EQUILIBRIUM – I

Equilibrium: It is the state of a process in which the properties like temperature, pressure, concentration of the system do not show any change with the passage of time.

This state is shown by a process which is reversible.

Physical Equilibrium: In this case opposing processes involve only physical changes.

Chemical Equilibrium: In this case opposing processes involve chemical changes.

Characteristics of Equilibrium

1. At equilibrium observable properties like pressure, temperature and concentration remain constant.
2. Equilibria involving gases can be attained only in a closed vessel.
3. Dynamic in nature i.e. Rate of forward process = Rate of backward process.
4. Equilibrium can be attained starting from either side.

Equilibria in Physical Processes

1. *Solid – Liquid equilibrium:* (Melting of Ice): If some ice tubes along with some water at 0^oC are placed in a thermos flask, the mass of ice and water remain constant for infinite time. In this case

   Rate of melting of ice = Rate of freezing of water.

   The equilibrium is represented as

   $H_2O\ (s) \rightleftharpoons H_2O\ (l)$

   The temperature at which solid and liquid are in equilibrium is known as melting point or freezing point of the substance.
2. *Liquid – Vapour Equilibrium:* (Evaporation of liquid in a closed vessel): When a liquid is taken in a closed container the molecules of the liquid leave the surface of the liquid and go into the atmosphere at the same time molecules of the liquid from vapour state condense to give liquid. In the beginning rate of evaporation is high and rate of condensation is low. With passage of time rate of evaporation decreases and rate of condensation increases till both become equal. It is the state of equilibrium.

   $H_2O\ (l) \rightleftharpoons H_2O\ (g)$

   At this state

   Rate of evaporation = Rate of condensation

   The pressure exerted by vapours of liquid in equilibrium with liquid is known as vapour pressure of liquid at a given temperature.
3. *Solid – Solution Equilibrium:* (Dissolution of solid in a liquid): When a solid is dissolved in a liquid a stage is reached when no more solid dissolves in the liquid at a given temperature. This is known as saturated solution. In this state two processes are going on (i) Dissolution of solid (ii) Crystallization. At this state

   Rate of dissolution = Rate of crystallization
4. *Gas – Solution Equilibrium:* (Dissolution of a gas in a liquid under pressure in a closed vessel): When CO_2 is dissolved in water under pressure in a closed vessel following equilibrium exists.

   $CO_2\ (g) \rightleftharpoons CO_2$ (in solution)

   The amount of gas dissolved in a solvent at a given temperature is directly proportional to the pressure of the gas above the solvent.

   $m \propto p$ or $m = kp$, where m = mass of gas dissolved, k = Henry's constant and p = pressure of the gas. This law is known as Henry's Law.

Chemical Equilibrium

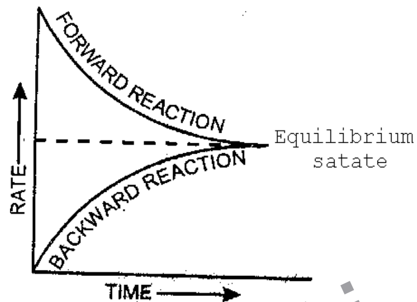
(a) *Reversible reactions*: The reaction in which reactants combine to give products but at the same time products also combine to give back reactants. i.e. reaction can be reversed.

(b) *Irreversible reaction*: Reaction in which products do not combine to give back reactants, i.e reaction which can not be reversed is known as irreversible reaction. A reversible reaction becomes irreversible if one of the products is allowed to escape out either in the form of gas or precipitate.

Chemical Equilibrium: If we start a reversible reaction

$A + B \rightleftharpoons C + D$

In the beginning conc. of reactants A and B is high, so rate of forward reaction is high and as conc. of C and D is zero, so rate of backward reaction is zero. With passage of time reactants combine to give products, so conc. of reactants goes on decreasing and conc. of products goes on increasing so rate of forward reaction goes on decreasing and rate of backward reaction goes on increasing and a state is reached when rate of forward reaction becomes equal to rate of backward reaction. This state is known as state of chemical equilibrium. This state is not static, both the processes are going on but as rate of forward reaction is equal to rate of backward reaction, so there is no change in conc. of reactants and products. So, this is a state of *Dynamic chemical equilibrium*.



