This Chapter “Concept Notes on Equilibrium for NEET” is taken from our Book:

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Product Description : NEET Chemistry 40 Days Score Amplifier 2nd Edition is developed for quick revision and practice of the complete syllabus of the NEET exams in a short span of 40 days. The book can prove to the ideal material for class 12 students as they can utilise this book to revise their preparation immediately after the board exams.

• The book follows the Syllabus and chapter plan as per the NCERT books of class 11 and 12.
• The book contains 32 chapters divided into 8 units. Each unit provides a Practice Test along with detailed solutions. At the end 2 Mock Tests based on the full syllabus are provided.
• Each chapter provides exhaustive theory explaining all fundamentals/concepts to build a strong base.
• This is followed by a set of 2 exercises for practice. The first exercise is a basic exercise whereas the second exercise is advanced.
• The solutions to the exercises have been provided immediately at the end of each chapter.
• The book covers past questions of the various entrance exams which have been incorporated in the exercises of the respective chapters.
Irreversible reactions: Such reactions which go only in the forward direction are called irreversible reactions. For example,

\[
Pb(NO_3)_2(aq) + K_2CrO_4(aq) \rightarrow PbCrO_4(s) + 2KNO_3(aq)
\]

The reaction in which the products do not react to give back the reactants are called irreversible reactions.

Reversible reaction: The reaction which can take place in both the directions under similar conditions of temperature and pressure are called reversible reaction. Such reactions are carried out in a closed vessel e.g.

(i) \[2H_2(g) + I_2(g) \rightleftharpoons 2HI(g)\]
(ii) \[N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)\]

EQUILIBRIUM:
The state at which the observable properties of system do not change with time is called state of equilibrium.

(i) Physical equilibrium: The state of equilibrium attained between two physical phases of any chemical compound is termed as physical equilibrium. e.g.

(a) Equilibrium between solid and its liquid.
   - Solid \(\rightleftharpoons\) liquid
   - For this equilibrium
   - Rate of melting = Rate of freezing.

(b) Equilibrium between liquid and its vapours.
   - Liquid \(\rightleftharpoons\) Gas
   - For this equilibrium
   - Rate of evaporation = Rate of condensation.

(c) Equilibrium between solids which sublime to vapour phase
   - \[I_2(solid) \rightleftharpoons I_2(vapour)\]
   - Rate of sublimation of solid = Rate of sublimation of vapours

Henry’s law: According to Henry’s law the mass of gas dissolved per unit mass of the solvent at a specific temperature is proportional to the pressure of the gas in equilibrium with the solution.

\[m \propto p \text{ or } m = kp\]

where \(m\) = mass of the gas dissolved in unit mass of solvent.

(ii) Chemical equilibrium: When a reversible reaction is carried out in a closed vessel a stage is reached when the speed of forward reaction equals the speed of the backward reaction and chemical equilibrium is said to be established.

General characteristic of physical and chemical equilibria:
(i) Equilibria can be attained only in a closed vessel.
(ii) An equilibrium is dynamic in nature (achieved when forward and backward both reactions takes place at equal speed).
(iii) It can be attained from either side of the reaction.
(iv) Equilibrium can be established only if none of the products is allowed to escape.
(v) The measurable properties at equilibrium are constant (concentration of reactants and products become constant).
(vi) Catalyst does not alter state of equilibrium. It changes time required to attain equilibrium.

LAW OF MASS ACTION:
The rate of a chemical reaction is proportional to the product of the active masses of the reactants, each raised to the power given by its coefficient as represented in the balanced chemical equation.

\[aA + bB \rightarrow r = K[A]^a[B]^b\]

LAW OF CHEMICAL EQUILIBRIUM
For reaction \[aA + bB \rightleftharpoons xX + yY\]

\[K = \frac{[X]^x[Y]^y}{[A]^a[B]^b}\]

where \(K\) = equilibrium constant,

\[\frac{[X]^x[Y]^y}{[A]^a[B]^b} = \text{concentration quotient (Q)}\]
EQUILIBRIUM CONSTANT

<table>
<thead>
<tr>
<th>Equilibrium constant in terms of concentration (K_c)</th>
<th>Equilibrium constant in terms of pressure (K_p)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( K_c = \frac{[X]^x[Y]^y}{[A]^a[B]^b} )</td>
<td>( K_p = \frac{[P_X]^x[P_Y]^y}{[P_A]^a[P_B]^b} )</td>
</tr>
</tbody>
</table>

Units \( K_c = (\text{mole} \cdot \text{L}^{-1})^{(a + b) - (a + b)} \)
Units of \( K_p = (\text{atm})^{(a + b) - (a + b)} \)

CHARACTERISTICS OF EQUILIBRIUM CONSTANT

(i) Its value depends on temperature. It has fixed value for given temperature.
(ii) The value of \( K \) is independent of
   (a) Catalyst
   (b) Initial concentration of reactants
   (c) Direction from which equilibrium is attained
   (d) Presence of inert material.
(iii) When reaction is reversed value of \( K \) changes to \( K' \)
   \( K' = \frac{1}{K} \)
(iv) When reaction is divided by 2
   \( K' = \sqrt{K} \)
(v) When reaction is multiplied by 2
   \( K' = (K)^2 \)
(vi) When reaction is written in two steps each having equilibrium constant as \( K_1 \) and \( K_2 \) then
   \( K = K_1 \times K_2 \)
(vii) The magnitude of equilibrium constant is helpful in predicting the relative amount of the reactants and the products of a reversible reaction.

Relation between \( K_p \) and \( K_c \)
\( K_p = K_c RT^{(\Delta n / n_{\text{gaseous}})} \)
where \( \Delta n = n_p - n_r \) gaseous
When \( \Delta n = 0 \) \( K_p = K_c \)
When \( \Delta n > 0 \) \( K_p > K_c \)
When \( \Delta n < 0 \) \( K_p < K_c \)

CONCENTRATION QUOTIENT OR REACTION QUOTIENT (Q)
\( aA + bB \rightleftharpoons xX + yY \)
\( Q = \frac{[X]^x[Y]^y}{[A]^a[B]^b} \)

(i) when \( Q = K \), the reaction is in equilibrium.
(ii) when \( Q > K \), the net reaction proceed in backward direction.
(iii) when \( Q < K \), the net reaction proceed in forward direction.

- A relationship between the equilibrium constant \( K \), reaction quotient and Gibbs energy.
  \( \Delta G = \Delta G^\circ + RT \ln Q \)
  At equilibrium \( \Delta G = 0 \) and \( Q = K \) then \( \Delta G^\circ = -RT \ln K_c \)
  \( \therefore \Delta G^\circ = -RT \ln K_p \)

LE CHATELIER’S PRINCIPLE
If a system in equilibrium is subjected to change in factors that determine the equilibrium conditions of a system, the equilibrium shifts in a direction as to nullify or undo the effect of change imposed.

FACTORS EFFECTING EQUILIBRIUM

- **Effect of change of concentration**:
  (i) Increase in concentration of any of the reactants, shifts the equilibrium in the forward direction.
  (ii) Increase in the concentration of any of the products, shifts the equilibrium in the backward direction.

- **Effect of change of temperature**:
  (i) Endothermic reactions shift the equilibrium in the forward direction with increase of temperature.
  (ii) Exothermic reactions shift the equilibrium in the forward direction with decrease of temperature.

- **Effect of change of pressure**:
  (i) Increase of pressure shifts the equilibrium in the direction where total number of moles decreases or \( n < 0 \)
  (ii) Decrease of pressure alters the equilibrium in the direction where total number of moles increases or \( n > 0 \)
  (iii) Change of pressure has no effect on equilibrium, if the number of moles of gaseous products is equal to moles of gaseous reactants i.e. \( n = 0 \)

- **Effect of addition of catalyst**:
  Addition of catalyst has no effect on equilibrium because the catalyst alters the rate of forward and backward reactions equally.

- **Effect of addition of inert gas (argon)**:
  **At constant volume**:
  No effect, what so ever is the value of \( \Delta n \)
  **At constant pressure**:
  Addition of inert gas favours forward reaction when \( \Delta n > 0 \)
  Addition of inert gas favours backward reaction when \( \Delta n < 0 \)
  Addition of inert gas has no effect when \( \Delta n = 0 \)
Effect of temperature, pressure, concentration and addition of inert gas on equilibrium:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Effect of increase in pressure</th>
<th>Effect of increase in concentration of reactant</th>
<th>Effect of increase in temperature</th>
<th>Effect of addition of inert gas</th>
</tr>
</thead>
<tbody>
<tr>
<td>2SO₂ + O₂ ⇌ 2SO₃ + x</td>
<td>Forward</td>
<td>Forward</td>
<td>Backward</td>
<td>Backward</td>
</tr>
<tr>
<td>2NH₃ ⇌ N₂ + 3H₂</td>
<td>Backward</td>
<td>Forward</td>
<td>Forward</td>
<td>Forward</td>
</tr>
<tr>
<td>N₂O₄ ⇌ 2NO₂ − 62 kJ</td>
<td>Backward</td>
<td>Forward</td>
<td>Forward</td>
<td>Forward</td>
</tr>
<tr>
<td>NO₂ + O₂ ⇌ 2NO + 180 kJ</td>
<td>No effect</td>
<td>Backward</td>
<td>Forward</td>
<td>Forward</td>
</tr>
<tr>
<td>PCl₅ ⇌ PCl₃ + Cl₂ − x kJ</td>
<td>Backward</td>
<td>Forward</td>
<td>Forward</td>
<td>Forward</td>
</tr>
<tr>
<td>H₂ + I₂ ⇌ 2HI − 12.4 kJ</td>
<td>No effect</td>
<td>Forward</td>
<td>Forward</td>
<td>Forward</td>
</tr>
<tr>
<td>ice + heat ⇌ water</td>
<td>Forward</td>
<td>Forward</td>
<td>Forward</td>
<td>Forward</td>
</tr>
<tr>
<td>water + heat ⇌ water(vapours)</td>
<td>Forward</td>
<td>Forward</td>
<td>Forward</td>
<td>Forward</td>
</tr>
</tbody>
</table>

Electrolyte

(Conducts electricity in molten and aqueous state)

Strong electrolyte dissociates completely
e.g., HCl, NaOH

Weak electrolyte dissociate to small extent
e.g., NH₄Cl, CH₃COOH

Conjugate acid-base pair:
(i) It is pair of acid and base which differ by H⁺ ion.

conjugate acid –H⁺ ⇌ conjugate base.

