d.

## Chapter - 7

- Equilibrium : It is a state in a process when two opposing processes (forward and reverse) occur simultaneously at the same rate.
The free energy change at equilibrium state is zero i.e., $\Delta \mathrm{G}=0$.
- Equilibrium constant : For a general reaction :

$$
\begin{aligned}
& a \mathrm{~A}+b \mathrm{~B} \leftrightharpoons c \mathrm{C}+d \mathrm{D} \\
& \mathrm{~K}_{c}=\frac{[\mathrm{C}]^{c}[\mathrm{D}]^{d}}{[\mathrm{~A}]^{a}[\mathrm{~B}]^{b}} \text { and } \mathrm{K}_{p}=\frac{\mathrm{P}_{\mathrm{C}}^{c} \times \mathrm{P}_{\mathrm{D}}^{d}}{\mathrm{P}_{\mathrm{A}}^{a} \times \mathrm{P}_{\mathrm{B}}^{b}}
\end{aligned}
$$

## - Relationship between $K_{p}$ and $K_{c}$ :

$$
\begin{aligned}
\mathrm{K}_{p} & =\mathrm{K}_{c}(\mathrm{RT})^{\Delta n g} \\
\Delta n_{g} & =n_{p}(g)-n_{r}(g)
\end{aligned}
$$

Magnitude of equilibrium constant depends upon the way in which a reaction is written :

## Chemical equation Equilibrium constant

$$
\begin{array}{ll}
a \mathrm{~A}+b \mathrm{~B} \leftrightharpoons c \mathrm{C}+d \mathrm{D} & \mathrm{~K} \\
c \mathrm{C}+d \mathrm{D} \leftrightharpoons a \mathrm{~A}+b \mathrm{~B} & \mathrm{~K}_{1}=\frac{1}{\mathrm{~K}} \\
n a \mathrm{~A}+n b \mathrm{~B} \leftrightharpoons n c \mathrm{C}+n d \mathrm{D} & \mathrm{~K}_{2}=\mathrm{K}^{n} \\
\frac{1}{n} a A+\frac{1}{n} b B \rightleftharpoons \frac{1}{n} c C+\frac{1}{n} d \mathrm{D} & \mathrm{~K}_{3}=\mathrm{K}^{1 / n}
\end{array}
$$

- Predicting the direction of reaction :

If $\mathrm{Q}_{c}=\mathrm{K}_{c} \Rightarrow$ the reaction is in a state of equilibrium.
$\mathrm{Q}_{c}>\mathrm{K}_{c} \Rightarrow$ the reaction proceeds in reverse direction.
$\mathrm{Q}_{c}<\mathrm{K}_{c} \Rightarrow$ the reaction proceeds in forward direction.

- Ostwald's dilution law : Degree of dissociation of weak electrolyte, $\alpha=\sqrt{\frac{\mathrm{K}}{\mathrm{C}}}$
- Ionic Product of water $\left(\mathrm{K}_{w}\right)=\left[\mathbf{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{OH}^{-}\right]=\mathbf{1 0}^{-\mathbf{1 4}}$ at $\mathbf{2 9 8 K}$

Le-Chatelier's Principle : When a system of equilibrium is subjected to a change in temperature, pressure or concentration, the equilibrium shifts itself in such a way so as to undo or counterout the effect of change.

- Outcomes of Le-Chatelier's Principle


## Change at equilibrium

Increase in temperature
Decrease in temperature
Increase in pressure
Decrease in pressure
Increase in Conc. of reactants
Increase in Conc. of products

## Shift in equilibrium

Endothermic direction
Exothermic direction
Towards lesser gaseous moles
Towards greater gaseous moles
Forward direction
Reverse direction

- Conjugate Acid or Base :

Species - $\mathrm{H}^{+}=$Conjugate base
Species $+\mathrm{H}^{+}=$Conjugate acid

- $\mathbf{p H}$ of solution :
$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$or $\left[\mathrm{H}^{+}\right]=10^{-\mathrm{pH}}$
$\mathrm{pH}+\mathrm{pOH}=\mathrm{pK}_{w}=14$ at 298 K
- Common ion effect : The depression of ionisation of weak electrolyte by the presence of common ion from a strong electrolyte is called common ion effect. For example degree of dissociation of $\mathrm{NH}_{4} \mathrm{OH}$ decreases in the presence of strong electrolyte $\mathrm{NH}_{4} \mathrm{CI}$.
- Hydrolysis of salts and pH of their solutions : Hydrolysis of salt is defined as the reaction of cation or anion with water as a result of which the pH of water changes.

