## Unit 7 (EQUILIBRIUM)

## Multiple Choice Questions

Single Correct Answer Type

Q1. We know that the relationship between $K_{c}$ and $K_{p}$ is $K_{p}=K_{c}(R T)^{\Delta n}$ What would be the value of An for the reaction $\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{s}) \leftrightarrows \mathrm{NH}_{3}(\mathrm{~g})+\mathrm{HCl}(\mathrm{g})$ ?
(a) 1
(b) 0.5
(c) 1.5
(d) 2

Sol: (d) The relationship between $K_{p}$ and $K_{c}$ is
$K_{p}=K_{c}(R T)^{\Delta n}$
Where $\Delta \mathrm{n}=$ (number of moles of gaseous products) - (number of moles of gaseous
reactants)
For the reaction,
$\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{s}) \leftrightarrows \mathrm{NH}_{3}(\mathrm{~g})+\mathrm{HCl}(\mathrm{g})$
$\Delta n=2-0=2$

Q2. For the reaction $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{g})$, the standard free energy is $\Delta \mathrm{G}^{\circ}>0$ The equilibrium constant $(\mathrm{K})$ would be
(a) $\mathrm{K}=0$
(b) $>1$
(c) $K=1$
(d)A:<1

Sol: (d) $\Delta G^{\circ}=-R T \ln K . \Delta G^{\circ}>0$ means $\Delta G^{\circ}$ is + ve. This can be so only if $\ln K$ is -ve, i.e., $K<1$.

Q3. Which of the following is not a general characteristic of equilibria involving physical processes?
(a) Equilibrium is possible only in a closed system at a given temperature.
(b) All measurable properties of the system remain constant.
(c) All the physical processes stop at equilibrium.
(d) The opposing processes occur at the same rate and there is dynamic but stable condition.
Sol: (c) All the physical processes like melting of ice and freezing of water, etc., do not stop at equilibrium.

Q4. $\mathrm{PC1}_{5}, \mathrm{PC1}_{3}$ and $\mathrm{Cl}_{2}$ are at equilibrium at 500 K in a closed container and their concentrations are $0.8 \times 10^{\times 3} \mathrm{molL}^{-1}, 1.2 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{1}$ and $1.2 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}$ The value of $\mathrm{K}_{\mathrm{c}}$ for the reaction $\mathrm{PCl}_{5}(\mathrm{~g}) \rightleftharpoons \mathrm{PCl}_{3}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})$ will be
(a) $8 \times 10^{3} \mathrm{molL}^{-1}$
(b) $1.8 \times 10^{-3} \mathrm{molL}^{-1}$
(c) $1.8 \times 10^{43} \mathrm{molL}^{-1}$
(d) $0.55 \times 10^{4} \mathrm{molL}^{-1}$

Sol: $(\mathrm{b}) \mathrm{PCl}_{5}(\mathrm{~g}) \rightleftharpoons \mathrm{PCl}_{3}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})$

$$
\begin{aligned}
K_{\mathrm{C}} & =\frac{\left[\mathrm{PCl}_{3}\right]\left[\mathrm{Cl}_{2}\right]}{\left[\mathrm{PCl}_{5}\right]}=\frac{1.2 \times 10^{-3} \times 1.2 \times 10^{-3}}{0.8 \times 10^{-3}} \\
& =1.8 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}
\end{aligned}
$$

Q5. Which of the following statements is incorrect?
(a) In equilibrium mixture of ice and water kept in perfectly insulated flask, mass of ice and water does not change with time.
(b) The intensity of red colour increases when oxalic acid is added to a solution containing iron (III) nitrate and potassium thiocyanate.
(c) On addition of catalyst the equilibrium constant value is not affected.
(d) Equilibrium constant for a reaction with negative AH value decreases as the temperature increases.

Sol: (b) $\mathrm{Fe}^{3+}+\mathrm{SCN}^{-} \rightleftharpoons \mathrm{FeSCN}^{2+}$ (Red)
When oxalic acid is added to a solution containing iron nitrate and potassium thiocyanate, oxalic acid reacts with $\mathrm{Fe}^{3+}$ ions to form a stable complex ion $\left[\mathrm{Fe}\left(\mathrm{C}_{2} \mathrm{O}_{4}\right)_{3}\right]^{3-}$, thus, decreasing the concentration of free $\mathrm{Fe}^{3+}$ ions which in mm decreases the intensity of red colour.
$\mathrm{Fe}^{3+}+\mathrm{SCN}^{-} \rightleftharpoons[\mathrm{Fe}(\mathrm{SCN})]^{2+}$ (Red)

Q6. When hydrochloric acid is added to cobalt nitrate solution at room temperature, the following reaction takes place and the reaction mixture becomes blue. On cooling the mixture, it becomes pink. On the basis of this information mark the correct answer.
$\left[\mathrm{Co}\left(\mathrm{H}_{2} \mathrm{O}\right)_{6}\right]^{2+}(\mathrm{aq})+4 \mathrm{Cl}^{-}(\mathrm{aq})\left[\mathrm{CoCl}_{4}\right]^{2}-(\mathrm{aq})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$
(Pink) (Blue)
(a) $\Delta \mathrm{H}>0$ for the reaction
(b) $\Delta \mathrm{H}<0$ for the reaction
(c) $\Delta \mathrm{H}=0$ for the reaction
(d) The sign of $\Delta \mathrm{H}$ cannot be predicted on the basis of this information.