LAW OF MASS ACTION

This law was given by *Guldberg and Waage*. According to this law

"The rate at which a substance reacts is proportional to its active mass and the rate of a chemical reaction is proportional to the product of active masses of reactants".

The active mass of a substance is taken as its *molar concentration*. i.e. conc. of the substance in gram moles per litre.

Mathematical expression

Let us consider the following reaction

$A + B \rightarrow$ Products

Active masses of A & B are represented as [A] & [B].

So rate of reaction α [A] × [B]

Rate of reaction = k [A] × [B] {where k = velocity constant.}

For the following reaction

$xA + yB \rightarrow$ Products

Rate of reaction = $k \times [A]^x \times [B]^y$

Law of Chemical Equilibrium

This is application of law of mass action to a reversible reaction at equilibrium. Let us consider the following reversible reaction at equilibrium.

$A + B \rightleftharpoons C + D$

Let the active masses of A, B, C & D be [A], [B], [C] & [D].

Applying law of mass action

Rate of forward reaction α [A] × [B]

= kf × [A] × [B] {kf = velocity constant for forward reaction}

Rate of backward reaction α [C] × [D]

= kb × [C] × [D] {kfb = velocity constant for backward reaction}

At equilibrium Rate of forward reaction = Rate of backward reaction

kf × [A] × [B] = kb × [C] × [D]

or $\frac{kf}{kb} \quad \frac{[C]\ [D]}{[A]\ [B]}$

or $\frac{kf}{kb} \quad k$ [k = equilibrium constant]

So, k = $\frac{[C]\ [D]}{[A]\ [B]}$

In case of a reaction,

$xA + yB \rightleftharpoons mC + nD$

k = $\frac{[C]^m\ [D]^n}{[A]^x\ [B]^y}$

So statement of law of chemical equilibrium is "the product of active masses of the products each raised by an exponent equal to its stoichiometric coefficient divided by the product of active masses of reactants each raised by an exponent equal to its stoichiometric coefficient is constant at a given temperature & is known as equilibrium constant.

Modification of Expression for Law of Chemical Equilibrium

If a reactant or product is in solid state or is a pure liquid then their active masses are taken as one and so are eliminated from the expression.

Example

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

Expected expression

K = $\frac{[Fe_3O_4(s)]\ H_2(g)^4}{[Fe(s)]^3\ [H_2O(g)]^4}$

As Fe & Fe_3O_4 are solids, so there active masses = 1, so the corrected expression will be

K = $\frac{H_2(g)^4}{[H_2O(g)]^4}$

Kp & Kc

Active masses may be represented in terms of

(i) Molar concentration than Equilibrium constant is known as Kc.

(ii) Partial pressure than Equilibrium constant is known as Kp. Partial pressure of a gaseous substance = Total pressure × Mole fraction of the substance.

For the reaction

xA + yB mC + nD

If molar conc. of A, B, C & D are C_A, C_B, C_C & C_D. Then

Kc = $\frac{C_C^m\ C_D^n}{C_A^x\ C_B^y}$.

If the respective partial pressures are p_A, p_B, p_C and p_D, then

Kp = $\frac{p_C^m\ p_D^n}{p_A^x\ p_B^y}$.

Relation between Kp and Kc

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

Δm = No. of molecules of products in gaseous state – No. of molecules of reactants in gaseous state.