1. Salts of strong and strong bases (e.g., NaCI) do not hydrolyse. The solution pH will be 7 .
2. Salts of weak acids and strong bases (e.g., $\mathrm{CH}_{3} \mathrm{COONa}$ ) hydrolyse, $\mathrm{pH}>7$ (The anion acts as a base).

$$
\mathrm{X}^{-}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{HX}+\mathrm{OH}^{-}
$$

$$
\mathrm{pH}=7+\frac{1}{2}\left(p \mathrm{~K}_{a}+\log \mathrm{C}\right)
$$

3. Salt of strong acids and weak bases (e.g., $\mathrm{NH}_{4} \mathrm{Cl}$ ) hydrolyse, $\mathrm{pH}<7$. (The cation acts as an acid).

$$
\begin{aligned}
& \mathrm{M}^{+}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{MOH}+\mathrm{H}^{+} \\
& \mathrm{pH}=7-\frac{1}{2}\left(p \mathrm{~K}_{a}+\operatorname{logC}\right)
\end{aligned}
$$

4. Salt of weak acids and weak base (e.g., $\mathrm{CH}_{3} \mathrm{COONH}_{4}$ ) hydrolyse. The cation acts as an acid and anion as a base but whether the solution is aodic or basic depends upon the relative values of $\mathrm{K}_{a}$ and $\mathrm{K}_{b}$ for these ions.

$$
\begin{aligned}
& \mathrm{M}^{+}+\mathrm{X}+\mathrm{H}_{2} \mathrm{O} \leftrightharpoons \mathrm{MOH}+\mathrm{HX} \\
& \mathrm{pH}=7+\frac{1}{2}\left(p \mathrm{~K}_{a}-p \mathrm{~K}_{b}\right)
\end{aligned}
$$

- Buffer solutions : The solutions, which resist the change in pH on dilution or addition of small amounts of acid or base, are called buffer solutions.
- Basic buffer : Solution of weak base and its salt with strong acid, For e.g., $\mathrm{NH}_{4} \mathrm{OH}+\mathrm{NH}_{4} \mathrm{CI}$
- Acidic buffer : Solution of weak acid and its salt with strong base, For e.g., $\mathrm{CH}_{3} \mathrm{COOH}+\mathrm{CH}_{3} \mathrm{COONa}$.
- Henderson's Equation for the $\mathbf{p H}$ of Buffer solution-

$$
\begin{array}{ll}
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \frac{[\text { Salt }]}{[\text { Acid }]} & \text { (for acidic buffer) } \\
\mathrm{pOH}=\mathrm{pK}_{\mathrm{a}}+\log \frac{[\text { Salt }]}{[\text { Base }]} & \text { (for basic buffer) }
\end{array}
$$

- Solubility Product $\left(\mathbf{K}_{s p}\right)$ : The equilibrium constant that represent the equilibrium between undissolved salt (solute) and its ions in a saturated solution is called solubility product constant $\left(\mathrm{K}_{s p}\right)$.
For $\mathrm{A}_{x} \mathrm{~B}_{y} \stackrel{a q}{\rightleftharpoons} x \mathrm{~A}^{y+}+y \mathrm{~B}^{x-}$

$$
\mathrm{K}_{s p}=\left[\mathrm{A}^{y+}\right]^{x}\left[\mathrm{~B}^{x-}\right]^{y}
$$

If ionic product $<\mathrm{K}_{s p}$; salt remain dissolve.
If ionic product $>\mathrm{K}_{s p}$; salt will be precipitated.

## - Relationship between solubility (S) and solubility product ( $\mathrm{K}_{s p}$ ).

$$
\mathrm{K}_{s p}=x^{x} \cdot y^{y} \cdot \mathrm{~S}^{x+y}
$$

For binary salts (e.g., $\mathrm{AgCl}, \mathrm{AgBr}, \mathrm{Agl}$ )

$$
\begin{array}{r}
\mathrm{K}_{s p}=\mathrm{S}^{2} \\
\mathrm{~K}_{s p}=4 \mathrm{~S}^{3}
\end{array}
$$

For Ternary salts (e.g., $\mathrm{Pbl}_{2}$ )

