2 HI(g) is

(b) 10

(c) 5 (d)
$$0.33$$

19. An equilibrium mixture of the reaction

 $2\mathrm{H}_2\mathrm{S}(g) \xrightarrow{} 2\mathrm{H}_2\left(g\right) + \mathrm{S}_2(g)$

had 0.5 mole H_2S , 0.10 mole H_2 and 0.4 mole S_2 in one litre vessel. The value of equilibrium constant (K) in mole litre⁻¹ is

20. For the equilibrium $N_2 + 3H_2 \rightleftharpoons 2NH_3$, K_c at 1000K is 2.37×10^{-3} If at equilibrium $[N_2] = 2M$, $[H_2] = 3M$, the concentration of NH_3 is (a) 0.00358 M (b) 0.0358 M (c) 0.358 M (d) 3.58 M

21. Two moles of NH_3 when put into a previously evacuated vessel (one litre), partially dissociate into N_2 and H_2 . If at equilibrium one mole of NH_3 is present, the equilibrium constant is

(a)
$$3/4 \text{ mol}^2 \text{ litre}^{-2}$$
 (b) $27/64 \text{ mol}^2 \text{ litre}^{-2}$

(c)
$$27/32 \text{ mol}^2 \text{ litre}^{-2}$$
 (d) $27/16 \text{ mol}^2 \text{ litre}^{-2}$

22. In Haber process 30 litres of dihydrogen and 30 litres of dinitrogen were taken for reaction which yielded only 50% of the expected product. What will be the composition of gaseous mixture under the aforesaid condition in the end (a) 20 litres ammonia, 25 litres nitrogen, 15 litres hydrogen (b) 20 litres ammonia, 20 litres nitrogen, 20 litres hydrogen (c) 10 litres ammonia, 25 litres nitrogen, 15 litres hydrogen (d) 20 litres ammonia, 10 litres nitrogen, 30 litres hydrogen
23. For the reaction equilibrium N₂O₄ → 2NO_{2(g)}, the concentrations of N₂O₄ and NO₂ at equilibrium are 4.8 × 10⁻² and 1.2 × 10⁻² mol litre⁻¹ respectively. The value

of
$$K_c$$
 for the reaction is
(a) 3.3×10^2 mole litre⁻¹
(b) 3×10^1 mol litre⁻¹
(c) 3×10^{-3} mol litre⁻¹
(d) 3×10^3 mol litre⁻¹

24. The equilibrium constant for the reaction

 $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ at temperature T is 4×10^{-4} . The value of K_c for the reaction

NO (g)
$$\longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g)$$
 at the same temperature is

(a)
$$4 \times 10^{-4}$$
 (b) 50
(c) 2.5×10^{2} (d) 0.02

25. In the reaction, $H_2 + I_2 \implies 2HI$. In a 2 litre flask 0.4 moles of each H_2 and I_2 are taken. At equilibrium 0.5 moles of HI are formed. What will be the value of equilibrium constant, K_c

(a) 20.2	(b)25.4
(c) 0.284	(d) 11.1

2 mol of N₂ is mixed with 6 mol of H₂ in a closed vessel of one litre capacity. If 50% of N₂ is converted into NH₃ at equilibrium, the value of Kc for the reaction N₂(g) + 3H₂(g) → 2NH₃(g) is
(a) 4/27 (b) 27/4

(c) 1/27	(d) 24

Equilibrium Constant : Effect of Stoichiometry

27. Equilibrium constants K_1 and K_2 for the following equilibria

$$NO(g) + \frac{1}{2}O_2 \xrightarrow{} NO_2(g)$$

and $2NO_2(g) \xrightarrow{} 2NO(g) + O_2(g)$ are related as

(a)
$$K_2 = \frac{1}{K_1}$$
 (b) $K_2 = K_1^2$
(c) $K_2 = \frac{K_1}{2}$ (d) $K_2 = \frac{1}{K_1^2}$

28. Two gaseous equilibria

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

and

 $2SO_3(g) \xrightarrow{} 2SO_2(g) + O_2(g)$ have equilibrium constants K_1 and K_2 respectively at 298 K. Which of the following relationships between K_1 and K_2 is correct

(a)
$$K_1 = K_2$$

(b) $K_2 = K_1^2$
(c) $K_2 = 1/K_1^2$
(d) $K_2 = 1/K_1$

29. At a given temperature, the equilibrium constant for reaction $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$ is 2.4×10^{-3} . At the same temperature, the equilibrium constant for reaction $PCl_3(g) + Cl_2(g) \longrightarrow PCl_5(g)$ is

(a)
$$2.4 \times 10^{-3}$$
 (b) -2.4×10^{-3}
(c) 4.2×10^{2} (d) 4.8×10^{-2}

Position of Equilibrium : Extent of a Reaction

30. In which of the following, the reaction proceeds towards completion

(a)
$$K = 10^3$$
 (b) $K = 10^{-2}$
(c) $K = 10$ (d) $K = 1$

31. A 1 M solution of glucose reaches dissociation equilibrium according to equation given below 6HCHO \rightleftharpoons C₆H₁₂O₆ What is the concentration of HCHO at equilibrium if equilibrium constant is 6×10^{22}

(a)
$$1.6 \times 10^{-8}$$
 M (b) 3.2×10^{-6} M
(c) 3.2×10^{-4} M (d) 1.6×10^{-4} M

Kp and Kc Relationship

32. In which of the following reaction, the value of K_p will be equal to K_c

(a)
$$H_2 + I_2 \rightleftharpoons 2HI$$
 (b) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$
(c) $2NH_3 \rightleftharpoons N_2 + 3H_2$ (d) $2SO_2 + O_2 \rightleftharpoons 2SO_3$

33. For
$$N_2 + 3H_2 \implies 2NH_3 + heat$$

(a)
$$K_p = K_c (RT)$$

(b) $K_c = K_p (RT)$
(c) $K_p = K_c (RT)^{-2}$
(d) $K_p = K_c (RT)^{-1}$

34. In which of the following equilibria, the value of K_p is less than K_c

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

(b) $N_2 + 3H_2 \rightleftharpoons 2NH_3$
(c) $N_2 + O_2 \rightleftharpoons 2NO$
(d) $CO + H_2O \rightleftharpoons CO_2 + H_2$

35. For the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ at 721K the value of equilibrium constant (K_c) is 50. When the equilibrium concentration of both is 0.5M, the value of K_p under the same conditions will be

36. The reaction between N₂ and H₂ to form ammonia has $K_c = 6 \times 10^{-2}$ at the temperature 500°C. The numerical value of K_p for this reaction is

(a)
$$1.5 \times 10^{-5}$$
 (b) 1.5×10^{5}
(c) 1.5×10^{-6} (d) 1.5×10^{6}

37. For the reversible reaction,

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

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_a with concentration in mole litre⁻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) $1.44 \times 10^{-5}/(0.082 \times 773)^{2}$
(d) $1.44 \times 10^{-5}/(0.082 \times 773)^{-2}$

Equilibrium : Analysis

(

38. A mixture of 0.3 mole of H_2 and 0.3 mole of I_2 is allowed to react in a 10 litre evacuated flask at 500°C. The reaction is $H_2 + I_2 \xrightarrow{} 2HI$, the K is found to be 64. The amount of unreacted I_2 at equilibrium is

(a) 0.15 mole	(b) 0.06 mole
(c) 0.03 mole	(d) 0.2 mole

39. 0.6 mole of NH_3 in a reaction vessel of 2dm^3 capacity was brought to equilibrium. The vessel was then found to contain 0.15 mole of H2 formed by the reaction

 $2NH_3(g) \longrightarrow N_2(g) + 3H_2(g)$

Which of the following statements is true

- (a) 0.15 mole of the original NH_3 had dissociated at equilibrium
- (b) 0.55 mole of ammonia is left in the vessel
- (c) At equilibrium the vessel contained 0.45 mole of N₂
- (d) The concentration of NH_3 at equilibrium is 0.25 mole per dm³
- 40. 5 moles of SO_2 and 5 moles of O_2 are allowed to react to form SO₃ in a closed vessel. At the equilibrium stage 60% of SO₂ is used up. The total number of moles of SO₂, O₂ and SO₃ in the vessel now is

(a) 10.0	(b) 8.5
(c) 10.5	(d) 3.9

41. The equilibrium $P_4(s) + 6 Cl_2(g) \implies 4 PCl_3(g)$ is attained by mixing equal moles of P₄ and Cl₂ in an evacuated vessel. Then at equilibrium

(a) [Cl2] > [PCl3]	(b) $[Cl_2] > [P_4]$
(c) $[P_4] > [Cl_2]$	(d) $[PCl_3] > [P_4]$

42. 40% of a mixture of 0.2 mol of N_2 and 0.6 mol of H_2 reacts to give NH, according to the equation :

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

at constant temperature and pressure. Then the ratio of the final volume to the initial volume of gases are

(a) 4 : 5	(b) 5 : 4
(c) 7 : 10	(d) 8 : 5

43. XY, dissociates as :

$$XY_2(g) \rightleftharpoons XY(g) + Y(g)$$

Initial pressure of XY, is 600 mm Hg. The total pressure at equilibrium is 800 mm Hg. Assuming volume of system to remain constant, the value of K is

(a) 50	(b) 100
(c) 200	(d) 400

15 mol of H₂ and 5.2 moles of I₂ are mixed and allowed to attain equilibrium at 500°C. At equilibrium, the concentration of HI is found to be 10 mol. The equilibrium constant for the formation of HI is.

(a) 50	(b) 25
(c)200	(d) 15

45. For the equilibrium AB (g) \rightleftharpoons A(g) + B(g). K_p is equal to four times the total pressure. Calculate the number moles of A formed if one mol of AB is taken initially.

(a) 0.45	(b) 0.30
(c) 0.60	(d) 0.90

 $I_2 + I^- \rightleftharpoons I_3^-$ **46**.

44.

This reaction is set-up in aqueous medium. We start with 1 mol of I, and 0.5 mol of I⁻ in 1L flask. After equilibrium is reached, excess of AgNO₂ gave 0.25 mol of yellow precipitate. Equilibrium constant is

(a) 1.33	(b) 2.66
(c) 2.00	(d) 3.00

47. One mole of $N_2O_4(g)$ at 100 K is kept in a closed container at 1.0 atm pressure. It is heated to 400 K, where 30% by mass of $N_2O_4(g)$ decomposes of $NO_2(g)$. The resultant pressure will be

(a) 4.2	(b) 5.2
(c) 3.2	(d) 6.2

Equilibrium Constant and ΔG

48.	$\Delta G^{o}(HI;g) \cong +1$.7 kJ. What is the equilibrium constant
	at 25°C for 2HI(g) \longrightarrow H ₂ (g) + I ₂ (g)	
	(a) 24.0	(b) 3.9
	(c) 2.0	(d) 0.5

49. Calculate ΔG° for conversion of oxygen to ozone $3/2 O_2(g) \rightarrow O_3(g)$ at 298 K, if K_p for this conversion is 2.47×10^{-29}

(a) 163 kJ mol ⁻¹	(b) $2.4 \times 10^2 \text{ kJ mol}^{-1}$
(c) 1.63 kJmol^{-1}	(d) 2.38×10^{6} kJ mol ⁻¹

Homogeneneous and Heterogeneous Equilibria, Degree of Dissociation

- **50.** Pure ammonia is placed in a vessel at temperature where its dissociation (α) is appreciable. At equilibrium
 - (a) K_{p} does not change significantly with pressure
 - (b) α does not change with pressure
 - (c) Concentration of NH₃ does not change with pressure
 - (d) Concentration of H_2 is less than that of N_2
- **51.** At a certain temp. $2\text{HI} \rightleftharpoons \text{H}_2 + \text{I}_2$ Only 50% HI is dissociated at equilibrium. The equilibrium constant is

(a) 0.25	(b) 1.0
(c) 3.0	(d) 0.50

52. 3.2 moles of hydrogen iodide were heated in a sealed bulb at 444°C till the equilibrium state was reached. Its degree of dissociation at this temperature was found to be 22%. The number of moles of hydrogen iodide present at equilibrium are

(a) 2.496	(b)1.87
(c) 2	(d) 4

53. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$ in closed container at equilibrium. What would be the effect of addition of $CaCO_3$ on the equilibrium concentration of CO_2 .