Sol:(a) Since the reaction shifts to backward direction on cooling, this means that the backward reaction is exothermic reaction. Therefore, the forward reaction is endothermic reaction and $\Delta H>0$.

Q7. The pH of neutral water at $25^{\circ} \mathrm{C}$ is 7.0 . As the temperature increases, ionization of water increases, however, the concentration of $\mathrm{H}^{+}$ions and $\mathrm{OH}^{-}$ions are equal. What will be the pH of pure water at $60^{\circ} \mathrm{C}$ ?
(a) Equal to 7.0
(b) Greater than 7.0
(c) Less than 7.0
(d) Equal to zero

Sol:(c) At $25^{\circ} \mathrm{C},\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right]=10^{7}$ and $\mathrm{K}_{\mathrm{w}}=\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]=10^{-14}$. On heating, $\mathrm{K}_{\mathrm{w}}$ increases, i.e.,
$\left[\mathrm{H}^{+}\right]\left[\mathrm{OH}^{-}\right]>10^{-14} \mathrm{As}\left[\mathrm{H}^{+}\right]=\left[\mathrm{OH}^{-}\right],\left[\mathrm{H}^{+}\right]^{2}>10^{-14}$ or $\left[\mathrm{H}^{+}\right]>10^{-7} \mathrm{M}$ or $\mathrm{pH}<7$.

Q8. The ionization constant of an acid, $K_{a}$ is the measure of strength of an acid. The $K_{a}$ values of acetic acid, hypochlorous acid and formic acid are $1.74 \times 10^{-5}, 3.0 \times 10^{-8}$ and 1.8 x $10^{-4}$ Which of the following orders of pH of $0.1 \mathrm{~mol} \mathrm{dm}^{-3}$ solutions of these acids is correct?
(a) acetic acid $>$ hypochlorous acid $>$ formic acid
(b) hypochlorous acid $>$ acetic acid $>$ formic acid
(c) formic acid $>$ hypochlorous acid $>$ acetic acid
(d) formic acid $>$ acetic acid $>$ hypochlorous acid

Sol. (d) $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\sqrt{K_{\mathrm{a}} \cdot C}$ for the same concentration, $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right] \propto \sqrt{K_{\mathrm{a}}}$. But $\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$
Larger the value of $K_{\mathrm{a}}$, larger will be $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]$and lower will be pH .
9. $K_{\mathrm{a}_{1}}, K_{\mathrm{a}_{2}}$ and $K_{\mathrm{a}_{3}}$ are the respective ionization constants for the following reactions.

$$
\begin{aligned}
& \mathrm{H}_{2} \mathrm{~S} \rightleftharpoons \mathrm{H}^{+}+\mathrm{HS}^{-} \\
& \mathrm{HS}^{-} \rightleftharpoons \mathrm{H}^{+}+\mathrm{S}^{2-} \\
& \mathrm{H}_{2} \mathrm{~S} \rightleftharpoons 2 \mathrm{H}^{+}+\mathrm{S}^{2-}
\end{aligned}
$$

The correct relationship between $K_{\mathrm{a}_{1}}, K_{\mathrm{a}_{2}}$ and $K_{\mathrm{a}_{3}}$ is
(a) $K_{\mathrm{a}_{3}}=K_{\mathrm{a}_{1}} \times K_{\mathrm{a}_{2}}$
(b) $K_{\mathrm{a}_{3}}=K_{\mathrm{a}_{1}}+K_{\mathrm{a}_{2}}$
(c) $K_{\mathrm{a}_{3}}=K_{\mathrm{a}_{1}}-K_{\mathrm{a}_{2}}$
(d) $K_{\mathrm{a}_{3}}=K_{\mathrm{a}_{1}} / K_{\mathrm{a}_{2}}$

Sol. (a) For the reaction, $\mathrm{H}_{2} \mathrm{~S} \rightleftharpoons \mathrm{H}^{+}+\mathrm{HS}^{-}$

$$
K_{\mathrm{a}_{1}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{HS}^{-}\right]}{\left[\mathrm{H}_{2} \mathrm{~S}\right]}
$$

For the reaction, $\mathrm{HS}^{-} \rightleftharpoons \mathrm{H}^{+}+\mathrm{S}^{2-}$

$$
K_{\mathrm{a}_{2}}=\frac{\left[\mathrm{H}^{+}\right]\left[\mathrm{S}^{2-}\right]}{\left[\mathrm{HS}^{-}\right]}
$$

When the above two reactions are added, their equilibrium constants are multiplied. Thus

$$
K_{\mathrm{a}_{3}}=\frac{\left[\mathrm{H}^{+}\right]^{2}\left[\mathrm{~S}^{2-}\right]}{\left[\mathrm{H}_{2} \mathrm{~S}\right]}=K_{\mathrm{a}_{1}} \times K_{\mathrm{a}_{2}}
$$

Hence, $K_{\mathrm{a}_{3}}=K_{\mathrm{a}_{1}} \times K_{\mathrm{a}_{2}}$
Q10. Acidity of BF3 can be explained on the basis of which of the following concepts?
(a) Arrhenius concept
(b) Bronsted Lowry concept
(c) Lewis concept
(d) Bronsted Lowry as well as Lewis concept

Sol: (c) According to Lewis concept, a positively charged or an electron deficient species acts as Lewis acid. $\mathrm{BF}_{3}$ is an electron deficient compound with B having 6 electrons only.