## Chemical Equilibrium

1-Mark Questions

1. Define physical equilibrium. Give an example also.
2. Why is there a fizz when soda water bottle is opened ?
3. Justify the statement : 'Both physical and chemical equilibria are dynamic in nature'
4. State Henry's law.
5. In a reversible reaction, the two substances are in equilibrium. If the concentration of each one is reduced to half, then what is the effect on the equilibrium constant?
6. $\mathrm{K}_{1}$ and $\mathrm{K}_{2}$ are equilibrium constant for reactions (1) and (2)

$$
\begin{aligned}
\mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) & \rightleftharpoons 2 \mathrm{NO}(\mathrm{~g}) \\
\mathrm{NO}(\mathrm{~g}) & \rightleftharpoons 1 / 2 \mathrm{~N}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g})
\end{aligned}
$$

then, calculate the relation between $\mathrm{K}_{1}$ and $\mathrm{K}_{2}$
7. Write the equilibrium constant expression for the following reaction :

$$
3 \mathrm{Fe}(\mathrm{~s})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{~g}) \rightleftharpoons \mathrm{Fe}_{3} \mathrm{O}_{4}(\mathrm{~s})+4 \mathrm{H}_{2}(\mathrm{~g})
$$

8. Classify the equilibrium as homogenous or heterogenous :

$$
\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(1) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\mathrm{aq})
$$

9. $\mathrm{K} p=\frac{\left(\mathrm{PNH}_{3}\right)}{\left(\mathrm{P}_{\mathrm{N} 2} / 2\right)\left(\mathrm{PH}_{2}\right)^{3 / 2}}$

Write the balanced chemical equation corresponding to the above expression.
10. Give the direction in which the reaction would proceed if $\mathrm{Qc}>\mathrm{Kc}$
11. $\mathrm{Hb}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{HbO}_{2}(\mathrm{~s})$

Predict the direction in which equilibrium gets shifted if partial pressure of $\mathrm{O}_{2}(\mathrm{~g})$ is lowered.
12. Discuss the position of equilibrium if the following reaction is carried out in the presence of catalyst.
$2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{SO}_{3}(\mathrm{~g})$
13. In which case the yield of the product will be more.

$$
\begin{array}{ll}
\mathrm{A} \rightleftharpoons \mathrm{~B} & \mathrm{~K}_{1}=1010 \\
\mathrm{X} \rightleftharpoons \mathrm{Y} & \mathrm{~K}_{2}=106
\end{array}
$$

14. Value of Kc at 500 K for $\mathrm{A}+2 \mathrm{~B} \rightleftharpoons \mathrm{C}$ is 10.6

Determine the value of $K c$ at the same temperature for $C \rightleftharpoons A+2 B$
15. Why do we sweat more on a humid day?
16. Why does a catalyst not affect the magnitude of equilibrium constant?
17. Write the relation between Kp and Kc for the given reaction.

$$
\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{~g})
$$

18. Write the expression of Kc for the following reaction

$$
\mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}(\mathrm{ac})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\mathrm{aq})
$$

19. Write the expression of Kp for the following reaction $\mathrm{Cu}\left(\mathrm{NO}_{3}\right)_{2}(\mathrm{~s}) \rightleftharpoons 2 \mathrm{CuO}(\mathrm{s})+4 \mathrm{NO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$
20. For an exothermic reaction, what happens to the equilibrium constant if temperature is increase?
21. Ka for HAl is 10 and Ka for $\mathrm{HA}_{2}$ is 12

Which acid is stronger.
22. For tribasic acid $\mathrm{Ka}_{1}>\mathrm{Ka}_{2}>\mathrm{Ka}_{3}$

What will happen to the acid strength of polyprotic acid if protons are lost?
23. $\mathrm{C}(\mathrm{s}) \rightleftharpoons \mathrm{C}(\mathrm{s})$

Diamond $\left(\right.$ Density $\left.=3.5 \mathrm{~g} / \mathrm{cm}^{3}\right)$ Graphite $\left(\right.$ Density $\left.=2.3 \mathrm{~g} / \mathrm{cm}^{3}\right)$
What will be the effect of increasing the pressure in this equilibrium.
24. Under what condition does the active mass becomes equal to the molarity?
25. In which expression of Kc or Keq, that only solutions and gases are involved?
26. What will be the change in the direction of equilibrium if Ne gas is added in a reaction at constant volume.
27. What will be the effect on the boiling point of liquid if pressure is increased?