(a) Increases	(b) Decreases
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- (c) Data is not sufficient (d) Remains unaffected
- 54. An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm. pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total

pressure in the flask rises to 0.84 atm. The equilibrium constant for NH_4HS decomposition at this temperature is

55. Calculate the partial pressure of carbon monoxide from the following

$$CaCO_{3}(s) \xrightarrow{\Delta} CaO(s) + CO_{2}\uparrow; K_{p} = 8 \times 10^{-2}$$

$$CO_{2}(g) + C(s) \rightarrow 2CO(g); K_{p} = 2$$
(a) 0.2
(b) 0.4
(c) 1.6
(d) 4

56. 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) $SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$

57. The equilibrium constant (K_p) for the reaction $PCl_5(g) \rightarrow PCl_3(g) + Cl_2(g)$ is 16. If the volume of the container is reduced to one half its original volume, the value of K_p for the reaction at the same temperature will be (a) 22

$$\begin{array}{c} (a) 32 \\ (c) 16 \\ \end{array} \qquad \qquad (b) 64 \\ (d) 4 \\ \end{array}$$

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

> 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_) and degree of dissociation (α) ?

- (a) neither K_n nor α changes
- (b) both V_n and α change
- (c) K_n changes but α does not change
- (d) K does not change but α changes
- **59.** Calculate the partial pressure of carbon monoxide from the following data :

$$CaCO_{3}(s) \xrightarrow{\Delta} CaO(s) + CO_{2} \uparrow, K_{p} = 8 \times 10^{-2}$$

$$CO_{2}(g) + C(s) \longrightarrow 2 CO(g), K_{p} = 2$$
(a) 0.2 (b) 0.4
(c) 1.6 (d) 4

60. A small amount of NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide

decomposes to yield NH_3 and H_2S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for NH_4HS decomposition at this temperature is

(a) 0.30	(b) 0.18
(c) 0.17	(d) 0.11

- 61. The vapour density of completely dissociated NH₄Cl is(a) double than that of NH₄Cl
 - (b) half than that of NH Cl
 - (c) same as that of NH₄Cl
 - (d) determined by the amount of solid NH₂Cl taken
- **62.** The following two equilibria exist simultaneously in a closed vessel :

$$PCl_{s}(g) \longrightarrow PCl_{s}(g) + Cl_{s}(g)$$

 $\text{COCl}_2(g) \Longrightarrow \text{CO}(g) + \text{Cl}_2(g)$

If some CO is added into the vessel, then after the equilibrium is attained again, concentration of

(a) PCl_{5} will increase (b) PCl_{5} will decrease

- (c) PCl₅ will remain unaffected
- (d) Cl_2 will increase
- **63.** The equilibrium constant (K_p) for the decomposition of gaseous H₂O

$$\mathrm{H_{2}O}\left(g\right) \rightleftharpoons \mathrm{H_{2}}(g) + \frac{1}{2} \mathrm{O_{2}}(g)$$

is related to degree of dissociation (α) at a total pressure p, given by

(a)
$$K_p = \frac{\alpha^3 p^{1/2}}{(1+\alpha) (2+\alpha)^{1/2}}$$

(b)
$$K_p = \frac{\alpha^3 p^{3/2}}{(1-\alpha) (2+\alpha)^{1/2}}$$

(c)
$$K_p = \frac{\alpha^{3/2} p^2}{(1-\alpha) (2+\alpha)^{1/2}}$$

(d)
$$K_p = \frac{\alpha^{3/2} p^{1/2}}{(1-\alpha) (2+\alpha)^{1/2}}$$

64. At the equilibrium of the reaction,

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

the observed molecular weight of N_2O_4 is 80 g mol⁻¹ at 350 K. The percentage of dissociation of N_2O_4 (g) at 350 K is

(a) 10%	(b) 15%
(c) 20%	(d) 18%

Le Chatelier's Principle

65. What is the effect of halving the pressure by doubling the volume on the following system at 500°C

 $H_2(g) + I_2(g) \xrightarrow{} 2HI(g)$

- (a) Shift to product side
- (b) Shift to product formation
- (c) Liquifaction of HI
- (d) No effect
- 66. In equilibrium $CH_3COOH + H_2O \rightleftharpoons CH_3COO^- + H^+$

The equilibrium constant may change when

- (a) CH_3COO^- are added (b) CH_3COOH is added
- (c) Catalyst is added (d) Mixture is heated
- **67.** Which of the following statements regarding a chemical equilibrium is wrong
 - (a) An equilibrium can be shifted by altering the temperature or pressure
 - (b) An equilibrium is dynamic
 - (c) The same state of equilibrium is reached whether one starts with the reactants or the products
 - (d) The forward reaction is favoured by the addition of a catalyst
- 68. In the reaction, $A_2(g) + 4 B_2(g) \xrightarrow{\sim} 2AB_4(g)$
 - $\Delta H < 0$ the formation of AB₄ is will be favoured at
 - (a) Low temperature, high pressure
 - (b) High temperature, low pressure
 - (c) Low temperature, low pressure
 - (d) High temperature, high pressure
- 69. The formation of SO_3 takes place according to the following reaction,

 $2SO_2 + O_2 \implies 2SO_3$; $\Delta H = -45.2$ kcal

The formation of SO₃ is favoured by

(a) Increasing in temperature

(b) Removal of oxygen

- (c) Increase of volume
- (d) Increasing of pressure
- 70. $N_2 + O_2 \implies 2NO Q$ cals

In the above reaction which is the essential condition for the higher production of NO

(a) High temperature(b) High pressure(c) Low temperature(d) Low pressure

71. Which of the following reactions proceed at low pressure

(a) $N_2 + 3H_2 \xrightarrow{} 2NH_3$ (b) $H_2 + I_2 \xrightarrow{} 2HI$

(c)
$$PCl_5 \longrightarrow PCl_3 + Cl_2$$
 (d) $N_2 + O_2 \longrightarrow 2NO$

72. In the following reversible reaction

 $2SO_2 + O_2 \implies 2SO_3 + QCal$

Most suitable condition for the higher production of SO_3 is

(a) High temperature and high pressure

(b) High temperature and low pressure

(c) Low temperature and high pressure

(d) Low temperature and low pressure

73. The reaction $A + B \rightleftharpoons C + D$ +heat has reached equilibrium. The reaction may be made to proceed forward by

(a) Adding more C

- (b) Adding more D
- (c) Decreasing the temperature
- (d) Increasing the temperature
- 74. According to Le-chatelier principle, if heat is given to solidliquid system, then
 - (a) Quantity of solid will reduce
 - (b) Quantity of liquid will reduce
 - (c) Increase in temperature
 - (d) Decrease in temperature
- 75. In the reaction $A(g) + 2B(g) \longrightarrow C(g) + Q kJ$, greater product will be obtained or the forward reaction is favoured by
 - (a) At high temperature and high pressure
 - (b) At high temperature and low pressure

- (c) At low temperature and high pressure
- (d) At low temperature and low pressure
- 76. Following gaseous reaction is undergoing in a vessel $C_2H_4 + H_2 \longrightarrow C_2H_6; \Delta H = -32.7 \text{ Kcal}$

Which will increase the equilibrium concentration of C_2H_6

- (a) Increase of temperature
- (b) By reducing temperature
- (c) By removing some hydrogen
- (d) By adding some C_2H_6
- 77. The effect of increasing the pressure on the equilibrium $2A+3B \longrightarrow 3A+2B$ is
 - (a) Forward reaction is favoured
 - (b) Backward reaction is favoured
 - (c) No effect
 - (d) None of the above
- **78.** The exothermic formation of C/F_3 is represented by the equation

 $Cl_2(g) + 3F_2(g) \longrightarrow 2ClF_3(g); \Delta H = -329 \text{ kJ}$

Which of the following will increase the quantity of ClF_3 in an equilibrium mixture of Cl_2 , F_2 and ClF_3

- (a) Increasing the temperature
- (b) Removing Cl₂
- (c) Increasing the volume of the container
- (d) Adding F_2
- **79.** In which of the following system, doubling the volume of the container cause a shift to the right

(a)
$$H_2(g) + Cl_2(g) \rightleftharpoons 2HCl(g)$$

- (b) $2CO(g) + O_2(g) \xrightarrow{} 2CO_2(g)$
- (c) $N_2(g) + 3H_2(g) \implies 2NH_3(g)$
- (d) $PCl_5(g) \xrightarrow{} PCl_3(g) + Cl_2(g)$
- **80.** Which of the following information can be obtained on the basis of Le-chatelier's principle
 - (a) Entropy change in a reaction
 - (b) Dissociation constant of a weak acid
 - (c) Equilibrium constant of a chemical reaction

- (d) Shift in equilibrium position on changing value of a constant
- 81. The equilibrium $SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed container and an inert gas helium is introduced which of the following statement is correct
 - (a) More chlorine is formed
 - (b) Concentration of SO_2 is reduced
 - (c) More SO₂Cl₂ is formed
 - (d) Concentration of SO₂Cl₂(SO₂) and Cl₂ does not change
- 82. $H_2(g) + I_2(g) \rightarrow 2HI(g) \Delta H = +q \text{ cal, then formation of HI}$
 - (a) Is favoured by lowering the temperature
 - (b) Is favoured by increasing the pressure
 - (c) Is unaffected by change in pressure
 - (d) Is unaffected by change in temperature
- 83. The formation of nitric oxide by contact process $N_2 + O_2 \implies 2NO. \Delta H = 43.200$ kcal is favoured by
 - (a) Low temperature and low pressure
 - (b) Low temperature and high pressure
 - (c) High temperature and high pressure
 - (d) High temperature and excess reactants concentration

- 84. The yield of product in the reaction
 - $A_2(g)+2B(g) \xrightarrow{} C(g) + Q.kJ.$ would be high at
 - (a) High temperature and high pressure
 - (b) High temperature and low pressure
 - (c) Low temperature and high pressure
 - (d) Low temperature and low pressure

EXERCISE - 2 : PREVIOUS YEAR JEE MAINS QUESTION

6.