Factors effecting Equilibrium constant

1. It is only temperature dependent. If the forward process is exothermic then with increase in temperature, value of K decreases and if forward reaction is endothermic then with increase in temperature the value of K increases.
2. Higher is the value of K, higher is the extent of forward reaction.
3. If the reaction is reversed, then the new equilibrium constant = 1/K.
4. If the no. of molecules of the reactants & products is doubled in the equation then the new equilibrium will be K^2.
5. If the no. of molecules reactants & products are halved in balanced chemical equation then new equilibrium constant = $\sqrt{K}$.
6. If a reaction takes place in no. of steps then the equilibrium constant for the overall reaction = Product of equilibrium constants for different steps.

Concentration quotient or reaction quotient

For a reaction, $xA + yB \rightleftharpoons mC + nD$

The following ratio of conc. at any time of chemical change other than equilibrium is known as concentration quotient or reaction quotient. [Qc]

Qc $\frac{[C]^m[D]^n}{[A]^x[B]^y}$ The beginning value of Qc is zero but with time it increases till equilibrium when Qc becomes equal to K.

If Q < K then reaction will proceed in forward direction.

If Q > K then the reaction will proceed in backward direction.

Le-Chatelier's Principle: *If a system in equilibrium is subjected to change in external conditions like temperature, pressure & concentration then system behaves (that reaction is favoured) in such a way so that effect of change is minimized (undone).*

Factors Effecting states of equilibrium

1. *Change of conc. of any reactant or product:* any of the reactant or product is added to the state of equilibrium then the reaction in which the substances added is consumed is favoured. Eg.
   $2N_2\,(g) + O_2\,(g) \rightleftharpoons 2N_2O\,(g)$
   If N_2 or O_2 is added to the equilibrium state, to minimize the effect of change more of N_2 and O_2 will react to give N_2O, i.e. forward reaction will be favoured and equilibrium will shift towards right hand side. If N_2O is added then backward reaction will be favoured and equilibrium will shift towards left hand side.
2. *Change of temperature:* Increase in temperature will favour a reaction in which heat is absorbed (endothermic reaction) and decrease in temperature will favour a reaction in which heat is given out (exothermic reaction).
   Eg. $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$; $\Delta H = -92.4$ kJ
   In this reaction, forward reaction is exothermic and backward reaction is endothermic. So increase in temperature will favour endothermic reaction i.e. more of NH_3 will dissociate to give N_2 & H_2 and equilibrium will shift towards left hand side. Decrease in temperature will favour exothermic reaction i.e. forward reaction and equilibrium will shift towards right hand side.
3. *Change of Pressure:* If reactants and products are in solid state, liquid state or in solution, then there is no effect of changing pressure on the state of equilibrium. If the reactants and products are gases then increase in pressure will favour a reaction in which volume decreases (no. of molecules decrease). Decrease in pressure will favour a reaction in which volume increases (i.e. no. of molecules increase).
   $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$;
   In this case, there is increase in no. of molecules increases in the backward reaction and decreases in the forward reaction. So increase in pressure will favour forward reaction and equilibrium will shift towards right hand side and decrease in pressure will favour backward reaction and equilibrium will shift towards left hand side.
   If the no. of molecules of gaseous reactants = no. of molecules of gaseous products.
   Eg. $N_2\,(g) + O_2\,(g) \rightleftharpoons 2NO\,(g)$
   There is no effect of pressure on the state of equilibrium.
4. *Addition of Catalyst:* There is no effect of catalyst on the state of equilibrium. The rates of both forward and backward reaction are increased but as increase in rate of forward reaction = increase in rate of backward reaction. So there is no effect on the state of equilibrium.
5. *Addition of inert gas:*

(a) At constant Volume: there is no effect of adding inert gas on the state of equilibrium as molar conc. of reactants and products remains same.

(b) At constant Pressure: Addition of inert gas will increase the total volume, so a reaction in which no. of molecules increase will be favoured.

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

In this case addition of inert gas will favoured backward reaction.