## 2-Mark Questions

1. What is Kc for the following equilibrium when the equilibrium concentration of each substance is :

$$
\begin{aligned}
& {\left[\mathrm{SO}_{2}\right]=0.60 \mathrm{M},\left[\mathrm{O}_{2}\right]=0.82 \mathrm{M} \text { and }\left[\mathrm{SO}_{3}\right]=1.90 \mathrm{M} ?} \\
& 2 \mathrm{SO}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{SO}_{3}(\mathrm{~g})
\end{aligned}
$$

2. At a certain temperature and total pressure of $10^{5} \mathrm{~Pa}$, iodine vapour contains $40 \%$ by volume of I atoms
$\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{I}(\mathrm{g})$
Calculate Kp for the equilibrium.
[NCERT] [2.67 $\times 104 \mathrm{~Pa}$ ]
3. Explain why pure liquids and solids can be ignored while writing the equilibrium constant expression?
4. A sample of $\mathrm{HI}(\mathrm{g})$ is placed in flask at a pressure of 0.2 atm . At equilibrium the partial pressure of $\mathrm{HI}(\mathrm{g})$ is 0.04 atm .
What is Kp for the given equilibrium?
$2 \mathrm{HI}(\mathrm{g}) \mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g})$
[NCERT] [4]
5. One mole of $\mathrm{H}_{2} \mathrm{O}$ and one mole of CO are taken in 10 L vessel and heated to 725 K . At equilibrium $40 \%$ of water (by mass) reacts with CO according to the equation,
$\mathrm{H}_{2} \mathrm{O}(\mathrm{g})+\mathrm{CO}(\mathrm{g}) \rightleftharpoons \mathrm{H}_{2}(\mathrm{~g})+\mathrm{CO}_{2}(\mathrm{~g})$
Calculate the equilibrium constant for the reaction. [NCERT] [0.444]
6. At 1127 K and 1 atm pressure, a gaseous mixture of CO and $\mathrm{CO}_{2}$ in equilibrium with soild carbon has $90.55 \% \mathrm{CO}$ by mass
$\mathrm{C}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{CO}(\mathrm{g})$
Calculate Kc for this reaction at the above temperature.[NCERT] [0.153]
7. Describe the effect of :
(a) addition of $\mathrm{H}_{2}$
(b) addition of $\mathrm{CH}_{3} \mathrm{OH}$
(c) removal of CO
(d) removal of $\mathrm{CH}_{3} \mathrm{OH}$
on the equilibrium of the reaction :
$2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{CO}(\mathrm{g}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{OH}(\mathrm{g})$
8. $\mathrm{A}+3 \mathrm{~B} \rightleftharpoons 2 \mathrm{XK}=\mathrm{x}$

What will be the equilibrium constant for the decomposition of 1 mol of x ?
9. $\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g}) \quad \mathrm{K}_{1}$
$\mathrm{N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}(\mathrm{g}) \quad \mathrm{K}_{2}$
$\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \quad \mathrm{K}_{3}$
Determine the equilibrium constant for
$\left.2 \mathrm{NH}_{3}(\mathrm{~g})+5 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}(\mathrm{g})+3 \mathrm{H}_{2} \mathrm{O}\right)(\mathrm{g})$
10. Kc for $\mathrm{PCl}_{5}(\mathrm{~g}) \rightleftharpoons \mathrm{PCl}_{3}(\mathrm{~g})+\mathrm{Cl}(\mathrm{g})$ is 0.04 at $25^{\circ} \mathrm{C}$

How much mole of $\mathrm{PCl}_{5}$ must be added to 3 L flask to obtain a chlorine concentration of 0.15 M ?

## 3-Mark Questions

1. Four moles of $\mathrm{PCl}_{5}$ are heated in a closed $4 \mathrm{dm}^{3}$ container to reach equilibrium at 400 K . At equilibrium $50 \%$ of $\mathrm{PCl}_{5}$ is dissociated. What is the value of Kc for the dissociation of $\mathrm{PCl}_{5}$ into $\mathrm{PCl}_{3}$ and $\mathrm{Cl}_{2}$ at 400 K
2. (a) How does the value of equilibrium constant predict the extent of a reaction?
(b) Equilibrium constant for a reaction is 10 . What will be the equilibrium constant for the reverse reaction?
3. (a) Define the equilibrium constant.
(b) For the general reaction :

$$
\mathrm{a} \mathrm{~A}(\mathrm{~g})+\mathrm{bB}(\mathrm{~g}) \rightleftharpoons \mathrm{cC}(\mathrm{~g})+\mathrm{dD}(\mathrm{~g})
$$

Derive the relationship between Kp and Kc
4. (a) What is meant by dynamic nature of equilibrium ?
(b) Consider the following transformation.
$\mathrm{A} \rightleftharpoons \mathrm{B}$
$\mathrm{K}_{1}=1$
$\mathrm{B} \rightleftharpoons \mathrm{C}$
$\mathrm{K}_{2}=2$
$\mathrm{C} \rightleftharpoons \mathrm{D}$
$\mathrm{K}_{3}=3$