7.

1. In which of the following equilibrium change in the volume of the system does not alter the number of moles (2002)

(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) $SO_2Cl_2 \rightleftharpoons SO_2(g) + Cl_2(g)$

2. For the reaction (2002)

$$CO(g) + \frac{1}{2}O_2(g) \xrightarrow{} CO_2(g), K_p/K_c \text{ is}$$
(a) RT
(b) (RT)⁻¹
(c) (RT)^{-1/2}
(d) (RT)^{1/2}

3. In which of the following reactions, increase in the pressure at constant temperature does not affect the moles at equilibrium (2002)

(a)
$$2NH_{3(g)} \xrightarrow{} N_{2(g)} + 3H_{2(g)}$$

(b) $C_{(g)} + 1/2O_{2(g)} \xrightarrow{} CO_{(g)}$
(c) $H_{2(g)} + 1/2O_{2(g)} \xrightarrow{} H_2O_{(g)}$
(d) $H_{2(g)} + I_{2(g)} \xrightarrow{} 2HI_{(g)}$

4. For the reaction equilibrium

$$N_2O_4(g) \Longrightarrow 2NO_2(g)$$

the concentrations of N2O4 and NO2 at equilibrium are 4.8×10^{-2} and 1.2×10^{-2} mol L⁻¹ respectively. The value of K_a for the reaction is (2003)(a) $2 \times 10^3 \text{ m s} 1 \text{ J} - 1$ $(1) 2 2 \dots 10^{2}$ 1 . 1

(a)
$$3 \times 10^{3} \text{ mol } L^{-1}$$
 (b) $3.3 \times 10^{2} \text{ mol } L^{-1}$

(c) 3×10^{-1} mol L⁻¹ (d) 3×10^{-3} mol L⁻¹

5. The conditions favourable for the reaction

$$2SO_{2(g)} + O_{2(g)} \xrightarrow{} 2SO_{3(g)}; \qquad \Delta H^{\circ} = -198 \text{ kJ}$$

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

What is the equilibrium expression for the reaction (2004)

(d) $K_c = \frac{[P_4 O_{10}]}{5[P_4][O_2]}$

$$P_4(s) + 5O_2(g) \xrightarrow{} P_4O_{10}(s)$$
?

(a)
$$K_c = \frac{[P_4O_{10}]}{[P_4][O_2]^5}$$
 (b) $K_c = \frac{1}{[O_2]^5}$

(c) $K_c = [O_2]^5$

For the reaction

$$CO(g) + Cl_2(g) \xrightarrow{} COCl_2(g)$$

the
$$\frac{K_p}{K_c}$$
 is equal to

(a)
$$\frac{1}{RT}$$
 (b) 1.0

(c)
$$\sqrt{\text{RT}}$$
 (d) RT

8. The equilibrium constant 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

(b) 0.02

$$NO_2(g) \xrightarrow{} \frac{1}{2} N_2(g) + \frac{1}{2} O_2(g)$$

at the same temperature is

(a) 2.5×102

(2004)

(2004)

(c) 4×10^{-4} (d) 50

- - A small amount of NH₄HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH₂ and H₂S gases in the flask. When the decomposition reaction reaches equilibrium, the total pressure in the flask rises to 0.84 atm. The equilibrium constant for NH₄HS decomposition at this temperature is (2005)

(a) 0.30	(b) 0.18
(c) 0.17	(d) 0.11

(2003)

10. For the reaction

 $2NO_{2}(g) \xrightarrow{} 2NO(g) + O_{2}(g)$ $(K_{c} = 1.8 \times 10^{-6} \text{ at } 184^{\circ}\text{C})$ (R = 0.0831 kJ/(mol.K))When K_p and K_c are compared at 184°C it is found that
(2005)

(a) Whether K_p is greater than, less than or equal of K_c depends upon the total gas pressure

(b) $K_p = K_c$

- (c) K_p is greater than K_c
- (d) K_{p}^{r} is greater than K_{c}
- 11. Phosphourus pentachloride dissociates as follows, in a closed reaction vessel,

 $\begin{array}{ll} PCl_{5}(g) & \longrightarrow PCl_{3}(g) + Cl_{2}(g) \\ \text{If total pressure at equilibrium of the reaction mixture is P} \\ \text{and degree of dissociation of PCl}_{5} \text{ is x, the partial pressure} \\ \text{of PCl}_{3} \text{ will be} \end{array}$

(a)
$$\left(\frac{x}{x+1}\right) P$$
 (b) $\left(\frac{2x}{1-x}\right) P$
(c) $\left(\frac{x}{x-1}\right) P$ (d) $\left(\frac{x}{1-x}\right) P$

12. The equilibrium constant for the reaction

$$SO_{3}(g) \xrightarrow{\longrightarrow} SO_{2}(g) + \frac{1}{2}O_{2}(g)$$

is $K_{c} = 4.9 \times 10^{-2}$. The value of K_{c} for the reaction
$$2SO_{2} + O_{2}(g) \xrightarrow{\longrightarrow} 2SO_{3}(g)$$
 will be (2006)
(a) 416 (b) 2.40×10^{-3}
(c) 9.8×10^{-2} (d) 4.9×10^{-2}

13. The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \xrightarrow{} 2Y$ and $Z \xrightarrow{} P+Q$, respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal then the ratio of total pressure at these equilibria is

(2008)

(a) 1 : 36	(b) 1 : 1
(c) 1 : 3	(d) 1 : 9

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

(1)
$$\operatorname{CO}_{(g)} + \operatorname{H}_2\operatorname{O}_{(g)} \xrightarrow{} \operatorname{CO}_{2(g)} + \operatorname{H}_{2(g)};$$
 K_1

(2)
$$\operatorname{CH}_{4(g)} + \operatorname{H}_2\operatorname{O}_{(g)} \xrightarrow{} \operatorname{CO}_{(g)} + 3\operatorname{H}_{2(g)};$$
 k

(3)
$$CH_{4(g)} + 2H_2O_{(g)} \longrightarrow CO_{2(g)} + 4H_{2(g)};$$
 K
Which of the following relations is correct ? (2008)

(a)
$$K_1 \sqrt{K_2} = K_3$$
 (b) $K_2 K_3 = K_1$
(c) $K_3 = K_1 K_2$ (d) $K_3 \cdot K_2^3 K_1^2$

- **15.** 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_p is (2011) (a) 1.8 atm (b) 3 atm (c) 0.3 atm (d) 0.18 atm
- 16. For the reaction $SO_{2(g)} + \frac{1}{2}O_{2(g)} \rightleftharpoons SO_{3(g)}$, if $Kp = K_{C}(RT)^{x}$ where the symbols have usual meaning then the value of x is :

(assuming ideality)

(2014)

(a)
$$-\frac{1}{2}$$
 (b) $\frac{1}{2}$
(c) 1 (d) -1

17. The standard Gibbs energy change at 300 K for the reaction $2A \rightleftharpoons B + C$ is 2494.2 J. At a given time, the composition of the reaction mixture is $[A] = \frac{1}{2}$, [B] = 2 and $[C] = \frac{1}{2}$. The reaction proceeds in the : (2015) [R = 8.314 J/K/mol, e = 2.718]

(a) forward direction because $Q < K_{c}$

- (b) reverse direction because $Q < K_c$
- (c) forward direction because $Q > K_c$
- (d) reverse direction because $Q > K_{c}$
- 18. The equilibrium constant at 298 K for reaction A+B ⇒ C+D is 100. If the initial concentration of all the four species were 1M each, then equilibrium concentration of D (in mol L⁻¹) will be: (2016)
 (a) 0.818 (b) 1.818
 - (c) 1.182 (d) 0.182
- 19. An aqueous solution contains 0.10 M H_2S and 0.20 M HCl. If the equilibrium constants for the formation of HS⁻ from H_2S is 1.0×10^{-7} and that of S²⁻ from HS⁻ ions is 1.2×10^{-13} then the concentration of S²⁻ ions in aqueous solution is: (2018)

(a)
$$5 \times 10^{-19}$$
(b) 5×10^{-8} (c) 3×10^{-20} (d) 6×10^{-21}

JEE MAINS ONLINE QUESTION

1. At a certain temperature, only 50% HI is dissociated into H_2 and I_2 at equilibrium. The equilibrium constant is:

Online 2014 SET (1)

6.

7.

8.

9.

10.

(a) 1.0	(b) 3.0
(c) 0.5	(d) 0.25

2. What happens when an inert gas is added to an equilibrium keeping volume unchanged? Online 2014 SET (3)

(a) More reactant will form

(b) More product will form

(c) Equilibrium will remain unchanged

- (d) Less product will form
- **3.** For the decomposition of the compound represented as

 $NH_{2}COONH_{4}(s) \Longrightarrow 2NH_{3}(g) + CO_{2}(g)$

The $K_{\rm p} = 2.9 \times 10^{-5} \, {\rm atm}^3$.

If the reaction is started with 1 mol of the compound, the total pressure at equilibrium would be :

Online 2014 SET (4)

(a) 5.82×10^{-2} atm	(b) 7.66×10^{-2} atm
(c) 38.8×10^{-2} atm	(d) 1.94×10^{-2} atm

4. The increase of pressure on ice water system at constant temperature will lead to :

Online 2015 SET (1)

(a) a decrease in the entropy of the system

(b)an increase in the Gibbs energy of the system

(c)no effects on the equilibrium

(d)a shift of the equilibrium in the forward direction

5. For the equilibrium, $A(g) \rightleftharpoons B(g), \Delta H \text{ is } -40 \text{ kJ/mol.}$ If the ratio of the activation energies of the forward (E_c)

and reverse (E $_{b})$ reactions is $\frac{2}{3}$ then :

Online 2015 SET (1)

(a)
$$E_f = 80 \text{ kJ/mol}; E_b = 120 \text{ kJ/mol}$$

(b) $E_f = 60 \text{ kJ/mol}; E_b = 100 \text{ kJ/mol}$
(c) $E_f = 30 \text{ kJ/mol}; E_b = 70 \text{ kJ/mol}$
(d) $E_f = 70 \text{ kJ/mol}; E_b = 30 \text{ kJ/mol}$

A solid XY kept in an evacuated sealed container undergoes decomposition to form a mixture of gases X and Y at temperature T. The equilibrium pressure is 10 bar in this vessel. Kp for this reaction is :

Online 2016 SET (2)

(a) 5	(b) 10
(c) 25	(d) 100

The following reaction occurs in the Blast Furnace where iron ore is reduced to iron metal :

 $Fe_2O_3(s) + 3CO(g) \rightleftharpoons 2Fe(l) + 3CO_2(g)$

Using the Le Chatelier's principle, predict which one of the following will not disturb the equilibrium?

Online 2017 SET (2)

(a) Removal of CO	(b) Removal of CO_2
(c) Addition of CO ₂	(d) Addition of Fe_2O_2

In which of the following reactions, an increase in the volume of the container will favour the formation of products ? Online 2018 SET (1)

(a)
$$2NO_2(g) \rightleftharpoons 2NO(g) + O_2(g)$$

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

(c) $4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(I)$

(d) $3O_2(g) \rightleftharpoons 2O_3(g)$

At a certain temperature in a 5L vessel, 2 moles of carbon monoxide and 3 moles of chlorine were allowed to reach equilibrium according to the reaction,

$$\operatorname{CO} + \operatorname{Cl}_2 \rightleftharpoons \operatorname{COCl}_2$$

At equilibrium, if one mole of CO is present then equilibrium constant (K_c) for the reaction is :

Online 2018 SET (2)

)2	.5
	o) 2.