Base + H⁺ ⇌ Conjugate acid

(ii) Weak acid has strong conjugate base and vice-versa
• Examples of Lewis acids
  (i) Molecules in which cation has incomplete octet e.g., AlCl₃, BF₃, FeCl₃
  (ii) Cations − Na⁺, Fe³⁺, Ag⁺
  (iii) Molecules having multiple bonds between different atoms e.g., SO₂, CO₂
  (iv) Molecules having empty d-orbitals, e.g., SnCl₄

• Examples of Lewis bases
  (i) Neutral molecules having lone pair of electrons on central atom e.g., NH₃, RNH₂
  (ii) Anions − CN⁻, Cl⁻, OH⁻

IONIC PRODUCT OF WATER (Kₘₐₙ)
Product of molar concentrations of H⁺ and OH⁻.

Kₘₐₙ = [H⁺][OH⁻]

Kₘₐₙ = 10⁻¹⁴ at 25°C.

• Value of Kₘₐₙ increases with temperature (dissociation of H₂O increases with increase in temperature)

• Value of Kₘₐₙ is not effected by addition of salt or acid or base if temperature is constant.

**pH SCALE (GIVEN BY SORENSEN)**

Used to express the acidic and basic strength of a solution.

\[ \text{pH} = -\log [\text{H}^+] \]

(i) if pH = 0, then solution is acidic.

(ii) if pH < 7 for acidic solution

(iii) if pH > 7 for basic solution

(iv) if pH = 7 for neutral solution

(vi) pH of water decreases with increase in temperature because ionic product of water increases.

**ACID-BASE INDICATORS (OSTWALD THEORY)**

(i) Acid-base indicators are complex organic molecules that change colour in solution when pH changes.

(ii) They are either weak organic acids (e.g., phenolphthalein) or weak organic-bases (e.g., methyl orange)

HPh ⇌ H⁺ + Ph⁻ (Pink)

MeOH ⇌ Me⁺ + OH⁻ (red)
IONISATION OF WEAK ACIDS

$$\text{HX(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{H}_3\text{O}^+ (\text{aq}) + \text{X}^- (\text{aq})$$

Initial C 0 0
At equilibrium C – C α Cα Cα

$$K_a = \frac{C^2\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{(1-2)}$$

Degree of hydrolysis, $$h = \frac{\sqrt{K_h}}{C} = \frac{\sqrt{K_w}}{K_aC}$$

$$p\text{H} = 7 + \frac{1}{2} pK_a - \frac{1}{2} \log \text{C} or \frac{1}{2} [\log K_w + \log K_a - \log C]$$

Here $$K_h$$ is hydrolysis constant of salt $$K_w$$ and $$K_a$$ are ionisation constants of water and weak acid respectively. C is the concentration of salt in mole/litre.

Relative Strength of Acids and Bases

<table>
<thead>
<tr>
<th>Strength of acid HA₁</th>
<th>Strength of acid HA₂</th>
<th>PKₐ + PKₐ = PKₜ = 14</th>
</tr>
</thead>
<tbody>
<tr>
<td>α₁</td>
<td>α₂</td>
<td></td>
</tr>
</tbody>
</table>

- Greater the value of $$K_a$$ stronger the acid.
- For polyprotic acids $$K_{a₁} > K_{a₂} > K_{a₃}$$ ($$K_{a₁}$$, $$K_{a₂}$$ and $$K_{a₃}$$ are first, second and third dissociation constants).
- Common ion effect means that dissociation of weak electrolyte is further suppressed in presence of strong electrolyte having common ion e.g., dissociation of CH₃COOH is suppressed in presence of CH₃COONa.
- Hydrolysis constant ($$K_h$$)

$$\text{BA(aq)} + \text{H}_2\text{O(l)} \rightleftharpoons \text{HA}^- (\text{aq}) + \text{BOH}^- (\text{aq})$$

$$K_h = \frac{[\text{HA}^-][\text{BOH}^-]}{[\text{BA}]}$$

Degree of hydrolysis ($$h$$) = \frac{\text{No. of moles of salt hydrolysed}}{\text{Total no. of moles of salt taken}}

SALT HYDROLYSIS

Salt hydrolysis is defined as “ a process in which a salt reacts with water to produce either acidic or basic or neutral solution.”

(i) Salts of strong acid and strong base e.g., NaCl, KNO₃, Na₂SO₄, KClO₄, etc. Such salts on hydrolysis produce equally strong acids and bases. Thus, their solutions are almost neutral with pH = 7.

(ii) Salts of weak acid and strong base e.g., Na₂CO₃, KCN, CH₃COONa, K₂CO₃, etc. Hydrolysis of these salts produce weak acid and strong base and thus their aqueous solutions are basic (pH > 7).

$$K_b = \frac{K_w}{K_a};$$

**BUFFER SOLUTION**

The solution which resists the change in hydrogen ion concentration on the addition of small amount of acid or base.

**Types of Buffers**

<table>
<thead>
<tr>
<th>Acidic buffer</th>
<th>Basic buffer</th>
</tr>
</thead>
<tbody>
<tr>
<td>(i) weak acid + salt of weak acid with strong base e.g., CH₃COOH + CH₃COONa</td>
<td>(i) weak base + salt of weak base with strong acid e.g., NH₄OH + NH₄Cl</td>
</tr>
<tr>
<td>(ii) pH &lt; 7</td>
<td>(ii) pH &gt; 7</td>
</tr>
</tbody>
</table>

- For acidic buffers:

$$p\text{H} = pK_a + \left[\frac{\text{salt}}{\text{acid}}\right] or p\text{H} = pK_a + \log \left[\frac{\text{conjugate base}}{\text{acid}}\right]$$

- For basic buffers:

$$p\text{OH} = pK_b + \left[\frac{\text{salt}}{\text{base}}\right] or p\text{H} = pK_b + \log \left[\frac{\text{conjugate acid}}{\text{base}}\right]$$

BUFFER CAPACITY OR BUFFER INDEX

$$= \frac{\text{No. of moles of acid or base added per litre}}{\text{Change in pH}}$$

- Buffer

Blood and sea water are examples of natural buffer.
SOLUBILITY PRODUCT ($K_{sp}$)

Defined as product of molar concentration of ions of an electrolyte in a concentrated solution, when each concentration term raised to the power equal to the number of ions produced on dissociation of one molecule of electrolyte.

$$A_xB_y \rightleftharpoons xA^{+} + yB^{-}$$

$$K_{sp} = [A^{+}]^x \times [B^{-}]^y = x^x \cdot y^y S^{x+y}$$

$$S^{(x+y)} = \frac{K_{sp}}{x^x \cdot y^y}$$

$$S = \left(\frac{K_{sp}}{x^x \cdot y^y}\right)^{\frac{1}{x+y}}$$

(i) Solubility product of a substance has constant value for given temperature.

(ii) Solubility product is used in qualitative salt analysis.

(iii) Ionic product $> K_{sp}$ precipitation occurs

$K_{sp}$ > ionic product no precipitation occurs

(iv) Solubility product is used for purification of common salt: When HCl is passed in solution of impure NaCl, pure NaCl precipitates when ionic product of NaCl exceeds its solubility product.

(v) Precipitation of soap by adding NaCl is called salting out of soap.

Important Results

1. (i) For **Endothermic reaction** $K$ increases with increase in $T$.
   (ii) For **Exothermic reaction** $K$ decreases with increase in $T$.

2. (i) **Melting of any solid other than ice** is accompanied by increase in pressure causes more solidification.
   (ii) **Ice** $\rightarrow$ **Heat** $\rightarrow$ **H₂O** (liquid)

   $\therefore$ Increase in pressure or temperature results in increased melting of ice.

3. **Increase in external pressure** always increases boiling point of liquid.

4. Solubility of all gases in water is exothermic process.

5. All organic acids are weak acids except sulphonic acids.

6. **Decreasing strength of acids** is

   HClO₄ > H₂SO₄ > HI > HBr > HCl > HNO₃ > H₂O⁺ > HSO₄⁻ > H₃PO₄ > HNO₂ > CH₃COOH > H₂CO₃ > H₂S > NH₄⁺ > HCN > H₂O > NH₃.

   The strength of conjugate base is reverse of it.

7. **Expression for solubility product and ionic product** are same but solubility product is for saturated solution and ionic product is for any solution.

8. **Substance**
   (a) Gastric juice 1.0 – 3.0
   (b) Vinegar 2.4 – 3.4
   (c) Soft drinks 2.0 – 4.0
   (d) Human blood 7.36 – 7.42

9. In **qualitative salt analysis** cations are arranged in increasing order of their solubility products.

10. Greater the buffer capacity, greater will be capacity to resist change in pH.

11. Serum proteins present in blood act as buffer.

12. **Active masses of solids** are taken as unity and that of gases and liquids is equal to their molar concentrations.