Calculate the value of K for $\mathrm{A} \rightleftharpoons \mathrm{D}$
5. Kc for $\mathrm{SO}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{SO}_{3}(\mathrm{~g})$ at $600^{\circ} \mathrm{C}$ is 61.7

Calculate Kp . What is the unit Kp for the above equilibrium. $[\mathrm{R}=0.0821$ L atm $\mathrm{K}^{-1} \mathrm{~mol}^{-1}$ ]
6. 3.2 mole of HI were heated in a sealed bulb at $444^{\circ} \mathrm{C}$ till the equilibrium state was reached. Its degree of dissociation was found to be $20 \%$. Calculate the number of moles hydrogen iodide, hydrogen and iodine present at the equilibrium point and also determine the equilibrium constant.
$2 \mathrm{HI}(\mathrm{g}) \rightleftharpoons \mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g})$
7. At $25^{\circ} \mathrm{C}$ and 1 atm , the partial pressure in an equilibrium mixture of $\mathrm{N}_{2} \mathrm{O}_{4}$ $\mathrm{NO}_{2}$ are 0.7 and 0.3 atm , respectively. Calculate the partial pressure when they are in equilibriums at $25^{\circ} \mathrm{C}$ and at a total pressure of 10 atm .
8. 13.8 g of $\mathrm{N}_{2} \mathrm{O}_{4}$ was placed in a 1 L reaction vessel at 400 K and allowed to attain equilibrium
$\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g})$
The total pressure at equilbrium was found to be 9.15 bar. Calculate Kc, Kp and partial pressure at equilibrium.
$[\mathrm{Kc}=2.6]$
9. The equilibrium constant for the following reaction is $1.6 \times 105$ at 1024 K
$\mathrm{H}_{2}(\mathrm{~g})+\mathrm{Br}(\mathrm{g}) \rightleftharpoons 2 \mathrm{HBr}(\mathrm{g})$
Find the equilibrium pressure of all gases if 10.0 bar a HBr is introduced into a sealed container at 1024 K .
[NCERT] $\left[\mathrm{P}_{\mathrm{H} 2}\right.$ eq. $=\mathrm{P}_{\mathrm{Br} 2}$ eq. $=2.5 \times 10^{-2}$ bar; $\left.\mathrm{P}_{\mathrm{HBr}}=10.0 \mathrm{bar}\right]$
10. In a reaction :

$$
\mathrm{CO}(\mathrm{~g})+2 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{OH}(\mathrm{l}) \Delta_{r} \mathrm{H}^{\mathrm{o}}=-92 \mathrm{kj} / \mathrm{mol}
$$

Indicate the direction in which equilibrium will shift when
(i) Temperature is decreased.
(ii) Pressure is decreased.
(iii) Ne gas is added at constant pressure.

## 5-Mark Questions

1. Dihydrogen gas is obtained from natural gas by partial oxidation with steam as per following endothermic reaction :
$\mathrm{CH}_{4}(\mathrm{~g})+\mathrm{H}_{2} \mathrm{O}(\mathrm{g}) \rightleftharpoons \mathrm{CO}(\mathrm{g})+3 \mathrm{H}_{2}(\mathrm{~g})$
(a) Write as expression for Kp for the above reaction.
(b) How will the values of Kp and composition of equilibrium mixture be affected by :
(i) increasing the pressure
(ii) increasing the temperature
(iii) using a catalyst?
2. At 473 K , equilibrium constant Kc for decomposition of phosphorus pentachloride, $\mathrm{PCl}_{5}$ is $8.3 \times 10^{-3}$. If decomposition is depicted as,
$\mathrm{PCl}_{5}(\mathrm{~g}) \rightleftharpoons \mathrm{PCl}_{3}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})$
$\Delta \mathrm{H}^{\mathrm{o}}=124.0 \mathrm{~kJ} \mathrm{~mol}^{-1}$
(a) Write an expression for Kc for the reaction.
(b) What is the value of Kc for the reverse reaction at the same temperature?
(c) What would be the effect on Kc if (i) more $\mathrm{PCl}_{5}$ is added (ii) pressure is increased (iii) the temperature is increased ? [(b) $\mathrm{K}_{\mathrm{C}}=120.48$ (c)
(i) No effect (ii) No effect (iii) Kc increase]
3. Ammonia is prepared by Haber's process is which the following reaction occurs
$\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g}) \Delta \mathrm{H}^{\mathrm{o}}=-93.6 \mathrm{~kJ}$
Mention the effect of following on the equilibrium concentration of ammonia.
(a) Increasing pressure
(b) Increasing temperature
(c) Use of catalyst at an optimum temperature.
(d) Addition of inert gas at constant volume.
(e) Addition of inert gas at constant pressure.
4. Ethyl acetate is formed by the reaction between ethanol and acetic acid and the equilibrium is represented as :
$\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{l})+\mathrm{C}_{2} \mathrm{H}_{5} \mathrm{OH}(\mathrm{l}) \rightleftharpoons \mathrm{CH}_{3} \mathrm{COOC}_{2} \mathrm{H}_{5}(\mathrm{l})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
(i) Write the concentration ratio (reaction quotient), Qc, 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 $293 \mathrm{~K}, 0.214 \mathrm{~mol}$ of ethyl acetate is found after sometime. Has equilibrium been reached ?
[(ii) 3.92 (iii) $\mathrm{Qc}=0.204$, Equilibrium has not been attained.]