(c) 3 (d) 4

- 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 : **Online 2018 SET (3)**
 - (a) lowering the temperature.
 - (b) increasing the pressure.
 - (c) addition of an inert gas at constant volume.
 - (d) addition of an inert gas at constant pressure.

EXERCISE - 3 : ADVANCED OBJECTIVE QUESTIONS

- 1. All questions marked "S" are single choice questions
- 2. All questions marked "M" are multiple choice questions
- 3. All questions marked "C" are comprehension based questions
- 4. All questions marked "A" are assertion–reason type questions
 - (A) If both assertion and reason are correct and reason is the correct explanation of assertion.
 - (B) If both assertion and reason are true but reason is not the correct explanation of assertion.
 - (C) If assertion is true but reason is false.
 - (D) If reason is true but assertion is false.
- 5. All questions marked "X" are matrix-match type questions
- 6. All questions marked "I" are integer type questions

Equilibrium : Definition and Expression

1.(A) Assertion : For a reaction at equilibrium, the free energy for the reaction is minimum.

Reason : The free energy for both reactants and products decreases and become equal.

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

2. (A) Assertion : Chemical equilibrium represents a state of a reversible reaction in which measurable properties of the system (pressure, concentration, colour etc.) become constant under the given set of conditions.

Reason : The chemical equilibrium is an apparent state of rest in which two opposing reactions are proceeding at the same rate.

(a) A (b) B

(c) C (d) D

3. (S) Which of the following statements about the reaction quotient, Q are correct ?

(a) the reaction quotient, Q and the equilibrium constant always have the same numerical value

- (b) Q may be lesser than, equal to or greater than K_{eq}
- (c) Q (numerical value) varies as reaction proceeds

(d) Q = 1 at equilibrium

4. (S) For a reversible reaction : $A + B \xrightarrow{} C$

$$\left(\frac{\mathrm{dx}}{\mathrm{dt}}\right) = 2.0 \times 10^3 \,\mathrm{L} \,\mathrm{mol}^{-1} \,\mathrm{s}^{-1} \,\mathrm{[A]} \,\mathrm{[B]} - 1.0 \times 10^2 \,\mathrm{s}^{-1} \,\mathrm{[C]}$$

where x is the amount of 'A' dissociated. The value of equilibrium constant (K_{eq}) is :

(a) 10	(b) 0.05
(c) 20	(d) Can't be calculated

5.(A) Assertion : The reaction quotient, Q has the same form as the equilibrium constant K_{eq} and is evaluated using any given concentrations of the species involved in the reaction, and not necessarily equilibrium concentrations.

Reason : If the numerical value of Q is not the same as the value of equilibrium constant, a reaction will proceed.

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

6.(A) Assertion : The active mass of pure solids and pure liquids is taken unity.

Reason : The active mass of pure solids and liquids depends on density and molecular mass. The density and molecular mass of pure liquids and solids are constant.

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

7.(A) Assertion : If some $PCl_5(g)$ containing labelled phosphorus p^{31} is added to a system with following equilibrium, after sometime the system was found to contain radioactive PCl_3 .

$$PCl_5(g) \xrightarrow{} PCl_3(g) + Cl_2(g)$$

Reason : Chemical equilibrium is dynamic in nature.

(a) A	(b) B
-------	-------

- (c) C (d) D
- **8.(A)** Assertion : As a reversible system approaches equilibrium, entropy of the system increases.

Reason : The state of equilibrium is the most disordered state of a reversible system.

9.(M)
$$N_2O_2 \rightleftharpoons 2KOK_1; \left(\frac{1}{2}\right)N_2 + \left(\frac{1}{2}\right)O_2 \rightleftharpoons NOK_2$$

$$2 \operatorname{NO} \rightleftharpoons \operatorname{N}_2 + \operatorname{O}_2 \operatorname{K}_3; \operatorname{NO} \rightleftharpoons \left(\frac{1}{2}\right) \operatorname{N}_2 + \left(\frac{1}{2}\right) \operatorname{O}_2 \operatorname{K}_4$$

Correct relation(s) between K₁, K₂, K₃ and K₄ is/are :

(a)
$$K_2 \times K_4 = 1$$
 (b) $\sqrt{K_1 \times K_4} = 1$
(c) $\sqrt{K_3} \times K_2 = 1$ (d) $\sqrt{K_3 \times K_2} = 1$

K_p and K_c

10.(X) Match the following systems with their K_p/K_c relationship

Equilibrium types

(a) NO(g) + NO₃(g) \rightleftharpoons 2NO₂(g) (p)K_p>K_c

K_n/K_c

- (b) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ (q) $K_p = K_c(RT)^2$
- (c) $2O_3(g) \rightleftharpoons 3O_2(g)$ (r) $K_p = K_c$
- (d) $\operatorname{BrF}_{5}(g) \rightleftharpoons \frac{1}{2}\operatorname{Br}_{2}(g) + \frac{5}{2}F_{2}(g)$ (s) $K_{p} < K_{c}$

11. (S) Equilibrium constant K_c for the following reaction at 800K is, 4.

$$\mathrm{NH}_3(\mathbf{g}) \rightleftharpoons \frac{1}{2}\mathrm{N}_2(\mathbf{g}) + \frac{3}{2}\mathrm{H}_2(\mathbf{g})$$

The value of k_p for the following reaction will be :

$$N_{2}(g) + 3H_{2}(g) \rightleftharpoons 2NH_{3}(g)$$
(a) $\left(\frac{800R}{4}\right)^{-2}$ (b) $16 \times (800R)^{2}$

(c)
$$\left[\frac{1}{4 \times 800 R}\right]^2$$
 (d) $(800 R)^{1/2} 4$

Equilibrium : Analysis

- **12. (S)** $N_2O_4 \implies 2NO_2$, $K_c = 4$. This reversible reaction is studied graphically as shown in the given figure. Select the correct statement out of I, II and III.
 - I : Reaction quotient has maximum value at point A
 - II : Reaction proceeds left to right at a point when $[N_2O_4] = [NO_2] = 0.1 \text{ M}$
 - III : $K_c = Q$ when point D or F is reached :



13. (S) $I_2 + I^- \rightarrow I_3^-$

This reaction is set-up in aqueous medium. We start with 1 mol of I_2 and 0.5 mol of I^- in 1L flask. After equilibrium is reached, excess of AgNO₃ gave 0.25 mol of yellow ppt. Equilibrium constant is : [Given : AgNO₃ gives yellow ppt with I^-]

(a) 1.33	(b) 2.66
(c) 2.00	(d) 3.00

14.(I) Given the hypothetical reaction :

 $2A(s) + nB(g) \rightleftharpoons 3C(g) \quad K_n = 0.0105$

and $K_c = 0.45$ at 250°C. What is the value of coefficient 'n'?

15. (S) In the reaction : $A + B \rightleftharpoons 2C + D$. The initial concentration of A and B are 1M each. The value of K_c is 10^8 . What is the equilibrium concentration of A?

(a) 2×10^{-4} M (b) 2×10^{4} M

- (c) 0.005 M (d) 0.0025 M
- 16. (S) Equilibrium constant for two complexes are :
 - $A: K_4 [Fe(CN)_6]$ 2.6×10^{37} (for dissociation) $B: K_3 [Fe(CN)_6]$ 1.9×10^{17} (for dissociation)
 - (a) A and B are equally stable
 - (b) A is more stable than A
 - (c) B is more stable than A
 - (d) the predictable stability
- **17. (S)** For the reaction, $[Ag(CN)_2]^- \rightleftharpoons Ag^+ + 2CN^-$, the equilibrium constant K_c at 25°C is 4×10^{-19} ; then Ag^+ concentration in a solution which has 0.1 M KCN and 0.03M AgNO₃ is :

(a) 7.5×10^{18} (b) 7.5×10^{-18} (c) 7.5×10^{19} (d) 7.5×10^{-19}

18. (S) A vessel at 1000 K contains CO_2 with a pressure of 0.5 atm. Some of the CO_2 is converted to CO on addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is :

(a) 0.18 atm	(b) 1.8 atm
(c) 3 atm	(d) 0.3 atm

19. (S) The equilibrium reaction : $2AB(aq) \rightleftharpoons 2A(aq) + B_2(g)$ has an equilibrium constant equal to 1.28. If the concentrations of AB and A are 5 mol/L and 4 mol/L respectively, what is [B₂]?

(a) 0.50 M	(b) 1.60 M
(c) 2.00 M	(d) 2.84 M

20. (S) Consider the reaction NaBr(aq) + $H_2SO_4(aq) \rightleftharpoons$ NaHSO₄(aq) + HBr(aq). The equilibrium constant is 8.3×10^{-2} . If the equilibrium concentrations of NaBr, H_2SO_4 and NaHSO₄ are 6.0 M, 9.0 M and 3.0 M respectively, what is the molarity of HBr ?

- (a) 1.8×10^{-2} M (b) 6.7×10^{-1} M (c) 1.5×10^{0} M (d) 3.6×10^{1} M
- **21. (S)** For the all gas reaction at 1000 K : $2HI \rightleftharpoons H_2 + I_2$, K = 0.0344. If you were to begin with 8.0 M of HI in a fixed volume container, what would be the equilibrium concentration of H₂?

(c) 5.8 M (d) 2.92 M

22.(8) In reversible reaction $A \xrightarrow[k_2]{k_1} B$, the initial

concentration of A and B are a and b in moles per litre and the equilibrium concentration are (a - x) and (b - x)respectively; express x in terms of k_1 , k_2 , a and b.

(a)
$$\frac{k_1 a - k_2 b}{k_1 + k_2}$$
 (b) $\frac{k_1 a - k_2 b}{k_1 - k_2}$

(c)
$$\frac{k_1 a - k_2 b}{k_1 k_2}$$
 (d) $\frac{k_1 a + k_2 b}{k_1 + k_2}$

Equilibrium Constant and ΔG

23. (S) If for the heterogeneous equilibrium $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$; K = 1 at 1 atm, the temperature is given by :

the temperature is given by .