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

14. $\alpha = \frac{D - d}{d} = \frac{M_e - M_o}{M_c}$

   where
   $\alpha$ = degree of dissociation
   $D$ = theoretical vapour density
   $d$ = observed density
   $M_e$ = calculated molecular weight
   $M_o$ = observed molecular weight

15. For calculating pH of very weak acidic solutions e.g. $10^{-8}$ M HCl consider H⁺ ions produced by water also because pH of HCl cannot be more than 7 (because it is an acid).

   $\therefore$ Total [H⁺] = $10^{-8} + 10^{-7} = 10^{-8}(1 + 10) = 11 \times 10^{-8}$

   $\therefore$ pH = $-\log 11 \times 10^{-8}$ = 6.958.

16. Greater the value of $K_a$ of an acid or lesser the value of $pK_a$, stronger is the acid.

17. pH relates to negative power of 10. So solution of pH = 1 has H⁺ concentration 100 times that of solution of pH = 3 (not 3 times).

18. While calculating solubility product always remember to consider common ion effect.

19. $\alpha = \sqrt{\frac{K}{C}} = \sqrt{K V}$.

20. Isoelectric point = $\frac{pK_{a1} + pK_{a2}}{2}$. 
Example 1:
6 gram hydrogen reacts with $9.023 \times 10^{-23}$ chlorine molecules to form HCl. If total pressure of the reaction is 800 mm then find the partial pressure of HCl.

**Sol.**

\[
\begin{align*}
\text{H}_2 + \text{Cl}_2 & \rightarrow 2\text{HCl} \\
\text{Initial mol} & = 3 \text{ moles} \\
9.023 \times 10^{23} & = \frac{6.023 \times 10^{23}}{0.3}
\end{align*}
\]

Moles at equilibrium = 3 - 1.5 moles = 1.5 - 1.5 moles = 3.0 moles

Total moles at equilibrium = 1.5 + 3.0 = 4.5 mole

Partial pressure of HCl = \[
\frac{3.0}{4.5} \times 800 = \frac{1600}{3} = 533 \text{ mm}
\]

Example 2:

20% part of N\(_4\)O\(_4\) is dissociated in NO\(_2\) at 1 atmospheric pressure, then find the value of $K_p$.

**Sol.**

\[
\text{N}_2\text{O}_4 \leftrightharpoons 2\text{NO}_2
\]

\[
P = 1 \text{ atm. pressure. } \alpha = 20\%
\]

\[
K_p = \frac{4x^2}{1-(0.2)^2} = \frac{0.16}{0.96} = 0.17
\]

Example 3:

0.1 mole of N\(_2\)O\(_4\) was sealed in a tube under atmospheric conditions at 25°C. Calculate the number of mole of NO\(_2\) present, if the equilibrium N\(_2\)O\(_4\) $\leftrightharpoons$ 2NO\(_2\), ($K_p = 0.14$) is reached after some time.

**Sol.**

\[
\text{NO}_2 \rightarrow \frac{1}{2} \text{N}_2\text{O}_4 + \frac{1}{2} \text{O}_2
\]

(a) 0.02 \quad (b) 2.5 \times 10^2 \quad (c) 4 \times 10^{-4} \quad (d) 50.0

Example 4:

Nicotinic acid ($K_a = 1.4 \times 10^{-5}$) has formula HNiC. Calculate its percent dissociation in a solution which contains 0.10 mole of nicotinic acid per 2.0 litre of solution.

**Sol.**

\[
\text{HNiC} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{NiC}^-
\]

\[
\text{Molar concentration of nicotinic acid} = 0.05 \text{ mole/lit.}
\]

\[
\% \text{ Degree of dissociation} = \frac{0.67 \times 10^{-5}}{0.1 \times 10^{-4}} = 0.67
\]

Example 5:

The pH of 0.1 M hydrocyanic acid solution is 5.2. What is the value of $K_a$ for hydrocyanic acid.

**Sol.**

\[
2\text{.5 pH} \Rightarrow \text{H}^+ \rightarrow 6.30 \times 10^{-6} \text{ M, } \text{H}^+ = C\alpha = \sqrt{C \times K_a}
\]

\[
(6.3 \times 10^{-6})^2 = K_a; \quad \because \sqrt{K_a} = 3.96 \times 10^{-10} \text{ M}
\]

Exercise 1

1. The standard state Gibb’s free energy change for the isomerisation reaction

\[
\text{cis-2-pentene } \rightarrow \text{trans-2-pentene} \quad \text{is } -3.67 \text{ kJ mol}^{-1} \text{ at 400 K. If more trans-2-pentene is added to the reaction vessel, then}
\]

(a) More cis-2-pentene is formed
(b) Equilibrium shifts in the forward direction
(c) Equilibrium remains unaltered
(d) More trans-2-pentene is produced

2. The equilibrium constant ($K_c$) for the reaction

\[
\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO(g)} \quad \text{at temperature T is } 4 \times 10^{-4}. \text{ The value of } K_c \text{ for the reaction}
\]

\[
\text{NO(g)} \rightarrow \frac{1}{2} \text{N}_2\text{(g)} + \frac{1}{2} \text{O}_2\text{(g)} \text{ at the same temperature is:}
\]

(a) 0.02 \quad (b) 2.5 \times 10^2 \quad (c) 4 \times 10^{-4} \quad (d) 50.0

3. For reaction PCl\(_3\) (g) + Cl\(_2\) (g) $\rightarrow$ PCl\(_5\) (g), the value of $K_p$ at 250°C is 26 mol\(^{-1}\) litre\(^1\). The value of $K_p$ at this temperature will be

(a) 0.61 atm\(^{-1}\) \quad (b) 0.57 atm\(^{-1}\) \quad (c) 0.83 atm\(^{-1}\) \quad (d) difficult to compute without more data

4. The equilibrium constant for the reaction

\[
\text{N}_2\text{(g)} + \text{O}_2\text{(g)} \rightarrow 2\text{NO(g)} \quad \text{is } 4 \times 10^{-4} \text{ at 2000 K.}
\]

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 \times 10^{-4} \quad (b) 4 \times 10^{-4} \quad (c) 4 \times 10^{-3} \quad (d) difficult to compute without more data
5. An acid HA ionises as

\[
\text{HA} \rightleftharpoons \text{H}^+ + \text{A}^{-1}
\]

The pH of 1.0 M solution is 5. Its dissociation constant would be:
(a) 5 \times 10^{-8} (b) 5 \times 10^{-5} (c) 1 \times 10^{-10} (d) 1 \times 10^{-10}

6. In a reaction, A + 2B \rightleftharpoons 2C. 2.0 mole of 'A' and 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

7. 4.5 moles each of hydrogen and iodine were heated in a sealed ten litre vessel. At equilibrium 3 moles of HI were found.
(a) 18 atm (b) 3 atm (c) 0.3 atm (d) 0.18 atm

8. When pressure is applied to the equilibrium system

\[
\text{Ice} \rightleftharpoons \text{Water}
\]

Which of the following phenomenon will happen?
(a) More ice will be formed (b) Water will evaporate (c) More water will be formed (d) Equilibrium will not be formed

9. 1 mole of N₂ and 2 moles of H₂ are allowed to react in a 1 dm³ vessel. At equilibrium, 0.8 mole of NH₃ is formed. The concentration of H₂ in the vessel is
(a) 0.6 mole (b) 0.8 mole (c) 0.2 mole (d) 0.4 mole

10. A vessel at 1000 K contains CO₂ with a pressure of 0.5 atm. Some of the CO₂ is converted into CO on the addition of graphite. If the total pressure at equilibrium is 0.8 atm, the value of K is:
(a) 1.8 atm (b) 3 atm (c) 0.3 atm (d) 0.18 atm

11. In which of the following, the forward reaction is favoured by use of high pressure?
(a) H₂ + I₂ \rightleftharpoons 2HI (b) N₂ + O₂ \rightleftharpoons 2NO (c) 2NH₃ \rightleftharpoons N₂ + 3H₂ (d) 2SO₂ + O₂ \rightleftharpoons 2SO₃

12. In which of the following equilibrium Kc and Kp are not equal?
(a) 2 NO(g) \rightleftharpoons N₂(g)+O₂(g) (b) SO₂(g) + NO₂(g) \rightleftharpoons SO₃(g) + NO(g) (c) H₂(g) + I₂(g) \rightleftharpoons 2HI(g) (d) 2C(s)+O₂(g) \rightleftharpoons 2CO₂(g)

13. The rate constant for forward and backward reaction of hydrolysis of ester are 1.1 × 10⁻² and 1.5 × 10⁻³ per minute respectively. Equilibrium constant for the reaction

\[
\text{CH₃COOC₂H₅ + H}^+ \rightleftharpoons \text{CH₃COOH} + \text{C₂H₅OH}
\]

is
(a) 4.33 (b) 5.33 (c) 6.33 (d) 7.33

14. The partial pressure of CH₂OH (g), CO (g) and H₂ (g) in equilibrium mixture for the reaction,

\[
\text{CO (g) + 2H₂ (g) \rightleftharpoons CH₃OH (g)}
\]

are 2.0, 1.0 and 0.1 atm respectively at 427°C. The value of Kp for the decomposition of CH₃OH to CO and H₂ is
(a) 10² atm⁻¹ (b) 2 × 10² atm⁻¹ (c) 50 atm⁻¹ (d) 5 × 10⁻³ atm⁻¹

15. The degree of dissociation of dinitrogen tetroxide N₂O₄ (g) \rightleftharpoons 2NO₂(g) at temperature T and total pressure P is α. Which one of the following is the correct expression for the equilibrium constant (Kp) at this temperature?
(a) \( \frac{2α}{1 - α} \) (b) \( \frac{α²}{1 - α} \) (c) \( \frac{4α²}{1 - α} \) (d) \( \frac{4α²}{1 - α} \)