Calculation degree of dissociation from vapour density measurements

$$\frac{D - d}{d[n - 1]} \quad \frac{M_c - M_0}{M_0[n - 1]}$$

α = degree of dissociation D = calculated vapour density

d = observed vapour density Mc = calculated molecular mass

Mo = observed molecular mass

n = no. of particles obtained by dissociation of one molecule

Assignment

1. For an equilibrium reaction, the rate constants for the forward and backward reaction are 2.38×10^{-4} and 8.15×10^{-5} respectively. Calculate the equilibrium constant for the reaction.
2. In the reaction between H_2 and I_2 at a certain temperature, the amounts of H_2, I_2 and HI at equilibrium were found to be 0.45 mole, 0.39 mole and 3.0 moles respectively. Calculate the equilibrium constant for the reaction at the given temperature.
3. For the reaction,
   $N_2O_4 (g) \rightleftharpoons 2NO_2 (g)$
   the concentration of an equilibrium mixture at 298 K are $N_2O_4 = 4.50 \times 10^{-2}$ mole/litre and $NO_2 = 1.61 \times 10^{-2}$ mole/litre. What is the value of equilibrium constant?
4. AB_2 dissociates as
   $AB_2 (g) \rightleftharpoons AB (g) + B (g)$
   If the initial pressure is 500 mm of Hg and the total pressure at equilibrium is 700 mm of Hg, calculate Kp for the reaction.
5. 0.1 mole of PCl_5 is vapourised in a litre vessel at 260°C. Calculate the concentration of Cl_2 at equilibrium, if the equilibrium constant for the dissociation of PCl_5 is 0.0414.
6. 3.00 mole of PCl_5 kept in 1L closed reaction vessel was allowed to attain equilibrium at 380 K. Calculate the composition of the mixture at equilibrium. [Kc = 1.80]
7. The value of Kp for the reaction,
   $CO_2 (g) + C (s) \rightleftharpoons 2CO (g)$, is 3.0 at 1000 K. If initially, $P_{CO2} = 0.48$ bar and $P_{CO} = 0$ bar and pure graphite is present, calculate the equilibrium partial pressures of CO and CO_2.
8. The value of Kc = 4.24 at 800 K for the reaction,
   $CO (g) + H_2O (g) \rightleftharpoons CO_2 (g) + H_2 (g)$
   Calculate equilibrium concentrations of CO_2, H_2, CO and H_2O at 800 K, if only H_2O and CO are present initially at concentration of 0.10 M each?
9. At 700 K, the equilibrium constant
   $2SO_3 (g) \rightleftharpoons 2SO_2 (g) + O_2 (g)$
   is 1.80×10^{-3} k Pa. What is the numerical value of Kc in moles per litre for this reaction at the same temperature?
10. At 773 K, the equilibrium constant Kc for the reaction
    $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$ is $6.02 \times 10^{-2}\ L^2\ mol^{-2}$. Calculate the value of Kp at the same temperature.
11. For the equilibrium, $2NOCl (g) \rightleftharpoons 2NO (g) + Cl_2 (g)$, the value of the equilibrium constant, Kc is 3.75×10^{-6} at 1069 K. Calculate Kp for the reaction at this temperature.
12. Kp for the reaction, $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$ is 49 at a certain temperature. Calculate the value of Kp at the same temperature for the reaction
    $$2NH_3 (g) \rightleftharpoons \frac{1}{2} N_2 (g) + \frac{3}{2} H_2 (g)$$

MCQs having only one answer is correct

1. The equilibrium constant for the reaction $N_2 + 3H_2 \rightleftharpoons 2NH_3$ is K. The equilibrium constant for

$\frac{1}{2} N_2 + \frac{3}{2} H_2 \rightleftharpoons NH_3$ will be

(a) K/2 (b) 2K

(c) $\sqrt{K}$ (d) K^2.

2. If an inert gas is added to the equilibrium mixture of the dissociation of PCl_5 in a closed vessel,
(a) the concentration of Cl_2 will increase
(b) the concentration of PCl_3 will increase
(c) the concentration of PCl_5 will increase
(d) the equilibrium concentrations will remain unaffected.