(a)
$$T = \frac{\Delta S^{\circ}}{\Delta H^{\circ}}$$
 (b) $T = \frac{\Delta H^{\circ}}{\Delta S^{\circ}}$

(c)
$$T = \frac{\Delta G^{\circ}}{R}$$
 (d) $T = \frac{\Delta G^{\circ}}{\Delta H^{\circ}}$

24. (X) Match the Column-I with Column-II:

Column-I	Column-II
(Equations)	(Type of process)
(a) $K_p > Q$	(p) Non spontaneous
(b) $\Delta G^{o} < RT \log_{e} Q$	(q) Equilibrium
(c) $K_p = Q$	(r) Spontaneous and
	endothermic
(d) $T > \frac{\Delta H}{\Delta S}$	(s) Spontaneous

Passage (For Questions 25 to 27)

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

.(ii)

$$\Delta G^{\circ} = -2.303 \text{ RT logK} \qquad \dots (i)$$

 ΔG^{o} : Standard free energy change

$$\Delta G^{o} = \Delta H^{o} - T \Delta S^{o} \qquad \dots$$

 ΔH^{o} : Standard heat of the reaction

From (i) and (ii)

$$-2.303 \text{ RT} \log \text{K} = \Delta \text{H}^{\circ} - \text{T} \Delta \text{S}^{\circ}$$

 ΔS^o : Standard entropy change

$$\Rightarrow \log K = -\frac{\Delta H^{\circ}}{2.303 \text{RT}} + \frac{\Delta S^{\circ}}{2.303 \text{R}}$$
 ...(iii)

If a plot of log K vs 1/T is made then it is a straight line

having slope
$$=\frac{-\Delta H^{\circ}}{2.303R}$$
 and Y intercept $=\frac{\Delta S^{\circ}}{2.303R}$

If at temperature T_1 , equilibrium constant be K_1 and at temperature T_2 , equilibrium constant be K_2 then the above equation reduces to :

$$\Rightarrow \log K_1 = -\frac{\Delta H^{\circ}}{2.303 RT_1} + \frac{\Delta S^{\circ}}{2.303 R}$$

$$\Rightarrow \log K_2 = -\frac{2\pi 1}{2.303 \text{RT}_2} + \frac{2\pi 3}{2.303 \text{RT}_2}$$

Substracting (iv) from (v) we get.

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

From the above relation we can conclude that the value of equilibrium constant increases with increase in temperature for an endothermic reaction and the same decreases with the increase in temperature for an exothermic reaction. Answer the following three questions based on the above information.

25. (C) If standard heat of dissociation of PCl₅ is 230 cal, then

slope of the graph of log k vs $\frac{1}{T}$ is

(a)
$$+50$$
 (b) -50

26. (C) For exothermic reaction is $\Delta S^{\circ} < 0$, then the sketch of log K vs 1/T may be



- 27. (C) If for a particular reversible reaction : $K_c = 57$ at 355°C and $K_c = 69$ at 450°, then
 - (a) $\Delta H < 0$ (b) $\Delta H > 0$
 - (c) $\Delta H = 0$
 - (d) Sign of ΔH can't be determined

28. (M) Variation of equilibrium constant K for the reaction

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

is plotted against absolute temperature T in figure as : ln K Vs (1/T)



ln K vs 1/T

- (a) the forward reaction is exothermic
- (b) the forward reaction is endothermic
- (c) the slope of line is proportional to ΔH
- (d) adding 'A' favours forward reaction
- **29. (M)** Which is/are correct ?

(a) 2.303 log K =
$$-\frac{\Delta H^{\circ}}{RT} + \frac{\Delta S^{\circ}}{R}$$

(b) $\Delta G^{\circ} = -2.303 \text{ RT} \log K$

(c) -2.303 log K =
$$-\frac{\Delta H^2}{RT^2} + \frac{\Delta S^2}{R}$$

(d) 2.303 log K =
$$\frac{1}{RT} (\Delta H^{\circ} + \Delta S^{\circ})$$

30. (S) The free energy of formation of NO is 78 kJ mol⁻¹ at the temperature of an automobile engine (1000 K). What is the equilibrium constant for this reaction at this reaction at 1000 K?

$$\frac{1}{2}N_{2}(g) + \frac{1}{2}O_{2}(g) \rightleftharpoons NO(g)$$
(a) 8.4×10^{-5} (b) 7.1×10^{-9}
(c) 4.2×10^{-10} (d) 1.7×10^{-19}

31.(M) The variation of equilibrium constant K with temperature is represented by :

(a)
$$\log_{e} K_{2} - \log_{e} K_{1} = -\frac{\Delta H}{R} \int_{T_{1}}^{T_{2}} \left(\frac{1}{T}\right) dT$$

(b)
$$\left\{\frac{d\log_{e} K}{dT}\right\}_{P} = -\frac{\Delta H}{RT}$$

(c)
$$\log_{e} K = \text{Constant} - \frac{RT}{\Delta H}$$

(d) $\log_{e} K = \text{Constant} - \frac{\Delta H}{RT}$

Homogeneneous and Heterogeneous Equilibria, Degree of Dissociation

- **32. (S)** Volume of the flask in which the following equilibria are separately established are transferred to a flask that is double the size of the earlier flask. In which of the following cases, equilibrium constants are affected ?
 - (a) $N_2 + 3H_2 \xrightarrow[g]{} 2NH_3$, exothermic (g) (g) (g)

(b)
$$N_2 + O_2 \xrightarrow[g]{} 2NO$$
, endothermic

(c)
$$\underset{(g)}{\text{PCl}_5} \xrightarrow{} \underset{(g)}{\text{PCl}_3} + \underset{(g)}{\text{Cl}_2}$$
, endothermic

(d) none of these

33. (S) In each of the following, total pressure set-up at equilibrium is assumed to be equal and is one atm with equilibrium constants K_p given :

$$I: CaCO_3(s) \longrightarrow CaO(s) + CO_2(g), K_1$$

II : $NH_4HS(s) \longrightarrow NH_3(g) + H_2S(g), K_2$

III:
$$NH_2COONH_4(s) \implies 2NH_3(g) + CO_2(g), K_3$$

In the increasing order :

(a)
$$K_1 = K_2 = K_3$$
 (b) $K_1 < K_2 < K_3$
(c) $K_3 < K_2 < K_1$ (d) None of these

34. (S) During thermal dissociation, the observed vapour density of $N_2O_4(g)$ is 26.0. The extent of dissociation of $N_2O_4(g)$ is :

- **35. (8)** For the reaction $N_2O_4(g) \xrightarrow{} 2NO_2(g)$, the value of K_p is 1.7×10^3 at 500 K and 1.78×10^4 at 600 K. Which of the following is correct ?
 - I. The proportion of NO_2 in the equilibrium mixture is increased by decreasing the pressure
 - II. The standard enthalpy change for the forward reaction is negative
 - III. units of K_p are atm
 - IV. at 500 K, the degree of dissociation N_2O_4 decreases by 50% by increasing the pressure by 100%.

The correct choice is :

(a) I, III	(b) I
(c) II, IV	(d) III

36. (S) Consider the equilibrium

$$CO_2 \rightleftharpoons CO(g) + \frac{1}{2}O_2(g)$$

The equilibrium constant K is given by (when $\alpha \ll 1$):

Column-II

(a)
$$K = \frac{\alpha^{3/2}}{\sqrt{2}}$$
 (b) $K = \frac{\alpha^3}{2}$
(c) $K = \frac{\alpha^{3/2}}{2}$ (d) $K = \frac{\alpha^{3/2}}{\sqrt{3}}$

$$\sim$$
 2 \checkmark

37.(X) Match the Column-I with Column-II :

Column-I

(Reaction) (Effect on equilibrium) (A) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3$ (q) Forward shift by lowering of

 $\Delta H = -ve$ temperature

 $(B) N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$ (q) Forward shift by rise in

$$\Delta H = +ve$$
 temperature

(c) $PCl_5(g) \rightleftharpoons PCl_3(g)+Cl_2(g)$ (r) No effect of pressure

 $\Delta H = +ve$ change

(d) $2SO_2(g)+O_2(g) \rightleftharpoons 2SO_3(g)$ (s) Forward shift by rise in

 $\Delta H = -ve$ pressure

- **38. (I)** For the equilibrium AB(g) \rightleftharpoons A(g) + B(g), at a given temperature $\frac{1}{3}$ rd of AB is dissociated, then $\frac{P}{K_p}$ will be numerically equal to
- SO₂Cl₂ and Cl₂ are introduced into a 3L vessel. Partial pressure of SO₂Cl₂ and Cl₂ at equilibrium are 1 atm and 2 atm respectively. The value of K_p for the following reaction

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$
 is 10.

The total pressure in atm at equilibrium would be _____.

- **40. (I)** What weight of solid ammonium carbamate (NH_2COONH_4) when vaporised at 200°C will have a volume of 8.96 litre at 1 atm ? Assume that solid completely decomposes into CO₂ and NH₃ at 200°C and 1 atm.
- **41.(A)** Assertion : The dissociation of $CaCO_3$ can be represented as, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$. Some solid $CaCO_3$ is placed in an evacuated vessel enclosed by a piston and heated so that a portion of it is decomposed. If the piston is moved so that the volume of the vessel is doubled, while the temperature is held constant, the number of moles of CO_2 in the vessel increases.

Reason : The pressure of CO_2 in the vessel will remain the same.

Passage : For Questions (42 to 44)

These 3 questions deal with the following chemical reaction:

$$Ni^{2+}(aq) + 6NH_3(aq) \rightleftharpoons [Ni(NH_3)_6]^{2+}(aq)$$
(green solution)

When $H^+(aq)$ is added, the colour green is favoured. Use one or more of the following interpretations to answer the questions.

- I. Some unreacted Ni²⁺ (aq) is present in the solution at equilibrium.
- II. Some unreacted NH₃ (aq) is present in the solution at equilibrium.

- III. The colour change indicates new equilibrium conditions with reduced $[Ni(NH_3)_6]^{2+}(aq)$.
- IV. The colour change indicates new equilibrium conditions with increased $[Ni(NH_3)_6]^{2+}(aq)$.
- **42.(C)** The deepening colour on dissolving more Ni(NO₃)₂ supports interpretation(s)
 - (a) I only (b) I and IV only
 - (c) II and IV only (d) I and II only
- **43.(C)** The deepening colour on addition of more NH₃(aq) supports intepretation(s)
 - (a) I only (b) I and IV only
 - (c) I and II only (d) II and IV only
- **44.(C)** The disappearance of colour on addition of H⁺ (aq) supports interpretation(s)
 - (a) I only (b) II and IV only
 - (c) I and II only (d) III only

Passage : For Questions (45 to 47)

These 3 questions refer to the following experiment. Some $Fe(NO_3)_3$ solution is added to KSCN solution and a dark red colour appears. This colour is caused by $FeSCN^{2+}$, which is formed by the reaction :

$$Fe^{3+}(aq) + SCN^{-}(aq) \rightleftharpoons FeCN^{2+}(aq).$$

Experiments show this colour becomes deeper upon addition of more $Fe(NO_3)_3$ or KSCN. The colour disappears when Na_2HPO_4 is added. Use one or more of the interpretations below.