Q11. Which of the following will produce a buffer solution when mixed in equal volumes?
(a) $1 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NH}_{4} \mathrm{OH}$ and $0.1 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HC} 1$
(b) $0.05 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NH}_{4} \mathrm{OH}$ and $0.1 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HC1}$
(c) $1 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NH}_{4} \mathrm{OH}$ and $0.05 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HC} 1$
(d) $1 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{CH}_{3} \mathrm{COONa}$ and $0.1 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{NaOH}$

Sol: (c) In (c), all HC 1 will be neutralized and $\mathrm{NH}_{4} \mathrm{C} 1$ will be formed. Also some $\mathrm{NH}_{4} \mathrm{OH}$ will be left unneutralized. Thus, the final solution will contain $\mathrm{NH}_{4} \mathrm{OH}$ and $\mathrm{NH}_{4} \mathrm{C} 1$ and hence will form a buffer.
Q12. In which of the following solvents is silver chloride most soluble?
(a) $0.1 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{AgNO}_{3}$ solution
(b) $0.1 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HC} 1$ solution
(c) $\mathrm{H}_{2} \mathrm{O}$
(d) Aqueous ammonia

Sol: (d) Silver chloride forms a soluble complex with aqueous ammonia.
$\mathrm{AgCl}+2 \mathrm{NH}_{3} \rightarrow\left[\mathrm{Ag}\left(\mathrm{NH}_{3}\right)_{2}\right] \mathrm{Cl}$

Q13. What will be the value of pH of $0.01 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{CH}_{3} \mathrm{COOH}\left(\mathrm{K}_{\cdot \mathrm{A}}-74 \times 10^{-5}\right)$ ?
(a) 3.4
(b) 3.6
(c) 3.9
(d) 3.0

Sol. (a)


$$
K_{\mathrm{a}}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]\left[\mathrm{CH}_{3} \mathrm{COO}^{-}\right]}{\left[\mathrm{CH}_{3} \mathrm{COOH}\right]}=\frac{x^{2}}{0.01-x}
$$

Since $x \ll 0.01$, therefore, $0.01-x \approx 0.01$

$$
\begin{aligned}
& \frac{x^{2}}{0.01}=1.74 \times 10^{-5} \\
& x^{2}=1.74 \times 10^{-7} \text { or } x=4.2 \times 10^{-4} \\
& \mathrm{pH}=-\log \left(4.2 \times 10^{-4}\right)=3.4
\end{aligned}
$$

Q14. $\mathrm{K}_{\mathrm{a}}$ for $\mathrm{CH}_{3} \mathrm{COOH}$ is $1.8 \times 10^{-5}$ and $\mathrm{K}_{\mathrm{b}}$ for $\mathrm{NH}_{4} \mathrm{OH}$ is $1.8 \times 10^{-5}$. The pH of ammonium acetate will be
(a) 7.005
(b) 4.75
(c) 7.0
(d) Between 6 and 7

Sol: (c) Ammonium acetate is a salt of weak acid and weak base.

$$
\begin{aligned}
\mathrm{pH} & =\frac{1}{2}\left[\mathrm{p} K_{\mathrm{w}}+\mathrm{p} K_{\mathrm{a}}-\mathrm{p} K_{\mathrm{b}}\right] \\
& =\frac{1}{2}\left[14-\log \left(1.8 \times 10^{-5}\right)+\log \left(1.8 \times 10^{-5}\right)\right]=7.0
\end{aligned}
$$

Q15. Which of the following options will be correct for the stage of half completion of the reaction $A \rightleftharpoons B$.
(a) $\Delta G^{\circ}=0$
(b) $\Delta G^{\circ}>0$
(c) $\Delta G^{\circ}<0$
(d) $\Delta \mathrm{G}^{\circ}=-\mathrm{RT} \ln 2$

Sol: (a) $A \rightleftharpoons B$
$\Delta G^{\circ}=-R T \ln K$

Q16. On increasing the pressure, in which direction will the gas phase reaction proceed to reestablish equilibrium, is predicted by applying the Le Chatelier's principle. Consider the reaction,
$\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})$
Which of the following is correct, if the total pressure at which the equilibrium is established, is increased without changing the temperature?
(a) K will remain same
(b) K will decrease
(c) K will increase
(d) K will increase initially and decrease when pressure is very high

Sol:(a) $\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})$
According to Le Chatelier's principle, at constant temperature, the equilibrium composition
will change but K will remain same.