## Ionic Equilibrium

## 1-Mark Questions

1. Which of the following are Lewis acids ?
$\mathrm{H}_{2} \mathrm{O}, \mathrm{BF}_{3}, \mathrm{H}^{+}, \mathrm{NH}_{4}^{+}$
2. Write the conjugate acids for the following Bronsted bases.
$\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{OH}, \mathrm{H}_{2} \mathrm{O}$
3. Write the conjugate bases for the following Bronsted acids.
$\mathrm{H}_{2} \mathrm{O}, \mathrm{CH}_{3} \mathrm{COOH}$
4. Which of the following are Lewis acids ?
(a) $\mathrm{H}_{2} \mathrm{O}$, (b) $\mathrm{AlCl}_{3}$
(c) $\mathrm{NH}_{4}^{+}$
5. Define the Ostwald's dilution law.
6. $\mathrm{SO}_{3}{ }^{2-}$ is Bronsted base or acid and why ?
7. Why pH of our blood remains almost constant at 7.4 though we quite often eat spicy food?
8. pH of black coffee is 5.0 at $25^{\circ} \mathrm{C}$. Is black coffee acidic or basic?
9. What will be the value of $(\mathrm{pKa}+\mathrm{pKb})$ at $25^{\circ} \mathrm{C}$.
10. What will be the pH of $1 \mathrm{M} \mathrm{KNO}_{3}$ solutions at $25^{\circ} \mathrm{C}$.
11. $\mathrm{CaCl}_{2}(\mathrm{~s})+\mathrm{sq} \rightleftharpoons \mathrm{CaCl}_{2}(\mathrm{aq})+$ Heat

Discuss the solubility of $\mathrm{CaCl}_{2}$ if temperature is increased.
12. Why does the solubility of $\mathrm{CO}_{2}$ decrease with rise in temperature?
13. The solubility of $A_{2} X_{3}$ is $y \mathrm{~mol} \mathrm{dm}-3$. Calculate its solubility product.
14. Write the Ksp expression for $\mathrm{Al}(\mathrm{OH})_{3}$
15. What is the condition for precipitation of a salt?
16. Pridict the nature of solution when $\mathrm{NH}_{4} \mathrm{NO}_{3}$ undergo hydrolysis.
17. Explain why pure NaCl precipitates out when HCl gas is passed through the solution of NaCl ?
18. Give the Henderson's -Hasselbalch equation for an acidic buffer solution.
19. On which of the factors the equilibrium depend :

Temperature, nature of reactant and product, initial concentration and pressure of the reactants.
20. What are amphoteric substances? Give one example.
21. What could be the temperature $15^{\circ} \mathrm{C}$ or $100^{\circ} \mathrm{C}$ for $\mathrm{Kw}=7.5 \times 10^{-14}$.
22. What happens to ionic product of water if some acid is added to it?
23. What is the conjugate base of $\left[\mathrm{Fe}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{3+}$

## 2-Mark Questions

1. Explain ionic product of water. What is the effect of temperature on ionic product of water?
2. What is pOH ? What is its value for neutral water at $25^{\circ} \mathrm{C}$
3. (a) Define buffer solution
(b) Give one example each of acidic and basic buffer
4. The solubility of $\mathrm{Ca}_{3}\left(\mathrm{PO}_{4}\right)_{2}$ in water is x moles / litre. Calculate its solubility product.
5. Calculate the pH of a 0.01 M solution of acetic acid. Ka for CH 3 COOH is $1.8 \times 10^{-5}$ at $25^{\circ} \mathrm{C}$.
6. Calculate pH when $9.8 \mathrm{~g} \mathrm{H}_{2} \mathrm{SO}_{4}$ is dissolved in 2 litre of solution [1]
7. Calculate the pH of $10^{-9} \mathrm{M} \mathrm{HCl}$.