- (a) Unreacted Fe³⁺ (aq) is present in the original equilibrium mixture.
- (b) Unreacted SCN⁻ (aq) is present in the original equilibrium mixture.
- (c) Colour change indicates a new equilibrium ; [FeSCN²⁺ (aq)] has been reduced.
- (d) Colour change indicates a new equilibrium ; [FeSCN²⁺ (aq)] has been increased.
- **45. (C)** The deepening of colour on addition of more $Fe(NO_3)_3$ supports

(c) A and B only (d) B and D only

46.(C) The deepening of colour on addition of KSCN supports

(a) A only	(b) A and D only
(c) A and B only	(d) B and D only

47.(C) The disappearance of colour on addition of Na_2HPO_4 supports

(a) A only	(b) A and D only
(c) A and B only	(d) C only

48. (M) An industrial fuel, 'water gas' which consists of a mixture of H_2 and CO can be made by passing steam over redhot carbon. The reaction is

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

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

- (a) raising the relative pressure of steam
- (b) adding hot carbon
- (c) raising the temperature

(d) reducing the volume of the system

49. (S) For the reaction, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$; if percentage dissociation of N_2O_4 are 25%, 50%, 75% and 100%, then the sequence of observed vapour densities will be :

(a)
$$d_1 > d_2 > d_3 > d_4$$
 (b) $d_4 > d_3 > d_2 > d_1$
(c) $d_1 = d_2 = d_3 = d_4$ (d) $(d_1 = d_2) > (d_3 = d_4)$

50. (S) The equilibrium constant for the decomposition of water,

$$H_2O(g) \rightleftharpoons H_2(g) + \frac{1}{4}O_2(g)$$

is given by :

(

(a)
$$K = \frac{\alpha^3 p^{1/2}}{(1-\alpha)(2-\alpha)^{1/2}}$$

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

c)
$$K = \frac{\alpha^3 p^{1/2}}{\sqrt{2}}$$
 (d) $K = \frac{\alpha^3 p^{3/2}}{(1-\alpha)(2+\alpha)^{1/2}}$

- **51.** (S) The equilibrium constants K_{p_1} and K_{p_2} for the reactions $X \rightleftharpoons 2Y$ and $Z \rightleftharpoons P + Q$; respectively are in the ratio of 1 : 9. If the degree of dissociation of X and Z be equal, then the ratio of total pressures at these equilibria is : (a) 1 : 9 (b) 1 : 36
 - (c) 1 : 1 (d) 1 : 3
- 52. (S) In the preparation of CaO from $CaCO_3$ using the equilibrium, $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$, (At 1 atm)

$$K_p$$
 is expressed as $\log K_p = 7.282 - \frac{8500}{T}$.

For complete decomposition of CaCO₃ the temperature is celsius to be used is :

(a) 1167	(b) 894
(c) 8500	(d) 850

Le Chatelier's Principle

53. (A) Assertion : For the reaction

$$A_{(g)} + B_{(g)} \longrightarrow C_{(g)} + D_{(g)}$$

at the given temperature, there will be no effect by addition of inert gas either at constant pressure or at constant volume.

Reason : For the reaction where $\Delta n = 0$, there is no effect of inert gas either at constant volume or at constant pressure because K_p becomes purely a number.

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

54. (A) Assertion : Addition of an inert gas at constant pressure equilibrium will support the dissociation of PCl_5 at the same temperature.

Reason : The addition of an inert gas will tend to increase the total pressure.

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

55. (A) Assertion : The addition of an inert gas under constant volume condition cause the total pressure of the system to increase. This would thus lower the degree of dissociation of PCl_5 .

Reason : Addition of inert gas at equilibrium increase the kinetic energy of molecules.

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

56. (M) Yield of NH₃ in Haber's process

$$N_{2(g)} + 3H_{2(g)} \longrightarrow 2NH_{3(g)}, \Delta H = -22$$
 kcal;

can be increased by

- (a) compressing the reaction system
- (b) raising the temperature
- (c) decreasing the temperature
- (d) using the catalyst to lower down the activation energy
- **57. (M)** The volume of the reaction flask is reduced to half of its initial value, temperature being constant. In which of the following cases the position of the equilibrium would shift ?

(a)
$$\operatorname{NH}_4\operatorname{HS}_{(s)} \xrightarrow{} \operatorname{NH}_{3(g)} + \operatorname{H}_2\operatorname{S}_{(s)}$$

(b) $2\operatorname{NOCl}_{(g)} \xrightarrow{} 2\operatorname{NO}_{(g)} + \operatorname{Cl}_{2(g)}$
(c) $\operatorname{CO}_{(g)} + \operatorname{H}_2\operatorname{O}_{(g)} \xrightarrow{} \operatorname{CO}_{2(g)} + \operatorname{H}_{2(g)}$
(d) $\operatorname{I}_{2(g)} \xrightarrow{} 2\operatorname{I}_{(g)}$

58.(M) KNO_{3(s)} dissociates on heating as :

$$\text{KNO}_{3(s)} \xrightarrow{} \text{KNO}_{2(s)} + \frac{1}{2}\text{O}_{2(g)}$$

At equilibrium in a closed container

(a) addition of $NaNO_{3(s)}$ favours forward reaction

(b) addition of $KNO_{2(s)}$ favours reverse reaction

(c) increasing temperature favours forward reaction

(d) decreasing pressure favours forward reaction

59.(M) The dissociation of phosgene, which occurs according to the reaction :

$$\operatorname{COCl}_{2(g)} \xrightarrow{} \operatorname{CO}_{(g)} + \operatorname{Cl}_{2(g)}$$

is an endothermic process. Which of the following factors will increase the degree of dissociation of COCl₂?

(a) Adding Cl_2 to the system

- (b) Adding helium to the system at constant pressure
- (c) Decreasing the temperature of the system
- (d) Reducing the total pressure

60.(M) The dissociation of ammonium carbamate may be represented by the equation

 $NH_4CO_2NH_{2(s)} \longrightarrow 2NH_{3(g)} + CO_{2(g)}$

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

- (a) a decrease in pressure
- (b) an increase in temperature
- (c) an increase in the concentration of ammonia
- (d) an increase in the concentration of carbon dioxide
- **61. (M)** Which of the following factors will increase solubility of a well known weak base, $NH_{3(g)}$, in H_2O ?
 - $NH_{3(g)} + H_2O_{(aq)} \xrightarrow{} NH_4OH_{(aq)}$
 - (a) increase in pressure (b) addition of water
 - (c) addition of an acid to water
 - (d) addition of a base to water
- **62. (M)** For the following endothermic equilibrium established by dissociation of NH_4HS to its components,

 $NH_4HS_{(s)} \xrightarrow{\sim} NH_{3(g)} + H_2S_{(g)}$

partial pressure of NH₃ will increase

(a) if NH₃ is added after equilibrium is established

- (b) if H₂S is added after equilibrium is established
- (c) temperature is increased
- (d) volume of the flask is decreased
- **63. (M)** Volume of the flask in which the following equilibria are separately established are transferred to a flask that is double the size of the earlier flask. In which of the following cases, equilibrium concentrations are affected ?

(a)
$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

(b) $N_2 + O_2 \rightleftharpoons 2NO$
(c) $N_2 = O_2$
(c) $N_$

(c)
$$\operatorname{PCl}_5 \xrightarrow{} \operatorname{PCl}_3 + \operatorname{Cl}_2 \atop (g) \qquad (g) \qquad (g)$$

(d) 2NOBr
$$\underset{(g)}{\longrightarrow}$$
 $N_2 + O_2$
(g) (g)

64. (S) To the system $H_2(g) + I_2(g) \implies 2HI(g)$

in equilibrium, some $\mathrm{N}_2\,$ gas was added at constant volume. Then,

(a) K_{p} will remain constant and K_{c} will change

(b) K_{c} will remain constant and K_{p} will change

(c) Both K_p and K_c will remain constant

(d) Both K_p and K_c will change

65. (S) In a 1.0 L aqueous solution when the reaction

$$2 \operatorname{Ag}_{(aq)}^{+} + \operatorname{Cu}_{(s)} \xrightarrow{} \operatorname{Cu}_{(aq)}^{2+} + 2 \operatorname{Ag}_{(s)}$$

reaches equilibrium, $[Cu^{2+}] = x M$ and $[Ag^{+}] = y M$.

If the volume of solution is doubled by adding water, then at equilibrium :

(a)
$$[Cu^{2+}] = \frac{x}{2}M, [Ag^+] = \frac{y}{2}M$$

(b) $[Cu^{2+}] > \frac{x}{2}M, [Ag^+] > \frac{y}{2}M$
(c) $[Cu^{2+}] < \frac{x}{2}M, [Ag^+] > \frac{y}{2}M$
(d) $[Cu^{2+}] < \frac{x}{2}M, [Ag^+] < \frac{y}{2}M$

66. (S) For the reaction $PCl_5(g) \longrightarrow PCl_3(g) + Cl_2(g)$

Which of the following sketch may represent above equilibrium? Assume equilibrium can be achieved from either side and by taking any one or more components initially. (Given K_c for the reaction < 2)?





For the following reaction through stages I, II and III 67. (S)



quantity of the product formed (x) varies with temperature (T) as given. Select correct statement :



(a) Stages I and III are endothermic but II is exothermic

(b) Stages I and III are exothermic but II is endothermic

(c) Stages II and III are exothermic but I is endothermic (d) Stage I is exothermic but stages II and III are

K_n/K_c

relationship

(p) System is at

equilibrium

(q) Goes to right

68. (X) Match the conditions on the left column with states on the right column.

Equilibrium types

endothermic

(a) $A_2(g) \rightleftharpoons 2A(g); K_c = 1.$ Mixture of 1.0 mole of each is prepared in a 1.0 L flask. (b) $A(g) + 2B(g) \Longrightarrow AB_2(g)$ $K_c = 2.$ A mixture of 2.0 moles of each A, B and AB,

is prepared in a 1.0 L flask.

$$A_2(g) \rightleftharpoons 2A(g)$$
; $K_p = 2$. At (r) $n(A) > n(A_2)$ at
equilibrium the total pressure equilibrium
is 2.0 atm

(d)
$$2A(g) \rightleftharpoons A_2(g)K_p = 2.A$$
 (s) $n(A) < n(A_2)$ at
mixture, initially containing equilibrium
both A and A₂ at 1.0 atm

69. (X) Match the Column–I with Column–II

Column-II

(p) Forward shift by

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

 $(B) N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

partial pressure is prepared.

(c)

Column-I

increase in pressure

(p) No effect of

pressure change

(r) No effect of inert gas addition at constant volume

g) (

(s) Addition of inert gas will favour backward direction (Not at constant volume)

Passage : For Questions (70 to 72)

Le-Chatelier's principle : If a system at equilbrium is subjected to a change of any one of the factors such as concentration, pressure or temperature, the system adjusts itself in such a way as to "Nullify" the effect of that change.

Change of Pressure :

If a system in equilibrium consists of gases, then the concentrations of all components can be altered by changing the pressure. When the pressure on the system is increased, the volume decreases proportionately. The total number of moles per unit volume will now be more and the equilibrium will shift in that direction in which there is decrease in number of moles i.e. towards the direction in which there is decrease in volume.

(D)
$$\text{NH}_2\text{COONH}_4(s) \rightleftharpoons 2\text{NH}_3(g)$$

(C) CaCO₂(s) \rightleftharpoons CaO(s)+CO₂(g)

 $+ CO_2(g)$

Effect of Pressure on Melting Point :

There are two types of solids :

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

Solid (higher volume) \rightleftharpoons liquid (lower volume)

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

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

Solid (lower volume) \rightleftharpoons liquid (higher volume)

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

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

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

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

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

In such cases, solubility decrease with increse in temperature.

(d) Solubility of gases in liquids : When a gas dissolves in liquid, there is decrease in volume. Thus, increase of pressure will favour the dissolution of gas in liquid. Answer the following three questions based on the above information.