Q17. What will be the correct order of vapour pressure of water, acetone and ether at $30^{\circ} \mathrm{C}$ ? Given that among these compounds, water has maximum boiling point and ether has minimum boiling point.
(a) Water < Ether < Acetone
(b) Water < Acetone < Ether
(c) Ether < Acetone < Water
(d) Acetone < Ether < Water

Sol: (b) Greater the boiling point, less is the vapour pressure. Hence, the correct order of vapour pressures will be:
water < acetone < ether.
18. At 500 K , equilibrium constant, $K_{\mathrm{C}}$, for the following reaction is 5 .

$$
\frac{1}{2} \mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{HI}(\mathrm{~g})
$$

What would be the equilibrium constant $K_{\mathrm{C}}$ for the reaction

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

(a) 0.04
(b) 0.4
(c) 25
(d) 2.5

Sol. (a) For the reaction,

$$
\frac{1}{2} \mathrm{H}_{2}(\mathrm{~g})+\frac{1}{2} \mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{HI}(\mathrm{~g}) ; K_{\mathrm{C}}=5
$$

For $\quad \mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{g}) ; K_{\mathrm{C}}=(5)^{2}=25$
For $\quad 2 \mathrm{HI}(\mathrm{g}) \rightleftharpoons \mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) ; K_{\mathrm{C}}=\frac{1}{25}=0.04$

Q19. In which of the following reactions, the equilibrium remains unaffected on addition of small amount of argon at constant volume?
(a) $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{HI}(\mathrm{g}) \cdot$
(b) $\mathrm{PCl}_{5}(\mathrm{~g}) \rightleftharpoons \mathrm{PCl}_{3}(\mathrm{~g})+\mathrm{Cl}_{2}(\mathrm{~g})$
(c) $\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})$
(d) The equilibrium will remain unaffected in all the three cases.

Sol: (d) The equilibrium will remain unaffected in all three cases on addition of small amount of inert gas at constant volume.

Q20. For the reaction $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NO}_{2}(\mathrm{~g})$, the value of K is 50 at 400 K and 1700 at 500 K .
Which of the following options is correct?
(a) The reaction is endothermic.
(b) The reaction is exothermic.
(c) If $\mathrm{NO}_{2}(\mathrm{~g})$ and $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})$ are mixed 400 K at partial pressures 20 bar and 2 bar respectively, more $\mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g})$ will be formed.
(d) The entropy of the system increases.

Sol: (a, c, d)
(a) As the value of $K$ increases with increase of temperature and $K=K_{f} / K_{b}$, this means that $k_{f}$ increases, i.e., forward reaction is favoured.
Hence, reaction is endothermic.
(c) At $400 \mathrm{~K}, Q=\frac{p_{\mathrm{NO}_{2}}^{2}}{P_{\mathrm{N}_{2} \mathrm{O}_{4}}}=\frac{(20)^{2}}{2}=200$. Thus, $Q>K$. Equilibrium will shift backward to form more $\mathrm{N}_{2} \mathrm{O}_{4}$.
(d) As reaction is accompanied by increase in the number of moles, entropy increases.

Q21. At a particular temperature and atmospheric pressure, the solid and liquid phases of a pure substance can exist in equilibrium. Which of the following term defines this temperature? .
(a) Normal melting point
(b) Equilibrium temperature
(c) Boiling point
(d) Freezing point

Sol: ( $a, d$ ) These are normal melting point and freezing point since they are measured at atmospheric pressure.

Q22. The ionization of hydrochloric acid in water is given below:
$\mathrm{HCl}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l}) \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})$
Label two conjugate acid-base pairs in this ionization.
$\begin{array}{lc}\text { Sol: } \mathrm{HCl} \text { (Acid) } & \mathrm{Cl}^{-} \text {(Conjugate base) } \\ \mathrm{H}_{2} \mathrm{O} \text { (Base) } & \mathrm{H}_{3} \mathrm{O}^{+} \text {(Conjugate acid }\end{array}$

Q23. The aqueous solution of sugar does not conduct electricity. However, when sodium chloride is added to water, it conducts electricity. How will you explain this statement on the basis of ionization and how is it affected by concentration of sodium chloride?
Sol: (i) Sugar being a non-electrolyte does not ionize in water, whereas NaCl ionizes completely in water and produces $\mathrm{Na}^{+}$and $\mathrm{Cl}^{-}$ions which help in the conduction of electricity.
(ii) When concentration of NaCl is increased, more $\mathrm{Na}^{+}$and Cl ions will be produced. Hence, conductance increases.

Q24. $\mathrm{BF}_{3}$ does not have proton but still acts as an acid and reacts with $\mathrm{NH}_{3}$. Why is it so? What type of bond is formed between the two?
Sol: $\mathrm{BF}_{3}$ is an electron deficient compound. Hence, it acts as Lewis acid. $\mathrm{NH}_{3}$ has a lone pair of electrons. Hence, acts as Lewis base. A coordinate bond is formed between the two.
$\mathrm{H}_{3} \mathrm{~N}: \rightarrow \mathrm{BF}_{3}$

Q25. Ionization constant of a weak base MOH, is given by the expression

$$
K_{\mathrm{b}}=\frac{\left[\mathrm{M}^{+}\right]\left[\mathrm{OH}^{-}\right]}{[\mathrm{MOH}]}
$$

Values of ionization constant of some weak bases at a particular temperature are given below:

| Base | Dimethylamine | Urea | Pyridine | Ammonia |
| :--- | :--- | :--- | :--- | :--- |
|  | $5.4 \times 10^{-4}$ | $1.3 \times 10^{-14}$ | $1.77 \times 10^{-9}$ | $1.77 \times 10^{-5}$ |

Arrange the bases in decreasing order of the extent of their ionization at equilibrium. Which of the above base is the strongest?
Sol: Greater is the ionization constant $\left(K_{b}\right)$ of a base, greater is the ionization of the base.
Order of extent of ionization at equilibrium is dimethylamine > ammonia > pyridine > urea.
Dimethylamine is the strongest base due to maximum value of $K_{b}$.