16. C₂H₅–O–C₂H₅ is
(a) Lewis acid (b) Arrhenius acid (c) Lewis base (d) None of these

17. The following equilibria are given:

\[
\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3 \quad K_1
\]
\[
\text{N}_2 + \text{O}_2 \rightleftharpoons 2\text{NO} \quad K_2
\]
\[
\frac{1}{2}\text{O}_2 \rightleftharpoons \text{H}_2\text{O} \quad K_3
\]

The equilibrium constant of the reaction

\[
2\text{NH}_3 + \frac{3}{2}\text{O}_2 \rightleftharpoons 2\text{NO} + 3\text{H}_2\text{O}
\]

in terms of K₁, K₂ and K₃ is
(a) \( \frac{K_1K_2}{K_3} \) (b) \( \frac{K_1K_2^2}{K_3} \) (c) \( \frac{K_2K_3^3}{K_1} \) (d) \( K_1K_2K_3 \)

18. The reaction quotient (Q) for the reaction

\[
\text{N}_2(g) + 3\text{H}_2(g) \rightleftharpoons 2\text{NH}_3(g)
\]

given by Q = \( \frac{[\text{NH}_3]^2}{[\text{N}_2][\text{H}_2]^3} \). The reaction will proceed from right to left if
(a) Q < Kc (b) Q > Kc (c) Q = 0 (d) Q = Kc

where Kc is the equilibrium constant.

19. Which will not affect the degree of ionization?
(a) Temperature (b) Concentration (c) Type of solvent (d) Current

20. If the concentration of OH⁻ ions in the reaction

\[
\text{Fe(OH)}_3(s) \rightleftharpoons \text{Fe}^{3+}(aq) + 3\text{OH}^−(aq)
\]

is decreased by \( \frac{1}{4} \) times, then equilibrium concentration of Fe³⁺ will increase by
(a) 8 times (b) 16 times (c) 64 times (d) 4 times
21. When hydrochloric acid is added to cobalt nitrate solution at room temperature, the following reaction takes place out the reaction mixture becomes blue. On cooling the mixture it becomes pink. On the basis of this information mark the correct answer.

\[
\text{CO}_3^{2-} (aq) + 4\text{H}^+ (aq) \rightleftharpoons \text{COCl}_4^{2-} (aq) + 6\text{H}_2\text{O}(l)
\]
\( \text{(pink)} \)
\( \text{(blue)} \)

(a) \( \Delta H > 0 \) for the reaction
(b) \( \Delta H < 0 \) for the reaction
(c) \( \Delta H = 0 \) for the reaction
(d) The sign of \( \Delta H \) cannot be predicted on the basis of this information.

22. For the reaction

\[
\text{CH}_4(g) + 2\text{O}_2(g) \rightleftharpoons \text{CO}_2(g) + 2\text{H}_2\text{O}(l),
\]
\( \Delta H = -170.8 \text{ kJ mol}^{-1} \)

Which of the following statements is not true?

(a) The equilibrium constant for the reaction is given by

\[ K_p = \frac{[\text{CO}_2] [\text{O}_2]}{[\text{CH}_4][\text{O}_2]} \]

(b) Addition of \( \text{CH}_4 \) or \( \text{O}_2 \) at equilibrium will cause a shift to the right
(c) The reaction is exothermic
(d) At equilibrium, the concentrations of \( \text{CO}_2 \) and \( \text{H}_2\text{O}(l) \) are not equal

23. Which of the following is not a Lewis acid?

(a) \( \text{CO} \)
(b) \( \text{SiCl}_4 \)
(c) \( \text{SO}_3 \)
(d) \( \text{Zn}^{2+} \)

24. In the equation, \( \text{I}_2 + \text{I}^- \rightleftharpoons \text{I}_3^- \), which is the Lewis base?

(a) \( \text{I}_2 \)
(b) \( \text{I}^- \)
(c) \( \text{I}_3^- \)
(d) None of these

25. Why are strong acids generally used as standard solutions in acid-base titrations?

(a) The \( \text{pH} \) at the equivalent point will always be 7.
(b) They can be used to titrate both strong and weak bases.
(c) Strong acids form more stable solutions than weak acids.
(d) The salts of strong acids do not hydrolyse.

26. To \( \text{Ag}_2\text{CrO}_4 \) solution over its own precipitate, \( \text{CrO}_4^{2-} \) ions are added. This results in

(a) increase in \( \text{Ag}^+ \) concentration.
(b) decrease in \( \text{Ag}^+ \) concentration.
(c) increase in solubility product
(d) shifting of \( \text{Ag}^+ \) ions from the precipitate into the solution.

27. Why only \( \text{As}^{3-} \) gets precipitated as \( \text{As}_2\text{S}_3 \) and not \( \text{Zn}^{2+} \) as \( \text{ZnS} \) when \( \text{H}_2\text{S} \) is passed through an acidic solution containing \( \text{As}^{5+} \) and \( \text{Zn}^{2+} \)?

(a) Solubility product of \( \text{As}_2\text{S}_3 \) is less than that of \( \text{ZnS} \).
(b) Enough \( \text{As}^{3-} \) are present in acidic medium.
(c) Zinc salt does not ionise in acidic medium.
(d) Solubility product changes in presence of an acid.

28. The oxidation of \( \text{SO}_2 \) by \( \text{O}_2 \) to \( \text{SO}_3 \) is an exothermic reaction. The yield of \( \text{SO}_3 \) will be maximum if

(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 decreased

29. Which of the following sulphides has the lowest solubility product?

(a) \( \text{FeS} \)
(b) \( \text{MnS} \)
(c) \( \text{PbS} \)
(d) \( \text{ZnS} \)

30. What is the solubility of calcium fluoride in a saturated solution if its solubility product is \( 3.2 \times 10^{-11} \)?

(a) \( 2.0 \times 10^{-4} \) mole/litre
(b) \( 12.0 \times 10^{-3} \) mole/litre
(c) \( 0.2 \times 10^{-4} \) mole/litre
(d) \( 2 \times 10^{-3} \) mole/litre

31. The ionisation 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 \( 1.8 \times 10^{-4} \) respectively. Which of the following orders of \( \text{pH} \) of 0.1 mol 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

32. The pH of blood does not appreciably change by a small addition of acid or a base because blood

(a) contains serum protein which acts as buffer
(b) contains iron as a part of the molecule
(c) can be easily coagulated
(d) is body fluid

33. Which of the following will produce a buffer solution when mixed in equal volumes?

(a) 0.1 mol dm\(^{-3} \) \( \text{NH}_4\text{OH} \) and 0.1 mol dm\(^{-3} \) \( \text{HCl} \)
(b) 0.05 mol dm\(^{-3} \) \( \text{NH}_4\text{OH} \) and 0.1 mol dm\(^{-3} \) \( \text{HCl} \)
(c) 0.1 mol dm\(^{-3} \) \( \text{NH}_4\text{OH} \) and 0.05 mol dm\(^{-3} \) \( \text{HCl} \)
(d) 0.1 mol dm\(^{-3} \) \( \text{CH}_3\text{COONa} \) and 0.1 mol dm\(^{-3} \) \( \text{NaOH} \)

34. 1 M \( \text{NaCl} \) and 1 M \( \text{HCl} \) are present in an aqueous solution. The solution is

(a) not a buffer solution with \( \text{pH} < 7 \)
(b) not a buffer solution with \( \text{pH} > 7 \)
(c) a buffer solution with \( \text{pH} < 7 \)
(d) a buffer solution with \( \text{pH} > 7 \)

35. pH of 4.0 gm/litre \( \text{NaOH} \) solution is

(a) 13
(b) 11
(c) 13.5
(d) 12

36. The \( \text{pOH} \) value of a solution whose hydroxide ion concentration is \( 6.2 \times 10^{-9} \) mol/litre is

(a) 0.21
(b) 6.21
(c) 7.75
(d) 7.21

37. Which of the following solution cannot act as a buffer?

(a) \( \text{NaH}_2\text{PO}_4 \) + \( \text{H}_2\text{PO}_4 \)
(b) \( \text{CH}_3\text{COOH} + \text{CH}_3\text{COONa} \)
(c) \( \text{HCl} + \text{NH}_4\text{Cl} \)
(d) \( \text{NH}_4\text{OH} + \text{NH}_4\text{Cl} \)

38. A certain buffer solution contains equal concentration of \( \text{X}^- \) and \( \text{HX} \). The \( K_b \) for \( \text{HX} \) is \( 10^{-9} \). The \( \text{pH} \) of the buffer is a)

(a) 3
(b) 8
(c) 11
(d) 14

39. What is \( [\text{H}^+] \) of a solution having 0.1 M \( \text{HCN} \) and 0.2 M \( \text{NaCN} \)? \( (K_b \text{for } \text{HCN} = 6.2 \times 10^{-10}) \)

(a) \( 3.1 \times 10^{10} \)
(b) \( 6.2 \times 10^{5} \)
(c) \( 6.2 \times 10^{-10} \)
(d) \( 3.1 \times 10^{-10} \)
40. In \( \text{HS}^–, \Gamma^–, \text{RNH}_2 \) and \( \text{NH}_3 \), order of proton accepting tendency will be
(a) \( \Gamma^– > \text{RNH}_2 > \text{NH}_3 > \text{HS}^– \)
(b) \( \text{HS}^– > \text{RNH}_2 > \text{NH}_3 > \Gamma^– \)
(c) \( \text{RNH}_2 > \text{HNH}_2 > \text{HS}^– > \Gamma^– \)
(d) \( \text{NH}_3 > \text{RNH}_2 > \text{HS}^– > \Gamma^– \)