- **70. (C)** When a gas "X" is dissolved in water, the heat is evolved. Then solubility of 'X' will increase at
 - (a) low pressure, high temperature
 - (b) low pressure, low temperature
 - (c) high pressure, high temperature
 - (d) high pressure, low temperature

71.(C) $Au(s) \rightleftharpoons Au(l)$

Above equilibrium is favoured at

- (a) high pressure low temperature
- (b) high pressure high temperature
- (c) low pressure, high temperature
- (d) low pressure, low temperature

72.(C) For the reaction :
$$\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons NO(g)$$

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

- (a) total pressure at equilibrium will change
- (b) concentration of all the components at equilibrium will change
- (c) concentration of all the components at equilibrium will remain same

(d) equilibrium will shift in the forward direction

73.(M) 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) increasing the volume of the container
- **74. (M)** Which of the following factors will favour the backward reaction ?

 $Cl_2(g) + 3F_2(g) \rightleftharpoons 2ClF_3(g); \Delta H = -ve$

(a) Addition of inert gas at constant pressure

(b) Addition of Cl, gas

- (c) Increase in the temperature of reaction
- (d) Increasing the volume of the container
- **75.(M)** For the gas phase reaction,

$$C_2H_4(g) + H_2(g) \rightleftharpoons C_2H_6(g); \Delta H^\circ = -136.8 \text{ kJ mol}^{-1}$$

carried out in a vessel, the equilibrium concentration of C_2H_4 can be increased by :

(a) increase in temperature(b) decrease in pressure

(c) removing some H₂ (d) adding some C_2H_6

Physical Equilibria

76. (S) Densities of diamond and graphite are 3.5 and 2.3 g/mL respectively. Increase of pressure on the equilibrium

C (diamond) $\rightleftharpoons C$ (graphite)

- (a) favours backward reaction
- (b) favours forward reaction
- (c) has no effect
- (d) increase the reaction rate

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



(a) increases (b) decrease

(c) remains same

(d) change unpredictably

- **78. (S)** Solubility of a substance which dissolves with a decrease in volume and absorption of heat will be favoured by
 - (a) high p and high T (b) low p and low T
 - (c) high p and Low T (d) low p and high T
- **79. (S)** A solution is transferred to a 1 L flask, some pure ice is added and a stopper is inserted to close the flask. After the system has reached constant temperature, there are still a few cubes of ice left in the flask, but no other solid. Which of the following statements is false relative to this system at equilibrium ?
 - (a) The system is a heterogeneous one.
 - (b) There are four phases present in the system, not including the container and stopper.
 - (c) The vapour pressure is constant.
 - (d) The temperature of the system is below 0°C.
- 80. (S) When a liquid in equilibrium with its vapour is heated
 - (a) the rate of the reaction, vapour \rightarrow liquid, is increased
 - (b) the same equilibrium mixture is re-established
 - (c) a new equilibrium mixture with a higher vapour pressure is established
 - (d) a new equilibrium mixture is established in which the rate of evaporation is greater than the rate of condensation

Simultaneous Equilibria

81. (I) Two equilibria are simultaneously existing in a vessel at 25°C

$$NO(g) + NO_2(g) \rightleftharpoons N_2O_3(g); K_{p_1}(say)$$

$$2NO_2(g) \rightleftharpoons N_2O_4(g); K_{p_2} = 8 \text{ atm}^{-1}$$

If initially only NO and NO₂ are present in a 3 : 5 mole ratio and the total pressure at equilibrium is 5.5 atm with the pressure of NO₂ is 0.5 atm, calculate K_{p_2} (in 10⁻¹).

82. (I) Two solids A and C dissociate into gas products as follows.

$$A(s) \rightleftharpoons B(g) + D(g); K_{p_1} = 400$$

 $C(s) \rightleftharpoons E(g) + D(g); K_{p_2} = 900$

At 25°C, the pressure over excess solid A only is 40 atm, and that over solid C only is 60 atm. Find the pressure over the solid mixture.

83. (S) On heating a mixture of SO_2Cl_2 and CO, two equilibria are simultaneously established :

$$SO_2Cl_2(g) \rightleftharpoons SO_2(g) + Cl_2(g)$$

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

On adding more SO₂ at equilibrium what will happen ?

(a) Amount of CO will decrese

(b) Amount of SO_2Cl_2 and $COCl_2$ will increase

(c) Amount of CO will remain unaffected

- (d) Amount of SO_2Cl_2 and CO will increase
- **84. (S)** Two solid compounds X(s) and Y(s) undergo dissociation as follows :

 $X(s) \rightleftharpoons A(g) + 2B(g); \quad K_{p_1} = 9 \times 10^{-3} \text{ bar}^3$

$$Y(s) \rightleftharpoons 2B(g) + C(g)$$
; $K_{p_2} = 4.5 \times 10^{-3} bar^3$

The total pressure of gaseous mixture at equilibrium will be :

85. (S) Given the following reactions and associated equilibrium constants, select the correct expression for the third equilibrium constant in terms of the first two.

(A)
$$2CO(g) + O_2(g) \rightleftharpoons 2CO_2(g)K_{c_1}$$

(B)
$$H_2(g) + \frac{1}{2}O_2(g) \rightleftharpoons H_2O(g)K_{c_2}$$

(C)
$$\operatorname{CO}(g) + \operatorname{H}_2\operatorname{O}(g) \rightleftharpoons \operatorname{CO}_2(g) + \operatorname{H}_2(g)\operatorname{K}_{c_3}$$

(a)
$$K_{c_3} = \frac{K_{c_1}}{K_{c_2}}$$
 (b) $K_{c_3} = \frac{\left(K_{c_1}\right)^{1/2}}{K_{c_2}}$
(c) $K_{c_3} = K_{c_1} \times \left(K_{c_2}\right)^{1/2}$
(d) $K_{c_3} = \left(K_{c_1}\right)^{1/2} \times \left(K_{c_2}\right)^{1/2}$

EXERCISE - 4 : PREVIOUS YEAR JEE ADVANCED QUESTION

6.

- The oxidation of SO₂ by O₂ to SO₃ is an exothermic reaction. The yield of SO₃ will be maximum if (1981)
 (a) temperature is increased and pressure is kept constant
 (b) temperature is reduced and pressure is increased
 (c) both temperature and pressure are increased
 (d) both temperature and pressure are reduced
- **2.** For the reaction :

 $H_2(g) + I_2(g) \xrightarrow{} 2HI(g)$

The equilibrium constant K_p changes with (1981)

- (a) total pressure (b) catalyst
- (c) the amounts of H_2 and I_2 present
- (d) temperature
- 3. Pure ammonia is placed in a vessel at a temperature where its dissociation constant (α) is appreciable. At equilibrium

$$N_2 + 3H_2 \longrightarrow NH_3$$
 (1984)

- (a) K_{p} does not change significantly with pressure
- (b) α does not change with pressure
- (c) concentration of NH₃ does not change with pressure
- (d) concentration of hydrogen is less than that of nitrogen
- 4. For the reaction ;

 $CO(g) + H_2O(g) \longrightarrow CO_2(g) + H_2(g),$

at a given temperature, the equilibrium amount of $CO_2(g)$ can be increased by (1998)

- (a) adding a suitable catalyst
- (b) adding an inert gas
- (c) decreasing the volume of the container
- (d) increasing the amount of CO(g)
- 5. For the chemical reaction

$$3X(g) + Y(g) \Longrightarrow X_{3}Y(g)$$

the amount of X_3 Y at equilibrium is affected by (1999)

- (a) temperature and pressure
- (b) temperature only
- (c) pressure only
- (d) temperature, pressure and catalyst

For the reversible reaction, $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$ 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_e , with concentration in mole litre⁻¹ is (2000)

(a)
$$\frac{1.44 \times 10^{-5}}{(0.082 \times 500)^{-2}}$$
 (b) $\frac{1.44 \times 10^{-5}}{(8.314 \times 773)^{-2}}$

(c)
$$\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^2}$$
 (d) $\frac{1.44 \times 10^{-5}}{(0.082 \times 773)^{-2}}$

- 7. 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 (2000)
 - (a) is zero (b) decreases with time
 - (c) is independent of time (d) increases with time
- 8. At constant temperature, the equilibrium constant (K_p) for the decomposition reaction $N_2O_4 \implies 2NO_2$ is expressed by $K_p = (4x^2P)(1-x^2)$, where P = pressure, x = extent of decomposition. Which one of the following statements is true ? (2001)
 - (a) K_{n} increases with increase of P
 - (b) K_{p} increases with increase of x
 - (c) K_n increases with decrease of x
 - (d) K_{n} remains constant with change in P and x
 - Consider the following equilibrium in a closed container

$$N_2O_4(g) 2 \implies 2NO_2(g)$$

At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements hold true regarding the equilibrium constant (K_p) and degree of dissociation (α)? (2008)

- (a) Neither K_p nor α changes
- (b) Both K_n and α changes
- (c) K_{n} changes but α does not change
- (d) K_{n} does not change but α changes

9.

10. $N_2 + 3H_3 \implies 2NH_3$

> Which is correct statement if N₂ is added at equilibrium condition ? (2006)

- (a) The equilibrium will shift to forward direction because according to IInd law of thermodynamics the entropy must increase in the direction of spontaneous reaction
- (b) The condition for equilibrium is $G_{N_2} + 3G_{H_2} = 2G_{NH_2}$

where G is Gibbs free energy per mole of the gaseous species measured at that partial pressure. The condition of equilibrium is unaffected by the use of catalyst, which increases the rate of both the forward and backward directions to the same extent

- (c) The catalyst will increase the rate of forward reaction bv β
- (d) Catalyst will not alter the rate of either of the reaction.