$$
[\mathrm{pH}=6.9957]
$$

8. An acid having $\mathrm{pH}=6$ is diluted 100 times. What will be the pH of the final solution? $\quad[\mathrm{pH}=6.98]$
9. Calculate the pH of $10^{-10} \mathrm{M} \mathrm{NaOH}$ solution. $[\mathrm{pH}=7.0004]$
10. Solid $\mathrm{Ba}\left(\mathrm{NO}_{3}\right)_{2}$ is gradually dissolved in a $1.0 \times 10^{-4} \mathrm{M} \mathrm{Na}_{2} \mathrm{CO}_{3}$ solution. At what concentration of $\mathrm{Ba}^{2+}$ will a precipitate begin to fotm? (Ksp for $\left.\mathrm{BaCO}_{3}=5.1 \times 10^{-9}\right)$
$\left[5.1 \times 10^{-5} \mathrm{M}\right]$
11. The pKa of acetic acid and pKb of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution.
[7.005]

## 3-Mark Questions

1. What is meant by the conjugate acid-base pair ? Find the conjugate acid/ base for the following species :
$\mathrm{HNO}_{2}, \mathrm{CN}^{-}, \mathrm{HClO}_{4}, \mathrm{~F}^{-}, \mathrm{OH}^{-}, \mathrm{OH}_{3}^{-}$, and $\mathrm{S}^{2-}$
2. Define solubility product. Calculate the solubility product of $\mathrm{Ca}(\mathrm{OH})_{2}$ if its solubility is 3 .
[ $\mathrm{Ksp}=108$ ]
3. Calculate the pH of the following mixture.

200 ml of $\mathrm{M} / 10 \mathrm{H}_{2} \mathrm{SO}_{4}+400 \mathrm{ml}$ of $\mathrm{M} / 10 \mathrm{H}_{3} \mathrm{PO}_{4}+400 \mathrm{ml}$ of M/10 HCl
4. The solubility product of AgCl in water is $1.5 \times 10-10$. Calculate its solubility in 0.01 M NaCl aqueous solution.
$[1.5 \times 10-8 \mathrm{M}]$
5. Predict whether a precipitate will be formed or not on mixing 20 ml of 0.001 M NaCl solution with 80 ml of $0.01 \mathrm{M} \mathrm{AgNO}_{3}$ solution, Ksp for AgCl is $1.5 \times 10^{-10}$.
[Yes, ppt. will be formed]
6. Equal volumes of three acids solution with $\mathrm{pH} 3,4$ and 5 are mixed in a vessel. What will be the $\mathrm{H}+$ ion concentration in the mixture?
7. Calculate the pH of a solution obtained by mixing 50 ml of 0.2 M HCl and 50 ml of 0.1 M NaOH .
8. The pH of 0.1 M hydrocyanic acid solution is 5.2 . What is the value of Ka for hydrocyanic acid? $\left[\mathrm{Ka}=3.69 \times 10^{-10}\right.$ ]
9. A buffer solution is prepared by mixing equal concentration of weak base and its salt with strong acid. For the base Kb is given as $10^{-9}$. Calculagte the pH of the buffer solution.
10. Calculate the pH of the resultant mixtures :
(a) 10 mL of $0.2 \mathrm{M} \mathrm{Ca}(\mathrm{OH})_{2}+25 \mathrm{~mL}$ of 0.1 M HCl
(b) 10 mL of $0.01 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}+10 \mathrm{~mL}$ of $0.01 \mathrm{M} \mathrm{Ca}(\mathrm{OH})_{2}$
(c) 10 mL of $0.1 \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}+10 \mathrm{~mL}$ of 0.1 M KOH
[NCERT]

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\text { [(a) } 12.632 \text { (b) } 7 \text { (c) } 1.3]
$$