41. Equimolar solutions of the following were prepared in water separately. Which one of the solutions will record the highest \( pH \)?
(a) \( \text{SrCl}_2 \)
(b) \( \text{BaCl}_2 \)
(c) \( \text{MgCl}_2 \)
(d) \( \text{CaCl}_2 \)

42. Solubility products of \( \text{Al(OH)}_3 \) and \( \text{Zn(OH)}_2 \) are \( 8.5 \times 10^{-23} \) and \( 1.8 \times 10^{-4} \) respectively. If both Al\(^{3+}\) and Zn\(^{2+}\) ions are present in a solution, which one will be precipitated first on addition of \( \text{NH}_4\text{OH} \)?
(a) \( \text{Al(OH)}_3 \)
(b) \( \text{Zn(OH)}_2 \)
(c) Both of them
(d) None of them

43. A 0.1 N solution of \( \text{Na}_3\text{CO}_3 \) is titrated with 0.1 N HCl solution. The best indicator to be used is
(a) Potassium ferricyanide
(b) Phenolphthalein
(c) Methyl red
(d) Litmus paper

44. The range of methyl orange as an indicator is in between \( pH \)
(a) 6 – 8
(b) 8 – 9
(c) 3 – 5
(d) 2 – 4

45. When \( \text{H}_2\text{S} \) is passed in acidic medium in solution having \( \text{CuS} \) and \( \text{ZnS} \), only CuS is precipitated because
(a) \( K_{sp}^{\text{ZnS}} = K_{sp}^{\text{CuS}} \)
(b) \( K_{sp}^{\text{CuS}} < K_{sp}^{\text{ZnS}} \)
(c) \( K_{sp}^{\text{CuS}} > K_{sp}^{\text{ZnS}} \)
(d) ZnS has lower melting point than CuS

46. \( \text{H}_2\text{S} \) gas when passed through a solution of cations containing HCl precipitates the cations of second group of qualitative analysis but not those belonging to the fourth group. It is because
(a) presence of HCl decreases the sulphide ion concentration.
(b) solubility product of group II sulphides is more than that of group IV sulphides.
(c) presence of HCl increases the sulphide ion concentration.
(d) sulphides of group IV cations are unstable in HCl.

47. The indicator used in titrating, weak acid (e.g. oxalic acid) with a strong base (e.g. caustic soda) solution is
(a) Methyl orange
(b) Methyl red
(c) Fluorescein
(d) Phenolphthalein

48. Starch can be used as an indicator for the detection of traces of
(a) glucose in aqueous solution
(b) proteins in blood
(c) iodine in aqueous solution
(d) urea in blood

49. 8 mole of a gas \( \text{AB}_3 \) are introduced into a 1.0 dm\(^3\) vessel. It dissociates as, \( 2\text{AB}_3(g) \rightleftharpoons \text{A}_2(g) + 3\text{B}_2(g) \). At equilibrium, 2 mole of \( \text{A}_2 \) are found to be present. The equilibrium constant of reaction is \( \ldots \) in mol\(^2\)L\(^{-2}\).
(a) 2
(b) 3
(c) 7
(d) 36

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**Exercise 2**

1. The solubility product of \( \text{PbCl}_2 \) is \( 2.3 \times 10^{-32} \). Its solubility will be:
   (a) \( 1.78 \times 10^{-11} \) g/lit.
   (b) \( 2.95 \times 10^{-9} \) g/lit.
   (c) \( 3.42 \times 10^{-9} \) g/lit.
   (d) \( 4.95 \times 10^{-9} \) g/lit.

2. An amount of solid \( \text{NH}_4\text{HS} \) is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield \( \text{NH}_3 \) and \( \text{H}_2\text{S} \) 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 \( \text{NH}_4\text{HS} \) decomposition at this temperature is
   (a) 0.11
   (b) 0.17
   (c) 0.18
   (d) 0.30

3. The reaction, \( \text{SO}_2 + \text{Cl}_2 \rightarrow \text{SO}_2 \text{Cl}_2 \) is exothermic and reversible. A mixture of \( \text{SO}_2 \) (g), \( \text{Cl}_2 \) (g) and \( \text{SO}_2\text{Cl}_2 \) (l) is at equilibrium in a closed container. Now a certain quantity of extra \( \text{SO}_2 \) 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

4. Which equilibrium can be described as an acid-base reaction using the Lewis acid-base definition but not using the Bronsted-Lowry definition?
   (a) \( 2\text{NH}_3 + \text{H}_2\text{SO}_4 \rightarrow 2\text{NH}_4^+ + \text{SO}_4^{2–} \)
   (b) \( \text{NH}_3 + \text{CH}_3\text{COOH} \rightarrow \text{NH}_4^+ + \text{CH}_3\text{COO}^- \)
   (c) \( \text{H}_2\text{O} + \text{CH}_3\text{COOH} \rightarrow \text{H}_2\text{O}^+ + \text{CH}_3\text{COO}^- \)
   (d) \( [\text{Cu(H}_2\text{O})_4]^{2–} + 4\text{NH}_3 \rightarrow [\text{Cu(NH}_3)_4]^{2+} + 4\text{H}_2\text{O} \)

5. The \( K_{sp} \) of \( \text{CuS} \), \( \text{Ag}_2\text{S} \) and \( \text{HgS} \) are \( 10^{-31}, 10^{-44} \) and \( 10^{-54} \) respectively. The solubility of these sulphides are in the order
   (a) \( \text{Ag}_2\text{S} > \text{CuS} > \text{HgS} \)
   (b) \( \text{AgS} > \text{HgS} > \text{CuS} \)
   (c) \( \text{HgS} > \text{Ag}_2\text{S} > \text{CuS} \)
   (d) \( \text{CuS} > \text{Ag}_2\text{S} > \text{HgS} \)

6. The solubility product of \( \text{AgCl} \) is \( 4.0 \times 10^{-10} \) at 298 K. The solubility of \( \text{AgCl} \) in 0.04 M \( \text{CaCl}_2 \) will be
   (a) \( 2.0 \times 10^{-5} \) M
   (b) \( 1.0 \times 10^{-4} \) M
   (c) \( 5.0 \times 10^{-9} \) M
   (d) \( 2.2 \times 10^{-4} \) M

7. It is found that 0.1 M solution of four sodium salts \( \text{NaA}, \text{NaB}, \text{NaC} \) and \( \text{NaD} \) have the following \( pH \) values 7, 9, 10 and 11 respectively. In which of the following salts corresponding acid is strongest?
   (a) \( \text{NaD} \)
   (b) \( \text{NaC} \)
   (c) \( \text{NaB} \)
   (d) \( \text{NaA} \)
8. \( K_b \) for the hydrolysis reaction

\[
\text{B}^+ + \text{H}_2\text{O} \rightleftharpoons \text{BOH} + \text{H}^-
\]

is \( 1.0 \times 10^{-6} \), the hydrolysis constant of the salt is

(a) \( 10^{-9} \)  \( \) (b) \( 10^{-6} \)  \( \) (c) \( 10^{-8} \)  \( \) (d) \( 10^{-7} \)

9. The equilibrium constants \( K_{p1} \) and \( K_{p2} \) for the reactions

\( \text{X} \rightleftharpoons 2\text{Y} \) and \( \text{Z} \rightleftharpoons \text{P} + \text{Q} \), 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 : 1  \( \) (b) 1.36  \( \) (c) 1 : 3  \( \) (d) 1 : 9

10. For preparing a buffer solution of pH 6 by mixing sodium acetate and acetic acid, the ratio of the concentration of salt and acid should be \( (K_a = 10^{-5} ) \)

(a) 1 : 10  \( \) (b) 10 : 1  \( \) (c) 100 : 1  \( \) (d) 1 : 100

11. Steam reacts with iron at high temperature to give hydrogen gas and Fe\(_3\)O\(_4\) (s). The correct expression for the equilibrium constant is

\[
\frac{p_{\text{H}_2}^2}{p_{\text{H}_2}^4} = \frac{(P_{\text{H}_2})^4}{(P_{\text{H}_2})^4} \cdot \frac{(P_{\text{Fe}})^4}{(P_{\text{Fe}})^4}
\]

(a) \( \) (b) \( \) (c) \( \) (d) \( \)

12. Consider the gaseous equilibrium of

\[
\text{H}_2(g) + \text{I}_2(g) \rightleftharpoons 2\text{HI}(g)
\]

In the following graphs the three gases are at equilibrium in a container. At some Time t, Extra \( \text{I}_2 \) is added. Which of the following sets will respond to this situation?

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

13. When hydrogen molecule decompose into it’s atoms which conditions gives maximum yields of H atoms?

(a) High temperature and low pressure  \( \) (b) Low temperature and high pressure  \( \) (c) High temperature and high pressure  \( \) (d) Low temperature and low pressure

14. The pH of a buffer solution containing 25 ml of 1M CH\(_3\)COONa and 25 ml of 1 M CH\(_3\)COOH will be appreciably affected by 5 ml of

(a) 1 M CH\(_3\)COOH  \( \) (b) 5 M CH\(_3\)COOH  \( \) (c) 5 M HCl  \( \) (d) 1 M NH\(_4\)OH

15. In a saturated solution of the sparingly soluble strong electrolyte AgIO\(_3\) (molecular mass = 283) the equilibrium which sets in is AgIO\(_3\) (s) \( \rightleftharpoons \) Ag\(^+\) (aq) + IO\(_3\)^–(aq). If the solubility product constant \( K_{sp} \) of AgIO\(_3\) at a given temperature is \( 1.0 \times 10^{-8} \), what is the mass of AgIO\(_3\) contained in 100 ml of its saturated solution?