Q26. Conjugate acid of a weak base is always stronger. What will be the decreasing order of basic strength of the following conjugate bases?
$\mathrm{OH}^{-}, \mathrm{RO}^{-}, \mathrm{ch}_{3} \mathrm{COO}^{-}, \mathrm{cl}^{-}$
Sol: Conjugate acids of given bases are $\mathrm{H}_{2} \mathrm{O}, \mathrm{ROH}, \mathrm{CH}_{3} \mathrm{COOH}, \mathrm{HC1}$.
Their acidic strength is in the order
$\mathrm{HCl}>\mathrm{CH}_{3} \mathrm{COOH}>\mathrm{H}_{2} \mathrm{O}>\mathrm{ROH}$ Hence, basic strength is in the order $\mathrm{RO}^{-}>\mathrm{OH}^{-}>\mathrm{CH}_{3} \mathrm{COO}^{-}>$ $\mathrm{Cl}^{-}$

Q27. Arrange the following in increasing order of pH .
$\mathrm{KNO}_{3}(\mathrm{aq}), \mathrm{CH}_{3} \mathrm{COONa}(\mathrm{aq}), \mathrm{NH}_{4} \mathrm{Cl}(\mathrm{aq}), \mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COONH}_{4}(\mathrm{aq})$
Sol: $\mathrm{KNO}_{3}$ : salt of strong acid-strong base, solution is neutral, $\mathrm{pH}=7$. CHjCOONa : salt of weak acid-strong base, solution is basic, $\mathrm{pH}>7$.
$\mathrm{NH}_{4} \mathrm{Cl}$ : salt of strong acid-weak base, solution is acidic, $\mathrm{pH}<7$.
$\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COONH}_{4}$ : both weak put $\mathrm{NH}_{4} \mathrm{OH}$ is slightly stronger than $\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COOH}$, pH close to 7 but slightly $>7$.
Hence, in order of $\mathrm{pH}, \mathrm{NH}_{4} \mathrm{C} 1<\mathrm{C}_{6} \mathrm{H}_{5} \mathrm{COONH}_{4}>\mathrm{KNO}_{3}<\mathrm{CH}_{3} \mathrm{COONa}$.

Q28. The value of $\mathrm{K}_{\mathrm{c}}$ for the reaction
$2 \mathrm{HI}(\mathrm{g}) \rightleftharpoons \mathrm{H}_{2}(\mathrm{~g})+\mathrm{I}_{2}(\mathrm{~g})$ is $1 \times 10^{-4}$. At a given time, the composition of reaction mixture is [ HI ] $=2 \times 10^{-5} \mathrm{~mol},\left[\mathrm{H}_{2}\right]=1 \times 10^{-5} \mathrm{~mol}$ and $\left[I_{2}\right]=1 \times 10^{-5} \mathrm{~mol}$. In which direction will the reaction proceed?

Sol. $Q=\frac{\left[\mathrm{H}_{2}\right]\left[\mathrm{I}_{2}\right]}{[\mathrm{HI}]^{2}}=\frac{1 \times 10^{-5} \times 1 \times 10^{-5}}{\left(2 \times 10^{-5}\right)^{2}}$.

$$
=\frac{1}{4}=0.25=2.5 \times 10^{-1}
$$

Value of $K_{\mathrm{C}}=1 \times 10^{-4}$
Since $Q>K_{\mathrm{C}}$, the reaction will proceed in backward direction.

Q29. On the basis of the equation $\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]$, the pH of $10^{-8} \mathrm{~mol} \mathrm{dm}^{-3}$ solution of HC 1 should be 8. However, it is observed to be less than 7.0. Explain the reason.
Sol: Concentration $10^{-8} \mathrm{~mol} \mathrm{dm}^{-3}$ indicates that the solution is very dilute. So, we cannot neglect the contribution of $\mathrm{H}_{3} \mathrm{O}^{+}$ions produced from $\mathrm{H}_{2} \mathrm{O}$ in the solution. Total $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=10^{-8}+$ $10^{-7} \mathrm{M}$. From this we get the value of pH close to 7 but less than 7 because the solution is acidic.
From calculation, it is found that pH of $10^{-8} \mathrm{~mol} \mathrm{dm}^{-3}$ solution of HC 1 is equal to 6.96 .

Q30. pH of a solution of a strong acid is 5.0 . What will be the pH of the solution obtained after diluting the given solution a 100 times?
Sol: $\mathrm{pH}=5$ i.e., $\left[\mathrm{H}^{+}\right]=10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}$
On dilution by 100 times $\left[\mathrm{H}^{+}\right]=10^{-7} \mathrm{~mol} \mathrm{~L}{ }^{-1}$ For a very dilute solution,
Total $\left[\mathrm{H}^{+}\right]=\left[\mathrm{H}_{3} \mathrm{O}^{+}\right.$ions from acid $]+\left[\mathrm{H}_{2} \mathrm{O}^{+}\right.$ions from water $]$
$=10^{-7}+10^{-7}$
$\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right]=-\log \left(2 \times 10^{-7}\right)=7-\log 2$
$=7-0.3010=6.6990$

Q31. A sparingly soluble salt gets precipitated only when the product of concentration of its ions in the solution $\left(\mathrm{Q}_{\mathrm{sp}}\right)$ becomes greater than its solubility product. If the solubility of $\mathrm{BaSO}_{4}$ in water is $8 \times 10^{-4} \mathrm{~mol} \mathrm{dm}^{-3}$, calculate its solubility in $0.01 \mathrm{~mol} \mathrm{dm}^{-3}$ of $\mathrm{H}_{2} \mathrm{SO}_{4}$.