11. Equal volumes of 0.002 M solutions of sodium iodate and cupric chlorate are mixed together. Will it lead to precipitation of copper iodate? (For cupric iodate $\mathrm{Ksp}=7.4 \times 10^{-8}$ ). [NCERT] [NO ppt. will ocurr]
12. What is the maximum concentration of equimolar solutions of ferrous sulphate and sodium sulphide so that when mixed in equal volumes, there is no precipitation of iron sulphide ? (For iron sulphide, $\mathrm{Ksp}=6.3$ $\times 10^{-18}$ )
[NCERT] $\left[5.02 \times 10^{-9} \mathrm{~mol} \mathrm{~L}^{-1}\right]$
13. The ionization constant of aniline is $3.69 \times 10-10$ :
(i) Calculate pH of 0.01 M solution of aniline.
(ii) Calculate the degree of dissociation of aniline in the solution.
(iii) Calculate the ionization constant of conjugate acid of the aniline.
14. The Ksp for $\mathrm{Al}(\mathrm{OH})_{3}$ is $2.7 \times 10^{-11}$. Calculate its solubility in $\mathrm{g} / \mathrm{L}$ and also pH of this solution.
15. Calculate the volume of water required to dissolve 0.3 gm of $\mathrm{Zn}(\mathrm{OH}) 2$ to get a saturated solution. $\mathrm{Ksp}\left[\mathrm{Zn}(\mathrm{OH})_{2}\right]=1 \times 10^{-15}$
[Atomic mass of $\mathrm{Zn}=65.3, \mathrm{O}=16, \mathrm{H}=1$ ]
16. The pH of an aqueous solution of ammonia is 11.5 . Find the molarity of the solution.
$\mathrm{Kb}\left(\mathrm{NH}_{4} \mathrm{OH}\right)=1.8 \times 10^{-5}$
17. What is the pH of the solution when 0.2 mole of HCl is added to 1 L of the solution containing 0.1 M each of $\mathrm{CH}_{3} \mathrm{COOH} \&$ acetate ion. Assume that volume is 1 L .
$\mathrm{Ka}\left(\mathrm{CH}_{3} \mathrm{COOH}\right)=1.8 \times 10^{-5}$

## 5-Mark Questions

1. Calculate the pH value of the following solutions.
(a) $10^{-2} \mathrm{M} \mathrm{HCl}$.
(b) $10^{-3} \mathrm{M} \mathrm{H}_{2} \mathrm{SO}_{4}$.
(c) $10^{-4} \mathrm{M} \mathrm{NaOH}$
(d) 0.04 M NaOH .
(e) 0.03 M HCl .
[(a) 2 (b) 2.6990 (c) 10 (d) 12.60 (e) 1.5229]
2. (i) Calculate the pH of a buffer solution containing $2.0 \mathrm{~mol} / \mathrm{LCH}_{3} \mathrm{COOH}$ in $1.0 \mathrm{~mol} / \mathrm{L}$ of $\mathrm{CH}_{3} \mathrm{COONa}$. [ Ka for $\mathrm{CH}_{3} \mathrm{COOH}$ is $1.8 \times 10^{-5}$ at $25^{\circ} \mathrm{C}$.]
(ii) Calculate the change in pH of the buffer after the addition of 0.01 mol NaOH .
(iii) Calculate the pH of the buffer after the addition of 0.01 M HCl ?
[H. O. T.S]
[(i) 4.4337, (ii) 0.0065 , (iii) 4,4372]
3. (a) What is solubility product? How is it different from ionic product?
(b) Calculate the solubility of $\mathrm{PbCl}_{2}$ if its solubility product is $1.0 \times 10^{-6}$ at 298 K .
$\left[6.3 \times 10^{-3} \mathrm{M}\right]$
4. (a) Write short notes on :
(i) Common ion effect
(ii) Buffer capacity
(b) Calculate the pH of a buffer solution containing 0.2 mole of NH 4 Cl and 0.1 mole of $\mathrm{NH}_{4} \mathrm{OH}$ per litre. Kb for $\mathrm{NH}_{4} \mathrm{OH}=1.8 \times 10^{-5}$
[8.966]
5. 500 ml saturated solution of $\mathrm{Ca}(\mathrm{OH})_{2}$ is mixed with equal volume of 0.4 M NaOH . How muchCa $(\mathrm{OH})_{2}$ in mg is precipitated?
$\left[\mathrm{Ka}\left(\mathrm{Ca}(\mathrm{OH})_{2}\right)=4.42 \times 10^{-5}\right.$ at $\left.25^{\circ} \mathrm{C}\right]$
[H.O.T.S]
6. Calculate the pH of 0.1 M ammonia solution. Calculate the pH after 50 ml of this solution is treated with 25 ml of 0.1 M HCl .
$\mathrm{Kb}\left(\mathrm{NH}_{3}\right)=1.77 \times 10^{-5}$ [11.12, 9.24]