(a) \( 1.0 \times 10^{-4} \) g  \( \) (b) \( 28.3 \times 10^{-2} \) g  \( \) (c) \( 2.83 \times 10^{-3} \) g  \( \) (d) \( 1.0 \times 10^{-7} \) g

16. The pH of a solution is 5.0. To this solution sufficient acid is added to decrease the pH to 2.0. The increase in hydrogen ion concentration is

(a) 100 times  \( \) (b) 1000 times  \( \) (c) 2.5 times  \( \) (d) 10 times

17. If the solubility of Li\(_3\)Na\(_3\)(AlF\(_6\))\(_2\) is ‘a’ mol/litre. Its solubility product is equal to

(a) \( a^8 \)  \( \) (b) \( 12a^3 \)  \( \) (c) \( 18a^3 \)  \( \) (d) \( 2916a^8 \)

18. Which solution will be strongly acidic?

(a) when pH = 0.0  \( \) (b) when pOH = 4.5  \( \) (c) when pOH = 14  \( \) (d) both (a) and (c)

19. The \( pK_a \) value for the A \( \rightarrow \) B, B \( \rightarrow \) C and C \( \rightarrow \) D dissociations are 2.09, 3.86 and 9.82 respectively. Since only B has an equal number of positive and negative charges, the value of the isoelectric point is

(a) 5.26  \( \) (b) 2.98  \( \) (c) 3.86  \( \) (d) 15.77

20. Four species are listed below:

\( \text{HCO}_3^- \) ii. \( \text{H}_2\text{O}^+ \) iii. \( \text{HSO}_4^- \) iv. \( \text{H}_2\text{SO}_4 \)

Which one of the following is the correct sequence of their acid strength?

(a) \( iv < ii < iii < i \)  \( \) (b) \( ii < iii < i < iv \)  \( \) (c) \( iii < i < iv < ii \)  \( \) (d) \( i < iii < ii < iv \)

21. Assuming that the buffer in the blood is \( \text{CO}_2 - \text{HCO}_3^- \). Calculate the ratio of conjugate base to acid necessary to maintain blood at its proper pH of 7.4.

\( K_1(\text{H}_2\text{CO}_3) = 4.5 \times 10^{-7} \)

(a) 11  \( \) (b) 8  \( \) (c) 6  \( \) (d) 14

22. Which one of the following statements is not true?

(a) \( \text{pH} + \text{pOH} = 14 \) for all aqueous solutions  \( \) (b) The pH of 1 \( \times 10^{-8} \) M HCl is 8  \( \) (c) 96,500 coulombs of electricity when passed through a CuSO\(_4\) solution deposits 1 gram equivalent of copper at the cathode  \( \) (d) The conjugate base of \( \text{H}_2\text{PO}_4^- \) is \( \text{HPO}_4^{2-} \)

23. Consider the following equilibrium in a closed container

\( \text{N}_2\text{O}_5(g) \rightleftharpoons 2\text{NO}_2(g) \)

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 (\( K_p \)) and degree of dissociation (\( \alpha \))?

(a) neither \( K_p \) nor \( \alpha \) changes  \( \) (b) both \( K_p \) and \( \alpha \) change  \( \) (c) \( K_p \) changes, but \( \alpha \) does not change  \( \) (d) \( K_p \) does not change, but \( \alpha \) changes
24. A reaction $A + 2B \rightleftharpoons 2C + D$ was studied using the initial concentrations of $B$ which was 1.5 times that of $A$. At the equilibrium, concentration of $A$ and $C$ were found to be equal.

Then $K_c$ for the equilibrium is

(a) 8  (b) 4  (c) 6  (d) 0.32

25. **Statement 1**: Pure liquids and solids can be ignored while writing the equilibrium constant expression.

**Statement 2**: The concentration of pure liquids and solids does not remain constant.

(a) Statement-1 is true, Statement-2 is true; Statement-2 is a correct explanation for Statement-1
(b) Statement-1 is true, Statement-2 is true; Statement-2 is not a correct explanation for Statement-1
(c) Statement-1 is true, Statement-2 is false
(d) Statement-1 is false, Statement-2 is true

26. **Statement 1**: In a reaction initially free energy decreases and attains a stage, the reaction becomes dynamic in either sides.

**Statement 2**: $G = 0$ and equilibrium is attained.

(a) Statement-1 is true, Statement-2 is true; Statement-2 is a correct explanation for Statement-1
(b) Statement-1 is true, Statement-2 is true; Statement-2 is not a correct explanation for Statement-1
(c) Statement-1 is true, Statement-2 is false
(d) Statement-1 is false, Statement-2 is true

27. **Statement 1**: The equilibrium (given below) attained in a closed vessel remains unaltered by the addition of $\text{CaCO}_3(s)$.

**Statement 2**: Heterogeneous reaction is unaffected by solid and liquid.

(a) Statement-1 is true, Statement-2 is true; Statement-2 is a correct explanation for Statement-1
(b) Statement-1 is true, Statement-2 is true; Statement-2 is not a correct explanation for Statement-1
(c) Statement-1 is true, Statement-2 is false
(d) Statement-1 is false, Statement-2 is true

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**Hints & Solutions**

**EXERCISE - 1**

1. (a) According to Le Chatelier’s principle, equilibrium is shifted in the backward direction.
2. (d) For the reaction

   $N_2 + O_2 \rightarrow 2NO$  $K = 4 \times 10^{-4}$

   Hence for the reaction

   $NO \rightarrow \frac{1}{2}N_2 + \frac{1}{2}O_2$

   $K' = \frac{\frac{1}{2}}{\frac{1}{4} \times 10^{-4}} = 50$

3. (a) Here $\Delta n = -1$, $K_p = 26 \times (0.0821 \times 523)^{-1} = 0.61 \text{ atm}^{-1}$
4. (b) $K_c$ remains constant at constant temperature.
5. (d) pH = 5 means
   $[H^+] = 10^{-5}$

   $\text{HA} \rightarrow H^+ + A^{-1}$

   $t=0$  $c$  0  0
   teq  $c(1-\alpha)$  $\alpha$  $\alpha$

   $K_a = \frac{[H^+][A^-]}{[HA]} = \frac{(c\alpha)^2}{c(1-\alpha)} = \frac{[H^+]^2}{c[H^+]}$

   But, $[H^+] << C$

   $\therefore K_a = (10^{-5})^2 = 10^{-10}$

6. (c) $\text{A} + 2\text{B} \rightleftharpoons 2\text{C}$

   Initial  2  3  2
   At equilibrium 2.5 4 1
   Molar conc. 1.25 2 0.5

   $K_c = \frac{(0.5)^2}{(1.25)^2} = 0.05$

7. (a) $\text{H}_2 + \text{l}_2 \rightleftharpoons 2\text{HI}$

   Initial moles 4.5 4.5 0
   Moles at equi. $(4.5 - 1.5) (4.5 - 1.5) 3$
   $= 3 = 3$

   $K = \frac{3^2}{3 \times 3} = 1$

   Since there is no change in no. of moles hence volume of the vessel can be ignored.

8. (c) On increasing the pressure on this system in equilibrium, the equilibrium tends to shift in a direction in which volume decreases. Ice melts with a reduction in volume.

9. (b) $\text{N}_2 + 3\text{H}_2 \rightleftharpoons 2\text{NH}_3$

   Initial 1 2 0
   At equi. $1 - 0.4 = 0.6$  $2 - 3 \times 0.4 = 0.8$  0.8

10. (a) $\text{CO}_2 + C(\text{graphite}) \rightleftharpoons 2\text{CO}

    \begin{align*}
    P_{\text{init}} & = 0.5 \text{ atm} \\
    P_{\text{final}} & = (0.5 - x) \text{ atm}  \\
    \text{Total P at equilibrium} & = 0.5 - x + 2x = 0.5 + x \text{ atm}
    \end{align*}

    $0.8 = 0.5 + x$  \therefore $x = 0.8 - 0.5 = 0.3 \text{ atm}$

    Now, $k_p = \frac{(P_{\text{CO}})^2}{P_{\text{CO}_2}} = \frac{(2 \times 0.3)^2}{(0.6)^2} = \frac{(0.6)^2}{(0.5 - 0.3)} = 1.8 \text{ atm}$

11. (d) Le Chatelier’s principle.

12. (d) $2\text{C}(s) + \text{O}_2(g) \rightleftharpoons 2\text{CO}_2(g)$

    $\Delta n = 2 - 1 = + 1$

    $\therefore K_c$ and $K_p$ are not equal.
13. (d) Rate constant of forward reaction \(K_f = 1.1 \times 10^{-2}\) and rate constant of backward reaction \(K_b = 1.5 \times 10^{-3}\) per minute. Equilibrium constant \(K_c\)
\[\frac{K_f}{K_b} = \frac{1.1 \times 10^{-2}}{1.5 \times 10^{-3}} = 7.33\]

14. (d) \(K_p = \frac{P_{CH_4} \ P_{O_2}}{P_{CO} \ P_{H_2}} = \frac{2}{1 \times (0.1)^2} = 200;\)
For reverse reaction,
\[\frac{1}{K_p} = \frac{1}{200} = 5 \times 10^{-3} \text{ atm}^2\]

15. (d) \(N_2O_4 \rightleftharpoons 2NO_2\)
\[1 - \alpha \quad 2\alpha\]
Total moles at equi. \(1 - \alpha + 2\alpha = 1 + \alpha\)
\[K_c = \frac{p_{NO_2}^2}{p_{N_2O_4}} = \frac{(2\alpha (1+\alpha) p)^2}{1+\alpha} = 4\alpha^2 p\]

16. (c) Electron rich compounds are Lewis bases. Diethyl ether has two lone pairs of electrons on oxygen atom.