Sol. $\mathrm{BaSO}_{4} \rightleftharpoons \mathrm{Ba}^{2+}+\mathrm{SO}_{4}^{2-}$
At $t=0 \quad 1 \quad 0$
At equilibrium in water $\quad 1-S \quad S \quad S$
At equilibrium in sulphuric acid $\quad 1-S \quad S \quad(S+0.01)$
$K_{\text {sp }}$ for $\mathrm{BaSO}_{4}$ in water $=\left[\mathrm{Ba}^{2+}\right]\left[\mathrm{SO}_{4}^{2-}\right]$

$$
\begin{gather*}
=S \times S=S^{2} \\
K_{\text {sp }}=\left(8 \times 10^{-4}\right)^{2}=64 \times 10^{-8} \tag{i}
\end{gather*}
$$

In presence of $\mathrm{H}_{2} \mathrm{SO}_{4}$,

$$
K_{\mathrm{sp}}=(S)(S+0.01)
$$

$$
\begin{aligned}
& K_{\text {sp }} \text { being constant } \\
& \qquad \begin{array}{l}
S(S+0.01)=64 \times 10^{-8} \\
S^{2}+0.01 \mathrm{~S}=64 \times 10^{-8} \\
S^{2}+0.01 \mathrm{~S}-64 \times 10^{-8}=0
\end{array}
\end{aligned}
$$

$$
\begin{aligned}
\Rightarrow & =\frac{-0.01 \pm \sqrt{(0.01)^{2}+\left(4 \times 64 \times 10^{-8}\right)}}{2} \\
& =\frac{-0.01 \pm \sqrt{10^{-4}+\left(256 \times 10^{-8}\right)}}{2} \\
& =\frac{-10^{-2}+\left(1.012 \times 10^{-2}\right)}{2}=\frac{(-1+1.012) \times 10^{-2}}{2} \\
& =6 \times 10^{-5} \mathrm{~mol} \mathrm{dm}^{-3}
\end{aligned}
$$

Q32. pH of $0.08 \mathrm{~mol} \mathrm{dm}^{-3} \mathrm{HOC} 1$ solution is 2.85 . Calculate its ionization constant.
Sol: pH of HOC1 $=2.85$
$-\mathrm{pH}=\log \left[\mathrm{H}^{+}\right]$or $-2.85=\log \left[\mathrm{H}^{+}\right]$
$=>\left[H^{+}\right]=1.413 \times 10^{-3}$

Q33. Calculate the pH of a solution formed by mixing equal volumes of two solutions A and B of a strong acid having $\mathrm{pH}=6$ and $\mathrm{pH}=4$ respectively.
Sol: pH of solution $\mathrm{A}=6$
$\left[\mathrm{H}^{+}\right]=10^{-6} \mathrm{~mol} \mathrm{~L}{ }^{1}$
pH of solution $\mathrm{B}=4$
$\left[\mathrm{H}^{+}\right]=10^{-4} \mathrm{molL}^{-1}$
On mixing one litre of each solution Total volume $=1 \mathrm{~L}+1 \mathrm{~L}=2 \mathrm{~L}$
Total amount of $\mathrm{H}^{+}$in 2 L solution formed by mixing solutions A and $\mathrm{B}=10^{-6}+10^{-4} \mathrm{~mol}$

$$
\begin{aligned}
& \text { Total } \begin{aligned}
{\left[\mathrm{H}^{+}\right] } & =\frac{10^{-4}(1+0.01)}{2}=\frac{1.01 \times 10^{-4}}{2} \\
& =5
\end{aligned} \begin{aligned}
& \times 10^{-5} \mathrm{~mol} \mathrm{~L}^{-1}
\end{aligned} \\
& \begin{aligned}
\mathrm{pH}=-\log \left[\mathrm{H}^{+}\right] & =-\log \left(5 \times 10^{-5}\right) \\
& =-\log 5-(-5 \log 10)=-\log 5+5 \\
& =5-\log 5=5-0.6990=4.3010=4.3
\end{aligned}
\end{aligned}
$$

Thus, the pH of resulting solution is 4.3.

Q34. The solubility product of $\mathrm{Al}(\mathrm{OH})_{3}$ is $2.7 \times 10^{-11}$. Calculate its solubility in $\mathrm{g}^{-} \mathrm{L}$ and also find out pH of this solution. (Atomic mass of A1 = 27 u ).