3. If pressure is increased on the equilibrium
$N_2 + O_2 \rightleftharpoons 2NO$, the equilibrium will
(a) shift in the forward direction
(b) shift in the backward direction
(c) remain undisturbed
(d) may shift in the forward or backward direction.

4. For the reaction
$PCl_3 (g) + Cl_2 (g) \rightleftharpoons PCl_5 (g)$ the value of Kp at 250°C is 26. The value of Kp at this temperature will be
(a) 0.61 (b) 0.57
(c) 0.83 (d) 0.46.

5. According to Le Chatelier's principle adding heat to a solid and liquid in equilibrium will cause the
(a) amount uf solid to decrease
(b) amount of liquid to decrease
(c) temperature to rise
(d) temperature to fall.

6. In a reaction $A_2 (g) + 4B_2 (g) \rightleftharpoons 2AB_4 (g)$, $\Delta H < 0$. The formation of AB_4 (g) will be favoured by
(a) low temperature and high pressure
(b) high temperature and low pressure
(c) low temperature and low pressure
(d) high temperature and high pressure.

7. The reaction which proceeds in the forward direction is
(a) $Fe_3O_4 + 6HCl = 2FeCl_3 + 3H_2O$
(b) $NH_3 + H_2O + NaCl = NH_4Cl + NaOH$
(c) $SnCl_4 + Hg_2Cl_2 = SnCl_2 + 2 HgCl_2$
(d) $2CuI + I_2 + 4 K^+ = 2Cu^{2+} + 4KI$.

8. For which of the following reaction, Kp = Kc?
(a) $2NOCl (g) \rightleftharpoons 2 NO (g) + Cl_2 (g)$
(b) $N_2 (g) + 3H_2 (g) \rightleftharpoons 2NH_3 (g)$
(c) $H_2 (g) + Cl_2 (g) \rightleftharpoons 2HCl (g)$
(d) $2N_2O_4 (g) \rightleftharpoons 2NO_2 (g)$

9. In a vessel containing SO_3, SO_2 and O_2 at equilibrium some helium gas is introduced so that the total pressure increases while temperature and volume remain constant According to Le-Chiitelier's principle, the dissociation of SO_3
(a) increases (b) decreases
(c) remains unaltered
(d) changes unpredictably.

10. In a reversible reaction, two substances are in equilibrium. If the concentration of each one is doubled, the equilibrium constant will be
(a) Reduced to half its original value
(b) Reduced to one fourth of its original value
(c) Doubled (d) Constant.

11. An equilibrium mixture for the reaction
$2 H_2S (g) \rightleftharpoons 2H_2 (g) + S_2 (g)$ had 1 mole of H_2S, 0.2 mole of H_2 and 0.8 mole of S_2 in a 2 litre flask. The value of Kc in mol L^{-1} is
(a) 0.004 (b) 0.08
(c) 0.016 (d) 0.160

12. In what manner will increase of pressure affect the following equilibrium?
$C (s) + H_2O (g) \rightleftharpoons CO (g) + H_2O (g)$
(a) Shift in the forward direction
(b) Shift in the reverse direction
(c) Increase in the yield of hydrogen
(d) No effect.

13. The reaction, $SO_2 + Cl_2 \rightleftharpoons SO_2Cl_2$ is exothermic and reversible. A mixture of
SO_2 (g), Cl_2 (g) and SO_2Cl_2 (g) is at equilibrium in a closed container, Now a certain quantity of extra SO_2 is introduced into the container, the volume remaining the same. Which of the following is/are true?
(a) The pressure inside the container will not change
(b) The temperature will not change
(c) The temperature will increase
(d) The temperature will decrease.