17. (c) (I) \(N_2 + 3H_2 \rightleftharpoons 2NH_3\)
\[K_1 = \frac{[NH_3]^2}{[N_2][H_2]^3}\]
(II) \(N_2 + O_2 \rightleftharpoons 2NO\)
\[K_2 = \frac{[NO]^2}{[N_2][O_2]}\]
(III) \(H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O\)
\[K_3 = \frac{[H_2O]}{[H_2][O_2]^\frac{1}{2}}\]
(IV) \(2NH_3 + \frac{5}{2} O_2 \rightleftharpoons 2NO + 3H_2O\)
\[K_c = \frac{K_2 K_3}{[NH_3]^2 [O_2]^\frac{5}{2}} = \frac{K_2 K_3}{K_1}\]

18. (b) If \(Q > K_c\), Q will tend to decrease so as to become equal to \(K_c\). As a result, the reaction will proceed in the backward direction.

19. (d) Degree of ionization increases with temperature. More the concentration of solution lesser will be degree of ionisation it increases with dilution. Solvents are of two types, polar and non-polar. Ionisation is more in case of polar solvent. Degree of ionisation is not affected by current.

20. (c) For this reaction \(K_{eq}\) is given by
\[K = \frac{[Fe^{3+}][OH^-]^3}{[Fe(OH)_3]} = (Fe^{3+})(OH^-)^3\]
\[\text{[solid]} = 1\].
If \((OH^-)\) is decreased by \(\frac{1}{4}\) times then for reaction equilibrium constant to remain constant, we have to increase the concentration of \([Fe^{3+}]\) by a factor of \(4^3\) i.e., \(4 \times 4 \times 4 = 64\).

21. (a)
22. (a) First option is incorrect as the value of \(K_p\) given is wrong. It should have been
\[K_p = \frac{P_{CO_2}}{P_{CH_4} \ P_{O_2}^2}\]

23. (a) CO can not accept electrons.
24. (b) \(I^-\) is electron donor.
25. (b) Strong acids can ionise the weak base also.
26. (b) To keep \(K_p\) constant, addition of \(CrO_4^{2-}\) will decrease \([Ag^+]\).
27. (a) \(K_{sp}\) of \(As_2S_3\) is less than ZnS.
28. (b) \(2SO_2 + O_2 \rightarrow 2SO_3 + \text{Heat}\);
Exothermic reaction with a reduction in number of moles is favoured by low temperature and high pressure.

29. (c) Sulphides of group II A and II B have low value of \(K_{sp}\) as compared to sulphides of group III and IV

30. (a) \(CaF_2 \rightleftharpoons Ca^{2+} + 2F^-\)
\[K_{sp} = [S][2S]^2\]
\[4S^3 = K_{sp}; \quad S = \left(\frac{3.2 \times 10^{-11}}{4}\right)^{\frac{1}{3}} = 2 \times 10^{-4} \text{ M}\]

31. (d)
32. (a) Blood contains serum protein which acts as buffer.
33. (c)
34. (a) It is not a buffer solution as buffer is a solution of weak acid or weak base and its salt. pH < 7.

35. (a) Molar concentration of \(NaOH = \frac{4}{40} = 0.1 \text{ M}\).
\[\text{[H}^+] = 10^{-13}; \quad \text{pH} = 13.\]
36. (a) \(-\log (OH^-) = pOH; \quad \text{log} 6.2 \times 10^{-9} = pOH; \quad \text{pOH} = 8.21\]

37. (c) \(HCl + NH_4Cl; \quad HCl\) is strong acid hence not used in buffer.

38. (b) \(\text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = -\log 10^{-8} + 0 = 8\]

39. (d) \(\text{pH} = -\log K_a + \log \frac{[\text{Salt}]}{[\text{Acid}]} = -\log [H^+] = -\log K_a - \log \frac{[\text{Acid}]}{[\text{Salt}]}\)
\[\text{pH} = -\log K_a + \log \frac{[\text{Acid}]}{[\text{Salt}]} = -\log [H^+] = -\log [K_a \times \frac{[\text{Acid}]}{[\text{Salt}]}]\]
\([H^+] = K_a \times \frac{[\text{Acid}]}{[\text{Salt}]} = 6.2 \times 10^{-10} \times \frac{0.1}{2} = 3.1 \times 10^{-10}\]
40. (c) Strong base has higher tendency to accept the proton. Increasing order of base and hence the order of accepting tendency of proton is

\[ \text{I}^- < \text{HS}^- < \text{NH}_3 < \text{RNH}_2 \]

41. (b) The highest pH will be recorded by the most basic solution. The basic nature of hydroxides of alkaline earth metals increase as we move from Mg to Ba and thus the solution of BaCl$_2$ in water will be most basic and so it will have highest pH.

42. (a) For Al(OH)$_3 \rightleftharpoons$ Al$^{3+}$ + 3OH$^-$

\[ K_{sp} = s \times (3s)^3 = 27s^4 \]

\[ [\text{OH}^-] = s \left( \frac{K_{sp}}{27} \right)^{1/4} = \left( \frac{8.5 \times 10^{-23}}{27} \right)^{1/4} \]

for Zn(OH)$_2 \rightleftharpoons$ Zn$^{2+}$ + 2OH$^-\quad 2s$

\[ K_{sp} = (2s)^2 \times s = 4s^3 \]

\[ [\text{OH}^-] = s \left( \frac{K_{sp}}{4} \right)^{1/3} = \left( \frac{1.8 \times 10^{-4}}{4} \right)^{1/3} \]

Al(OH)$_3$ required lower concentration of OH$^-$ ions for precipitation and hence precipitated.

43. (c) The pH at the equivalence point will be on the acidic side, the pH range of methyl red.

44. (c) Methyl orange is used as an indicator in the pH range of 4 - 5. pH range of other indicators are given below.

methyl red - 4.2 - 6.3
phenolphthalein - 8.0 - 9.8

45. (b) The compound with lower K$_{sp}$ is precipitated first.

46. (a) IV$^\text{th}$ group needs higher S$^{2-}$ ion concentration. In presence of HCl, the dissociation of H$_2$S decreases hence produces less amount of sulphide ions due to common ion effect, thus HCl decreases the solubility of H$_2$S which is sufficient to precipitate II$^\text{nd}$ group radials.

47. (d) The pH of the solution at the equivalence point will be greater than 7 due to salt hydrolysis So, an indicator giving colour on the basic side will be suitable.

48. (c) I$_2$ gives blue colour with starch.

49. (c) 2AB$_3 \rightleftharpoons$ A$_2$ (g) + 3B$_2$ (g)

Initial moles 8 0 0
Moles at eqb. 8 - x 3x/2 3x/2

given 3x/2 = 2 \therefore x = 4 \quad K = \frac{[B_2]^3[A_2]}{[AB_3]^2} = \frac{(6)^3 \times 2}{(4)^2} = 27

\[ K = \frac{[B_2]^3[A_2]}{[AB_3]^2} \]

EXERCISE - 2

1. (d) Let s be the solubility of PbCl$_2$.

Now, solubility equilibria of PbCl$_2$ can be represented as

\[ \text{PbCl}_2 \rightleftharpoons \text{Pb}^{2+} + 2\text{Cl}^- \]

\[ K_{sp} = \left[ \text{Pb}^{2+} \right] \left[ \text{Cl}^- \right]^2 = (s) (2s)^2 \]

\[ \Rightarrow s^3 = \frac{K_{sp}}{4} \]

\[ = \frac{\sqrt[3]{1.78 \times 10^{-11}} \text{mol/lit}}{4} \]

2. (a) NH$_4$HS (s) $\rightleftharpoons$ NH$_3$(g) + H$_2$S(g)

\[ \text{start} \quad 0.5 \text{ atm} \quad 0 \text{ atm} \quad x \text{ atm.} \]

Then 0.5 + x + x = 2x + 0.5 = 0.84 (given)

\[ \Rightarrow x = 0.17 \text{ atm.} \]

\[ p_{\text{NH}_3} = 0.5 + 0.17 = 0.67 \text{ atm} ; \quad p_{\text{H}_2\text{S}} = 0.17 \text{ atm} \]

3. (c) By addition of SO$_2$, equilibrium will shift to RHS which is exothermic. Hence temperature will increase.

4. (d) [Cu(H$_2$O)$_4$]$^{2+} + 4\text{NH}_3$ $\rightleftharpoons$ [Cu(NH$_3$)$_4$]$^{2+} + 4\text{H}_2\text{O}$ involves lose and gain of electrons.

5. (a) For CuS, solubility = ($10^{-11}$)$^{1/2}$;

\[ \text{For Ag}_2\text{S} = \left( \frac{K_{sp}}{4} \right)^{1/3} = \left( \frac{10^{-44}}{4} \right)^{1/3} \]

6. (c) Solubility of AgCl

\[ \text{[Ag}^+\text{]}_0 = \frac{K_{sp}}{[\text{Cl}^-]} = 4 \times 10^{-10} = 5.0 \times 10^{-9} \text{ M} \]

0.08 M of concentration of [Cl$^-$] comes from CaCl$_2$.

7. (d) The pH values indicate that NaD, NaC and NaB are salts of strong base and weak acid. pH of NaA = 7 indicates that it is a salt of strong acid and strong base.