Paragraph

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

 $X_2(g) \rightleftharpoons 2X(g)$

The standard reaction Gibbs energy, $\Delta_{c}G^{\circ}$, of this reaction is positive. At the start of the reaction, there is one mole of X, and no X. As the reaction proceeds, the number of moles of X formed is given by β . Thus, $\beta_{equilibrium}$ is the number of moles of X formed at equilibrium. The reaction is carried out at a constant total pressure of 2 bar. Consider the gases to behave ideally. (Given : $R = 0.083 L bar K^{-1} mol^{-1}$) (2016)

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

(a)
$$\frac{8\beta_{equilibrium}^2}{2-\beta_{equilibrium}}$$
(b)
$$\frac{8\beta_{equilibrium}^2}{4-\beta_{equilibrium}^2}$$
(c)
$$\frac{4\beta_{equilibrium}^2}{2-\beta_{equilibrium}}$$
(d)
$$\frac{4\beta_{equilibrium}^2}{4-\beta_{equilibrium}^2}$$

- 12. The INCORRECT statement among the following, for this reaction, is
 - (a) Decrease in the total pressure will result in formation of more moles of gaseous X
 - (b) At the start of the reaction, dissociation of gaseous X₂ takes place spontaneously

(c)
$$\beta_{\text{equilibrium}} = 0.7$$

(d) $K_{\text{C}} < 1$

Objective Questions (One or more than one correct option)

- 13. For the gas phase reaction $C_2H_4 + H_2 \longrightarrow C_2H_6 (\Delta H = -32.7 \text{ kcal})$ carried out in a vessel, the equilibrium concentration of $C_{2}H_{4}$ can be increased by (1984) (a) Increasing the temperature (b) decreasing the pressure (c) removing some H_2 (d) adding some C_2H_6 14. When NaNO₃ is heated in a closed vessel, oxygen is liberated and NaNO, is left behind. At equilibrium (1986) (a) addition of NaNO₂ favours reverse reaction (b) addition of NaNO₂ favours forward reaction (c) increasing temperature favours forward reaction
 - (d) increasing pressure favours reverse reaction
- 15. The equilibrium $SO_2Cl_2(g) \implies SO_2(g) + Cl_2(g)$ is attained at 25°C in a closed container and an inert gas, helium is introduced. Which of the following statements are correct? (1989) (a) Concentration of SO_2 , Cl_2 and SO_2Cl_2 change
 - (b) More chlorine is formed
 - (c) Concentration of SO₂ is reduced
 - (d) All the above are incorrect
- For the reaction, $PCl_{s}(g) \implies PCl_{s}(g) + Cl_{s}(g)$ 16. The forward reaction at constant temperature is favoured by (1991) (a) introducing chlorine gas at constant volume (b) introducing an inert gas at constant pressure
 - (c) increasing the volume of the container
 - (d) introducing PCl_5 at constant volume
- 17. For a reaction, $A \rightleftharpoons P$, the plots of [A] and [P] with time at temperatures T_1 and T_2 are given below. (2018)



If $T_2 > T_1$, the correct statement(s) is (are)

(Assume ΔH^- and ΔS^- are independent of temperature and ratio of lnK at T_1 to lnK at T_2 is greater than T_2/T_1 . Here H, S, G and K are enthalpy, entropy, Gibbs energy and equilibrium constant, respectively.)

(a) $\Delta H^- < 0, \Delta S^- < 0$	(b) $\Delta G^- < 0, \Delta H^- > 0$
(c) $\Delta G^- < 0, \Delta S^- < 0$	(d) $\Delta G^- < 0, \Delta S^- > 0$

Fill in the Blanks

- 18. For a given reversible reaction at a fixed temperature, equilibrium constant K_p and K_c are are related by (1994)
- 19. A ten-fold increase in pressure on the reaction, $N_2(g)$ + $3H_2(g) \implies 2NH_3(g)$ at equilibrium, results in in K_v. (1996)
- 20. For a gaseous reaction 2B \longrightarrow A, the equilibrium constant K_p is to/than K_c.

True/False

- When a liquid and its vapour are at equilibrium and the 21. pressure is suddenly decreased, cooling occurs. (1984)
- 22. If equilibrium constant for the reaction, $A_2 + B_2 \implies$

2AB, is K, then for the backward reaction AB $\implies \frac{1}{2}$

$$A_2 + \frac{1}{2}B_2$$
, the equilibrium constant is $\frac{1}{K}$. (1984)

- 23. (1987) Catalyst makes a reaction more exothermic.
- 24. The rate of an exothermic reaction increases with (1993) increasing temperature.

Subjective Questions

One mole of nitrogen is mixed with three moles of 25. hydrogen in a four litre container. If 0.25 per cent of nitrogen is converted to ammonia by the following reaction

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

calculate the equilibrium constant, $\tilde{K_{\rm c}}$ in concentration units. What will be the value of K for the following equilibrium?

$$\frac{1}{2}N_2(g) + \frac{3}{2}H_2(g) \Longrightarrow NH_3(g)$$
(1981)

- 26. One mole of Cl, and 3 moles of PCl, are placed in a 100 litre vessel heated at 227°C. The equilibrium pressure is 2.05 atmosphere. Assuming ideal behaviour, calculate the degree of dissociation for PCl₅ and K_n for the reaction $PCl_{s}(g) \xrightarrow{} PCl_{s}(g) + Cl_{2}(g)$ (1984)
- 27. The equilibrium constant of the reaction $A_2(g) + B_2(g) \implies 2AB(g)$ at 100°C is 50. If a one litre flask containing one mole of A, is connected to a two litre flask containing two moles of B2, how many mole of AB will be formed at 373°C? (1985)
- 28. At a certain temperature, equilibrium constant (K) is 16 for the reaction ;

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

If we take one mole of each of all the four gases in a one litre container, what would be the equilibrium concentration of NO and NO₂? (1987)

 $\mathrm{N_2O_4}$ is 25% dissociated at 37°C and one atmosphere 29. pressure. Calculate (i) K_p and (ii) the percentage dissociation at 0.1 atmosphere and 37°C. (1988)

30. The equilibrium constant K_p of the reaction,

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

is 900 atm at 800 K. A mixture containing SO₂ and O₂ having initial pressure of 1 and 2 atm respectively is heated at constant volume to equilibrate. Calculate the partial pressure of each gas at 800 K. (1989)

31. For the reaction

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

hydrogen gas is introduced into a five litre flask at 327°C, containing 0.2 mole of CO(g) and a catalyst, until the pressure is 4.92 atm. At this point 0.1 mole of CH₂OH(g) is formed. Calculate the equilibrium constant, K_p and K_c . (1990) 0.15 mole of CO taken in a 2.5 L flask is maintained at 750 K

32. along with a catalyst so that the following reaction can take place :

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

Hydrogen is introduced until the total pressure of the system is 8.5 atm at equilibrium and 0.08 mole of methanol is formed. Calculate (i) K_p and K_c and (ii) the final pressure if the same amount of CO and H₂ as before are used, but with no catalyst so that the reaction does not take place. (1993)

33. The progress of reaction,

> $A \Longrightarrow nB$ with time, is represented in fig. given below. Determine



(i) the value of n

(ii) the equilibrium constant, K and

(1994)

- (iii) the initial rate of conversion of A. 34. The degree of dissociation is 0.4 at 400 K and 1.0 atm for the gaseous reaction $PCl_5 \implies PCl_3 + Cl_2$. Assuming ideal behaviour of all the gases, calculate the density of equilibrium mixture at 400 K and 1.0 atm (relative atomic mass of P = 31.0 and Cl = 35.5) (1998)
- 35. When 3.06 g of solid NH₄SH is introduced into a two litre evacuated flask at 27°C, 30% of the solid decomposes into gaseous ammonia and hydrogen sulphide.

(i) Calculate K_c and K_p for the reaction at 27°C.

(ii) What would happen to the equilibrium when more solid (1999) NH₄SH is introduced into the flask ?

ANSWER KEY

		. (Basic O		cstionsj						
	1. (c)	2. (b)	3. (d)	4. (d)	5. (d)	6. (c)	7. (a)	8. (a)	9. (c)	10. (d)
	11. (d)	12. (b)	13. (b)	14. (d)	15. (a)	16. (b)	17. (b)	18. (a)	19. (c)	20. (c)
	21. (d)	22. (c)	23. (c)	24. (b)	25. (d)	26. (a)	27. (d)	28. (c)	29. (c)	30. (a)
	31. (d)	32. (a)	33. (c)	34. (b)	35. (c)	36. (a)	37. (d)	38. (b)	39. (d)	40. (b)
	41. (c)	42. (a)	43. (b)	44. (a)	45. (d)	46. (a)	47. (b)	48. (d)	49. (a)	50. (a)
	51. (a)	52. (a)	53. (d)	54. (d)	55. (b)	56. (a)	57. (c)	58. (d)	59. (b)	60. (d)
	61. (b)	62. (b)	63. (d)	64. (b)	65. (d)	66. (d)	67. (d)	68. (a)	69. (d)	70. (a)
	71. (c)	72. (c)	73. (c)	74. (a)	75. (c)	76. (b)	77. (c)	78. (d)	79. (d)	80. (d)
	81. (d)	82. (c)	83. (d)	84. (c)						
EXE	RCISE - 2	: (Previou	s year JEE I	Mains Qu	estions)					
	1. (a)	2. (c)	3. (d)	4. (d)	5. (a)	6. (b)	7. (a)	8. (d)	9. (d)	10. (d)
	11. (a)	12. (a)	13. (a)	14. (c)	15. (a)	16. (a)	17. (d)	18. (b)	19. (c)	
JEE	Mains On	line								
	1. (d)	2. (c)	3. (a)	4. (d)	5. (a)	6. (c)	7. (d)	8. (a)	9. (b)	10. (d)
EXE	RCISE - 3	: (Advanc	ed Objectiv	ve Questi	ons)					
	1. (a)	2. (a)	3. (b,c)	4. (c)	5. (b)	6. (a)	7. (a)	8. (a)	9. (a,c)	11. (c)
	12. (a)	13. (a)	14. (0004)	15. (a)	16. (c)	17. (b)	18. (b)	19. (c)	20. (c)	21. (a)
	22. (a)	23. (b)	24. (A–s),	(B–p), (C–c	l), (D−r)	25. (b)	26. (b)	27. (b)	28. (a,c,d)	
	29. (a,b)	30. (a)	31. (a,d)	32. (d)	33. (c)	34. (c)	35. (a)	36. (a)		

EXERCISE - 1 : (Basic Objective Questions)

37. (A–p,q,s	s), (B-q,r), (C-	-q), (D–p,s)	38. (0008)	39. (0008)	40. (0006)	41. (b)	42. (c)	43. (b)	44. (d)
45. (d)	46. (b)	47. (d)	48. (a,c)	49. (a)	50. (b)	51. (b)	52. (b)	53. (a)	54. (a)
55. (d)	56. (a,c)	57. (a,b,d)	58. (c,d)	59. (b,d)	60. (b,c,d)	61. (a,b,c)	62. (a,c)	63. (a,c)	64. (c)
65. (c)	66. (d)	67. (a)	69. (A-p,r,s),	(B-q,r), (C-r)	,(D-r)	70. (d)	71. (c)	72. (b)	
73. (c,d)	74. (a,c,d)	75. (a,b,c,d)	76. (a)	77. (b)	78. (a)	79. (b)	80. (c)	81. (0004)	
82. (0072)	83. (d)	84. (b)	85. (b)						

EXERCISE - 4 : (Previous year JEE Advanced Questions)

1. (b)	2. (d)	3. (a)	4. (d)	5. (a)	6. (d)	7. (d)	8. (d)	9. (d)	10. (b)
11. (b)	12. (c)	13. (a,b,c,d)	14. (c,d)	15. (d)	16. (bcd)	17. (a,c)	18. $K_p = K_c$	$(RT)^{\Delta n}$	
19. no chan	ge	20. smaller	21. (T)	22. (F)	23. (F)	24. (F)	25. 0.468 L ²	mol ⁻² , 0.68	
26. 0.33	27. 1.76	29. 0.266 atm	n; 63%	30. $\frac{175}{87}$ atm	, $\frac{85}{87}$ atm	31. $K_p = 0.1$	$1 \text{ atm}^{-2}, \text{K}_{c} =$	277.77 M ⁻²	
32. 220	33. (i) n = 2,	(ii) 1.2	34. 4.54g/L		35. 8.1 × 10 ⁻	5 , 4.84 × 10 ⁻²	, (ii) No effec	et	