14. The equilibrium constant for the reaction,
$N_2 (g) + O_2 (g) \rightleftharpoons 2NO (g)$ is 4×10^{-4} at 2000 K. In presence of a catalyst, equilibrium is attained ten times faster. Therefore, the equilibrium constant, in presence of the catalyst, at 2000 K is:
(a) 40×10^{-4} (b) 4×10^{-4}
(c) 4×10^{-3}
(d) difficult to compute without more data.

15. In $2HI \rightleftharpoons H_2 + I_2$, the forward reaction is affected by change in
(a) Catalyst (b) Pressure
(c) Volume (d) Temperature.

16. 64 g of HI are present in a 2 litre vessel. The active mass of HI is

(a) 0.5 (b) 0.25
(c) 1.0 (d) None of the three.

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

(a) 32 (b) 64
(c) 16 (d) 4.

18. In a reaction, $A + 2B \rightleftharpoons 2C$, 2.0 mole of 'A' 3.0 mole of 'B' and 2.0 mole of 'C' are placed in a 2.0 L flask and the equilibrium concentration of 'C' is 0.5 mole/L. The equilibrium constant (K) for the reaction is

(a) 0.073 (b) 0.147
(c) 0.05 (d) 0.026.

19. One mole of N_2O_4 (g) at 300 K is kept in a closed container under one atmosphere. It is heated to 600 K when 20% by mass of N_2O_4 (g) decomposes to NO_2 (g). The resultant pressure is

(a) 1.2 atm (b) 2.4 atm
(c) 2.0 atm (d) 1.0 atm.

20. If the concentration of the reactants is increased by x, then equilibrium constant K becomes

(a) $\ln \frac{K}{x}$ (b) $\frac{K}{x}$
(c) K + x (d) K

21. In which case Kp is less than Kc

(a) $PCl_5 \rightleftharpoons PCl_3 + Cl_2$

(b) $H_2 + Cl_2 \rightleftharpoons 2HCl$

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

(d) All of these

22. Formation of SO_3 takes place according to the reaction

$2\ SO_2 + O_2 \rightleftharpoons 2\ SO_3$, $\Delta H = -45.2$ kcal

Which of the following factors favours the formation of SO_3?

(a) Increase in temperature
(b) Increase in pressure
(c) Removal of oxygen
(d) Increase in volume

23. Kp / Kc for the reliction

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

(a) 1 (b) RT
(c) $\frac{1}{\sqrt{RT}}$ (d) $(RT)^{1/2}$

24. What would happen to a reversible dissociation reaction at equilibrium when an inert gas is added while the pressure remains unchanged?

(a) Less of the product will be formed
(b) More of the product wilt be formed
(c) More of the reactants will be formed
(d) It remains unaffected.

25. For the reaction $H_2\ (g) + I_2\ (g) \rightleftharpoons 2HI\ (g)$, the equilibrium constant Kp changes with

(a) temperature (b) total pressure
(c) catalyst (d) amount of H_2 and I_2

26. For a reversible reaction, if the concentrations of the reactants are doubled, the equilibrium constant will be

(a) halved (b) doubled
(c) the same (d) one fourth.

27. 500 ml vessel contains 1.5 M each of A, B, C and D at equilibrium. If 0.5 M each of C and D are taken out, the value of Kc for $A + B \rightleftharpoons C + D$ will be

(a) 1.0 (b) 1/9
(c) 4/9 (d) 8/9.

28. At 25°C the value of Kc for the reaction $\frac{1}{2} N_2 + O_2 \rightleftharpoons NO_2$ is 2×10^4.What will be the value of Kc for $2NO_2 \rightleftharpoons N_2 + 2O_2$?

(a) $\sqrt{2} \times 10^2$ (b) $\frac{1}{4\ \ 10^8}$
(c) 2×10^4 (d) 10^4.