8. (c) For hydrolysis of $\bar{B}$,$$

\[ K_h = \frac{K_w}{K_b} = 10^{-14} \quad 10^{-6} = 10^{-8} \]

9. (b) Let the initial moles of X be ‘a’ and that of Z be ‘b’ then for the given reactions, we have

\[ X \rightleftharpoons 2Y \quad \text{Initial} \quad a \text{ (moles)} \quad 0 \]

\[ \text{At equilibrium} \quad a(1 - \alpha) \quad 2\alpha \alpha \]

Total no. of moles = a (1 - $\alpha$) + 2a$\alpha$

\[ = a - a\alpha + 2a\alpha = a(1 + \alpha) \]
Now,
\[ K_{P_1} = \left( \frac{n_y}{n_x} \right)^2 \left( \frac{P_{T_1}}{\Sigma n} \right)^{2m} \]
or,
\[ K_{P_1} = \frac{(2a)^2 \cdot P_{T_1}}{[a(1-a)][a(1+a)]} \]

Initial
\[ b \text{ moles} \]
At equi (moles)
\[ b(1 - \alpha) \quad b\alpha \quad b\alpha \]
Total no. of moles
\[ = b(1 - \alpha) + b\alpha + b\alpha \]
\[ = b(1 + \alpha) \]

Now
\[ K_{P_2} = \frac{n_Q \times n_P}{n_2} \left( \frac{P_{T_2}}{\Sigma n} \right)^{n_2} \]
or
\[ K_{P_2} = \frac{(b\alpha)(b\alpha) \cdot P_{T_2}}{[b(1-\alpha)][b(1+\alpha)]} \]
or
\[ K_{P_2} = \frac{4a^2 \cdot P_{T_1} - (1 - \alpha)^2}{P_{T_2} \cdot a^2} \]
or
\[ \frac{P_{T_1}}{P_{T_2}} = \frac{1}{9} \quad \text{given} \]
or
\[ \frac{P_{T_1}}{P_{T_2}} = \frac{1}{36} \]
i.e., (b) is the correct answer.

10. (b) \[ 6 = -\log 10^{-5} + \log \left( \frac{[\text{Salt}]}{[\text{Acid}]} \right) = 5 + \log \left( \frac{[\text{Salt}]}{[\text{Acid}]} \right); \]
\[ \log \left( \frac{[\text{Salt}]}{[\text{Acid}]} \right) \text{ must be } 1, \quad \therefore \quad \frac{[\text{Salt}]}{[\text{Acid}]} = \frac{10}{1} \text{ or } 10:1 \]

11. (b) \[ 3 \text{Fe}(s) + 4 \text{H}_2\text{O}(steam) \rightarrow \text{Fe}_2\text{O}_4(s) + 4 \text{H}_2(g) \]
\[ K_p = \frac{[\text{H}_2]^4}{[\text{H}_2\text{O}]^4} \]
only gaseous products and reactants.

By convention, we put \([\text{Fe}_2\text{O}_4(s)] = 1\) and \([\text{Fe}(s)] = 1\)

12. (b) \[ K_p = \frac{P_{HI}^2}{P_{H}^2 \times P_{I_2}} \]

Addition of \(I_2\) will increase \(P_{I_2}\), hence to keep \(K_p\)
constant, either \(P_{HI}\) should decrease or \(P_{HI}\) should increase. Hence the graph (B).

13. (a) \[ \text{H}_2 \rightarrow 2 \text{H}^- + \Delta \text{H} \]
According to Le-Chatelier’s Principal, to increase the rate of forward reaction, temperature should be
increased in case of endothermic reactions and pressure should be decreased in given case.

14. (c) Initial \(\text{pH} = pK_a + \log \left( \frac{[\text{Salt}]}{[\text{Acid}]} \right) \]
\[ = pK_a + \log \left( \frac{25 \times 1}{25 \times 1} \right) = pK_a \]

(a) \(\text{pH} = pK_a + \log \left( \frac{25 \times 1}{25 \times 1 + 5 \times 1} \right) \]
\[ = pK_a + \log \left( \frac{25}{30} \right) \]

(b) \(\text{pH} = pK_a + \log \left( \frac{25 \times 1}{25 \times 1 + 5 \times 5} \right) \]
\[ = pK_a + \log \left( \frac{25}{50} \right) \]

(c) \[ \text{CH}_3\text{COONa} + \text{HCl} \rightarrow \text{CH}_3\text{COOH} + \text{NaCl} \]
moles \(25 \times 1 \quad 5 \times 5 \)
Therefore, \([\text{Salt}]\) decreases to almost zero and pH decreases appreciably.

(d) \[ \text{CH}_3\text{COOH} + \text{NH}_4\text{OH} \rightarrow \text{CH}_3\text{COONH}_4 + \text{H}_2\text{O} \]
\[ 25 \times 1 \quad 5 \times 1 \quad 30 \text{ pH} \]
\[ = pK_a + \log \left( \frac{25 \times 1 + 5 \times 1}{25 \times 1 + 5 \times 5} \right) = pK_a + \log \left( \frac{30}{20} \right) \]

15. (c) Let \(s = \text{solubility} \)
\[ \text{AgIO}_3 \rightarrow \text{Ag}^+ + \text{IO}_3^- \]
\[ \text{K}_s = [\text{Ag}^+] \cdot [\text{IO}_3^-] = s \times s = s^2 \]
Given \(\text{K}_s = 1 \times 10^{-8} \]
\[ = \sqrt{\text{K}_s} = \sqrt{1 \times 10^{-8}} = 1.0 \times 10^{-4} \text{ mol/lit} \]
\(\therefore \quad \text{Molecular mass of Ag IO}_3 = 283 \)
\[ = 1.0 \times 10^{-4} \times 283 \times 100 \text{ g/lit} \]
\[ = 1000 \]
\[ = 2.83 \times 10^{-3} \text{ g/mmol} \]

16. (b) \[ [\text{H}^+]_{\text{initial}} = 10^{-5}; \quad [\text{H}^+]_{\text{final}} = 10^{-2}; \]
Increase in \([\text{H}^+] = \frac{10^{-2}}{10^{-5}} = 1000 \text{ times}. \]

17. (d) \[ \text{Li}_3\text{Na}_5[\text{AlF}_6]_2 \rightarrow 3\text{Li}^+ + 3\text{Na}^+ + 2[\text{AlF}_6]^{3-}; \]
\[ [\text{Li}^+] = 3a; \quad [\text{Na}^+] = 3a; \quad [\text{AlF}_6^{3-}] = 2a \]
Hence, \(\text{K}_s = [\text{Li}^+]^3 \cdot [\text{Na}^+]^3 \cdot [\text{AlF}_6^{3-}]^2 = (3a)^3 \cdot (3a)^3 \cdot (2a)^2 \]
\[ = 2916 \times 8 \]

18. (d) When pH of solution is zero, then conc. of \(\text{H}^+\) is 1M.
When pH of solution is 14, then \(\text{pH} = 14 - 14 = 0 \)
Both solutions will have same conc. of \(\text{H}^+\), which are strongly acidic.

19. (b) The pH at which the dipolar ion does not migrate in the electric field is called isoelectric point. It is given by
\[ \frac{pK_{a_1} + pK_{a_2}}{2} = 2.09 + 3.86 \]
\[ = 2.98. \]
20. (d) The correct order of acidic strength of the given species

\[ \text{in } \text{HSO}_3^- > \text{H}_2\text{O}^+ > \text{HSO}_4^- > \text{HCO}_3^- \]

or (i) < (iii) < (ii) < (iv)

It corresponds to choice (d) which is correct answer.

21. (a) \( \text{CO}_2 \) with \( \text{H}_2\text{O} \) forms \( \text{H}_2\text{CO}_3 \)

\[ \text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}^+ + \text{HCO}_3^- \]

\[ K_1 = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{CO}_2]} = 4.5 \times 10^{-7} \]

Again \( \text{pH} = -\log[\text{H}^+] = 7.4 \)

\[ \therefore [\text{H}^+] = 4.0 \times 10^{-8} \]

\[ \frac{4 \times 10^{-8} \cdot [\text{HCO}_3^-]}{[\text{CO}_2]} = 4.5 \times 10^{-7} \]

\[ \therefore \frac{[\text{HCO}_3^-]}{[\text{CO}_2]} = \frac{4.5 \times 10^{-7}}{4 \times 10^{-8}} = 11 \]

22. (b) An acidic solution cannot have a pH > 7.

23. (d) For the equilibria: \( \text{N}_2\text{O}_4(g) \leftrightarrow 2\text{NO}_2(g) \)

\[ K_p = K_c \times (RT)^n \]

Since temperature is constant so \( K_c \) or \( K_p \) will remain constant. Further since volume is halved, the pressure will be doubled so \( \alpha \) will decrease so as to maintain the constancy of \( K_c \) or \( K_p \).

24. (d) \( A + 2B \leftrightarrow 2C + D \)

\[
\begin{array}{c|c|c|c}
\text{A} & \text{B} & \text{C} & \text{D} \\
\hline
2 & 3 & 0 & 0 \\
\end{array}
\]

Initial conc.

\[ 2 - x \quad 3 - 2x \quad 2x \quad x \quad \text{equilibrium conc.} \]

Again \( 2 - x = 2x \)

\[ \therefore x = 2/3 \]

\[ K_c = \frac{(2x)^2 [x]}{(2 - x)(3 - 2x)^2} \]

Put \( x = 2/3 \)

\[ \therefore K_c = 0.32 \]

25. (c) The concentration of pure liquids and solids remain constant, and these terms are amalgamated (or merged) in the equilibrium constant. That is why, pure liquids and solids are ignored while writing the equilibrium constant expressions.

26. (a) When reaction becomes dynamic from other side an equilibrium is attained. At equilibrium change in free energy (\( \Delta \text{Br} \)) becomes zero.

27. (a) For given reaction \( K_p = \text{PCO}_2 \)

thus equilibrium is not affected by addition of \( \text{CaCO}_3(s) \).