Sol.
Conc. at $\mathrm{t}=0$
Conc. at equilibrium $1-S \quad S \quad 3 S$

$$
\begin{aligned}
& K_{\text {sp }}=\left[\mathrm{Al}^{3+}\right]\left[\mathrm{OH}^{-}\right]^{3}=(S)(3 S)^{3}=27 S^{4} \\
& S^{4}=\frac{K_{\text {sp }}}{27}=\frac{2.7 \times 10^{-11}}{27}=1 \times 10^{-12} \\
& S=1 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}
\end{aligned}
$$

(i) Solubility of $\mathrm{Al}(\mathrm{OH})_{3}$

Molar mass of $\mathrm{Al}(\mathrm{OH})_{3}=78 \mathrm{~g}$

$$
\begin{aligned}
\therefore \quad \text { Solubility of } \mathrm{Al}(\mathrm{OH})_{3} \text { in } \mathrm{g}^{-1} & =1 \times 10^{-3} \times 78 \\
& =78 \times 10^{-3}=7.8 \times 10^{-2} \mathrm{~g} \mathrm{~L}^{-1}
\end{aligned}
$$

(ii) pH of the solution

$$
\begin{aligned}
& S=1 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1} \\
& {\left[\mathrm{OH}^{-}\right]=3 S=3 \times 1 \times 10^{-3}=3 \times 10^{-3}} \\
& \mathrm{pOH}=-\log \left[\mathrm{OH}^{-}\right]=-\log \left(3 \times 10^{-3}\right) \\
& \mathrm{pOH}=3-\log 3=3-0.4771=2.552 \\
& \mathrm{pH}=14-\mathrm{pOH}=14-2.522=11.4771
\end{aligned}
$$

Q35. Calculate the volume of water required to dissolve 0.1 g lead (II) chloride to get a saturated solution. ( $\mathrm{K}_{\mathrm{sp}}$ of $\mathrm{PbCl}_{2}=3.2 \times 10^{-8}$, atomic mass of $\mathrm{Pb}=207 \mathrm{u}$ ).
Sol.

$$
\mathrm{PbCl}_{2} \rightleftharpoons \mathrm{~Pb}^{2+}+2 \mathrm{Cl}^{-}
$$

$\begin{array}{lllll}\text { Conc. at } t=0 & 1 & 0 & 0\end{array}$
Conc. at equilibrium $1-S \quad S \quad 2 S$

$$
\begin{aligned}
& K_{\mathrm{sp}}=\left[\mathrm{Pb}^{2+}\right]\left[\mathrm{Cl}^{-}\right]^{2}=(S)(2 S)^{2}=4 S^{3} \\
& S^{3}=\frac{K_{\mathrm{sp}}}{4}=\frac{3.2 \times 10^{-8}}{4}=8 \times 10^{-9} \mathrm{~mol} \mathrm{~L}^{-1} \\
& S=\sqrt[3]{8 \times 10^{-9}}=2 \times 10^{-3} \mathrm{~mol} \mathrm{~L}^{-1}
\end{aligned}
$$

Solubility of $\mathrm{PbCl}_{2}=2 \times 10^{-3} \times 278\left(\right.$ molar mass of $\left.\mathrm{PbCl}_{2}\right)=556 \times 10^{-3} \mathrm{gL}^{-1}$ $=0.556 \mathrm{~g} \mathrm{~L}^{-1}$
To get saturated solution, $0.556 \mathrm{~g} \mathrm{PbCl}_{2}$ is dissolved in 1 L water.
0.1 g of $\mathrm{PbCl}_{2}$ is dissolved in $\frac{0.1}{0.556}=0.1798 \mathrm{~L}$ water

To make a saturated solution, $0.1 \mathrm{~g} \mathrm{PbCl}_{2}$ is dissolved in $0.1798 \approx 0.2 \mathrm{~L}$ water

Q36. A reaction between ammonia and boron trifluoride is given below:
$: \mathrm{NH}_{3}+\mathrm{BF}_{3} \rightarrow \mathrm{H}_{3} \mathrm{~N}: \mathrm{BF}_{3}$
Identify the acid and base in this reaction. Which theory explains it? What is the hybridization of $B$ and $N$ in the reactants?
Sol:Although $\mathrm{BF}_{3}$ does not have a proton but acts as Lewis acid as it is an electron deficient compound. It reacts with $\mathrm{NH}_{3}$ by accepting the lone pair of electrons from $\mathrm{NH}_{3}$ and completes its octet. The reaction can be represented by
$\mathrm{BF}_{3}+: \mathrm{NH}_{3} \rightarrow \mathrm{BF}_{3} \leftarrow: \mathrm{NH}_{3}$
Lewis electronic theory of acids and bases can explain it. Boron in $\mathrm{BF}_{3}$ is $\mathrm{sp}^{2}$ hybridised,
whereas N in $\mathrm{NH}_{3}$ is $\mathrm{sp}^{3}$ hybridised.
$\mathrm{CaCO}_{3}(\mathrm{~s}) \rightarrow \mathrm{CaO}(\mathrm{s})+\mathrm{CO}_{2}(\mathrm{~g})$
$\Delta_{\mathrm{f}} \mathrm{H}^{\circ}[\mathrm{CaO}(\mathrm{s})]=-635.1 \mathrm{~kJ} \mathrm{~mol}^{-1}$
$\Delta_{\mathrm{f}} \mathrm{H}^{\circ}\left[\mathrm{CO}_{\mathrm{z}}(\mathrm{g})\right]=-393.5 \mathrm{~kJ} \mathrm{~mol}^{-1}$
$\Delta_{\mathrm{f}} \mathrm{H}^{\circ}\left[\mathrm{CaCO}_{3}(\mathrm{~s})\right]=-1206.9 \mathrm{~kJ} \mathrm{~mol}^{-1}$
Predict the effect of temperature on the equilibrium constant of the above reaction.
Sol: $\Delta_{\mathrm{r}} \mathrm{H}^{\circ}=\Delta_{\mathrm{f}} \mathrm{H}^{\circ}[\mathrm{CaO}]+\Delta_{\mathrm{f}} \mathrm{H}^{\circ}\left[\mathrm{CO}_{2}\right]-\Delta_{\mathrm{f}} \mathrm{H}^{\circ}\left[\mathrm{CaCO}_{3}\right]$
$=[-635.1]+[-393.5]-[-1206.9]=178.3 \mathrm{~kJ} \mathrm{~mol}^{-1}$ Thus, the reaction is endothermic. Hence, according to Le Chatelier's principle, on increasing the temperature, the equilibrium will proceed in the forward direction.
Matching Column Type Questions
Q38. Match the following equilibria with the corresponding condition