29. For the reversible reaction, $N_2\ (g) + 3\ H_2\ (g) \rightleftharpoons 2\ NH_3\ (g)$ at 500°C, the value of Kp is 1.44×10^{-5} when partial pressure is measured in atmospheres. The corresponding value of Kc, with concentration in mole litre^{-1}, is

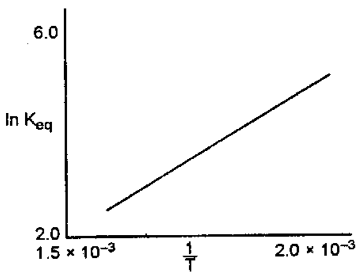
(a) $1.44 \times 10^{-5} / (0.082 \times 500)^{-2}$
(b) $1.44 \times 10^{-5} / (8.314 \times 773)^{-2}$

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

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

30. 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
    (a) is zero
    (b) decreases with time
    (c) is independent of time
    (d) increases with time.
31. In which of the following equilibrium, change in the volume of the system does not alter the number of moles?
    (a} $N_2\,(g) + O_2\,(g) \rightleftharpoons 2\,NO\,(g)$
    (b) $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$
    (c) $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$
    (d) $SO_2Cl_2\,(g) \rightleftharpoons SO_2\,(g) + Cl_2\,(g)$
32. 1 mole of N_2 and 2 moles of H_2 are allowed to react in a 1 dm^3 vessel. At equilibrium, 0.8 mole of NH_3 is formed. The concentration of H_2 in the vessel is
    (a) 0.6 mole (b) 0.8 mole
    (c) 0.2 mole (d) 0.4 mule
33. Consider the following equilibrium in a closed container: $N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$
    At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements, holds true regarding the equilibrium constant (Kp) and degree of dissociation
    (a) neither Kp nor a changes
    (b) both Kp and a change
    (c) Kp changes but a does not change
    (d) Kp does not change but a change
34. The reaction quotient (Q) for the reaction
    $N_2\,(g) + 3H_2\,(g) \rightleftharpoons 2NH_3\,(g)$
    is given by $Q = \frac{NH_3^{\ 2}}{N_2\ \ H_2^{\ 3}}$
    The reaction will proceed from right to left if
    (a) Q = Kc (b) Q < Kc
    (c) Q > Kc (d) Q = 0
35. The following equilibria are given
    $N_2 + 3H_2 \rightleftharpoons 2NH_3,\ K_1$
    $N_2 + O_2 \rightleftharpoons 2\,NO,\ K_2$
    $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O,\ K_3$
    The equilibrium constant of the reaction
    $2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O$
    in terms of K_1, K_2 and K_3 is
    (a) $K_1\,K_2\,K_3$ (b) $K_1\,K_2 / K_3$
    (c) $K_1\,K_3^2 / K_2$ (d) $K_2\,K_3^3 / K_1$
36. In the reaction $PCl_5\,(g) \rightleftharpoons PCl_3\,(g) + Cl_2\,(g)$,
    the equilibrium concentrations of PCl_5 and PCl_3 are 0.4 and 0. 2 mole/litre respectively. If the value of Kc is 0.5, what is the concentration of Cl_2 in moles/litre?
    (a) 2.0 (b) 1.5
    (c) 1.0 (d) 0.5
37. Of the following which change will shift the reaction towards the product?
    $I_2\,(g) \rightleftharpoons 2I\,(g),\ \Delta H^o_r\,(298\ K) = +150\ kJ$
    (a) increase in concentration of I
    (b) decrease in concentration of I_2
    (c) increase in temperature
    (d) increase in total pressure
38. The equilibrium $P_4\,(s) + 6Cl_2\,(g) \rightleftharpoons 4PCl_3\,(g)$ is attained by mixing equilibrium moles of P_4 and Cl_2 in an evacuated vessel. Then at equilibrium
    (a) $[Cl_2] > [PCl_3]$ (b) $[Cl_2] > [P_4]$
    (c) $[P_4] > [Cl_2]$ (d) $[PCl_3] > [P_4]$
39. In the given reaction $2\,X\,(g) + Y\,(g) \rightleftharpoons 2Z\,(g) + 80$ kcal, which combination of pressure and temperature will give the highest yield of X sit equilibrium?
    (a) 1000 atm and 200°C
    (b) 500 atm and 500°C
    (c) 1000 atm and 200°C
    (d) 500 atm and 100°C
40. Kp for the following reaction will be equal to
    $Fe\,(s) + 4H_2O\,(g) \rightleftharpoons Fe_3O_4\,(s) + 4H_2\,(g)$
    (a) $(p_{H2})^4\,(p_{Fe3O4})$ (b) $\frac{p_{H2}}{p_{H2O}}$
    (c) $\frac{p_{H2}^{\ 4}}{p_{H2O}^{\ 4}}$ (d) $\frac{p_{H2}\ p_{Fe3O4}}{p_{Fe}}$
41. A schematic plot of In K_{eq} versus inverse of temperature for a reaction is shown below:

The reaction must be



(a) exothermic
(b) endothermic
(c) one with negligible enthalpy change
(d) highly spontaneous at ordinary temperature

42. A small amount of NH_4HS is placed in n 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

43. Equilibrium constants K1 and K2 for the following equilibria:

$NO\ (g) + \frac{1}{2} O_2\ (g) \overset{K_1}{\rightleftharpoons} NO_2\ (g)$ and

$2NO_2\ (g) \overset{K_2}{\rightleftharpoons} 2NO + O_2\ (g)$

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

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

44. $NH_4COONH_2\ (s) \rightleftharpoons 2NH_3\ (g) + CO_2\ (g)$.
equilibrium pressure is 3 atm for tile above reaction, Kp for the reaction is

(a) 4 (b) 27
(c) 4/27 (d) 1/27

45. For the reaction $N_2\ (g) + O_2\ (g) \rightleftharpoons 2\ NO\ (g)$,
the value of Kc at 800°C is 0.1. When the equilibrium concentration of both the readmits is 0.5 mol, what is the value of Kp at this temperature ?

(a) 0.5 (b) 0.1
(c) 0.01 (d) 0.025

46. The equilibrium constant for the reaction

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

is Kc = 4.9 × 10─2. The value of Kc for the reaction
$SO_3 + O_2 \rightleftharpoons 2SO_3\ (g)$
will be

(a) 9.8×10^{-2} (b) 4.9×10^{-2}
(c) 416 (d) 2.40×10^{-3}

47. 2 litre vessel. The number of moles of H_2 at equilibrium is 0.2. Then the number of moles of I_2 and HI at equilibrium is

(a) 1.2, 1.6 (b) 1.8, 1.0
(c) 0.4, 2.4 (d) 0.8, 2.0

48. The equilibrium constant of a reaction is 300. If the volume of the reaction flask is tripled, the equilibrium constant will be

(a) 100 (b) 900
(c) 600 (d) 300

49. For the reaction, $H_2 + I_2 \rightleftharpoons 2HI$, K= 47.6.
If the initial number of moles of each reactant and product is 1 mole, then at equilibrium

(a) $[I_2] = [H_2]$, $[I_2] > [HI]$
(b) $[I_2] < [H_2]$, $[I_2] = [HI]$
(c) $[I_2] = [H_2]$, $[I_2] < [HI]$
(d) $[I_2] > [H_2]$, $[I_2] = [HI]$

50. A mixture of NO_2 and N_2O_4 has a vapour density of 38.3 at 300 K. What is the no of moles of NO_2 in 100 g of the mixture?

(a) 0.043 (b) 4.4
(c) 3.4 (d) 0.437

Answer

c	d	c	a	a
a	a	c	b	d
c	b	c	b	d
b	c	b	b	d
c	b	c	b	a
c	a	b	d	d
a	b	d	c	d
c	c	c	a	a
a	d	c	a	b
c	a	d	c	d