| Column I |  | Column II |  |
| :--- | :--- | :--- | :--- |
| (i) | Liquid $\rightleftharpoons$ Vapour | (a) | Saturated solution |
| (ii) | Solid $\rightleftharpoons$ Liquid | (b) | Boiling point |
| (iii) | Solid $\rightleftharpoons$ Vapour | (c) | Sublimation point |
| (iv) | Solute(s) $\rightleftharpoons$ Solute (solution) | (d) | Melting point ' |

Sol: (i) $\rightarrow$ (b), (ii) $\rightarrow$ (d), (iii) $\rightarrow$ (c), (iv) $\rightarrow$ (a)
(i) Liquid $\rightleftharpoons$ Vapour equilibrium exists at the boiling point.
(ii) Solid $\rightleftharpoons$ Liquid equilibrium exists at the melting point.
(iii) Solid $\rightleftharpoons$ Vapour equilibrium exists at the sublimation point.
(iv) Solute(s) $\rightleftharpoons$ Solute (solution) equilibrium exists in saturated solution.

Q39. For the reaction: $\mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 2 \mathrm{NH}_{3}(\mathrm{~g})$ equilibrium constant,

$$
K_{\mathrm{C}}=\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}
$$

Some reactions are written below in Column I and their equilibrium constants in terms of $\mathrm{K}_{\mathrm{C}}$ are written in Column II. Match the following reactions with the corresponding equilibrium constant.

| Column I (Reaction) |  | Column II <br> (Equilibrium constant) |  |
| :--- | :--- | :--- | :--- |
| (i) | $2 \mathrm{~N}_{2}(\mathrm{~g})+6 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 4 \mathrm{NH}_{3}(\mathrm{~g})$ | (a) | $2 K_{\mathrm{C}}$ |
| (ii) | $2 \mathrm{NH}_{3}(\mathrm{~g}) \rightleftharpoons \mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g})$ | (b) | $K_{\mathrm{C}}^{1 / 2}$ |
| (iii) | $\frac{1}{2} \mathrm{~N}_{2}(\mathrm{~g})+\frac{3}{2} \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{NH}_{3}(\mathrm{~g})$ | (c) | $\frac{1}{K_{\mathrm{C}}}$ |
|  |  | (d) | $K_{\mathrm{C}}^{2}$ |

$$
K_{\mathrm{C}}=\frac{\left[\mathrm{NH}_{3}\right]^{2}}{\left[\mathrm{~N}_{2}\right]\left[\mathrm{H}_{2}\right]^{3}}
$$

(i) $2 \mathrm{~N}_{2}(\mathrm{~g})+6 \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons 4 \mathrm{NH}_{3}(\mathrm{~g}) ; K_{\mathrm{C}}^{\prime}=K_{\mathrm{C}}^{2}$
(ii) $2 \mathrm{NH}_{3}(\mathrm{~g}) \rightleftharpoons \mathrm{N}_{2}(\mathrm{~g})+3 \mathrm{H}_{2}(\mathrm{~g}) ; K_{\mathrm{C}}^{\prime}=\frac{1}{K_{\mathrm{C}}}$
(iii) $\frac{1}{2} \mathrm{~N}_{2}(\mathrm{~g})+\frac{3}{2} \mathrm{H}_{2}(\mathrm{~g}) \rightleftharpoons \mathrm{NH}_{3}(\mathrm{~g}) ; K_{\mathrm{C}}^{\prime}=K_{\mathrm{C}}^{1 / 2}$

Q40. Match standard free energy of the reaction (Column I) with the corresponding equilibrium constant (Column II).

| Column I |  | Column II |  |
| :---: | :--- | :---: | :--- |
| (i) | $\Delta G^{\circ}>0$ | (a) | $K>1$ |
| (ii) | $\Delta G^{\circ}<0$ | (b) | $K=1$ |
| (iii) | $\Delta G^{\circ}=0$ | (c) | $K=0$ |
|  |  | (d) | $K<1$ |

Sol. (i) $\rightarrow$ (d), (ii) $\rightarrow$ (a), (iii) $\rightarrow$ (b)
As we know that, $\Delta G^{\circ}=-\mathrm{R} T \ln K$
(i) If $\Delta G^{\circ}>0$, i.e., $\Delta G^{\circ}$ is positive, then $\ln K$ is negative i.e., $K<1$
(ii) If $\Delta G^{\circ}<0$, i.e., $\Delta G^{\circ}$ is negative then $\ln K$ is positive i.e., $K>1$.
(iii) If $\Delta G^{\circ}=0, \ln K=0$, i.e., $K=1$

