DAY EIGHT

Equilibrium

Learning & Revision for the Day

- Equlibrium in Physical and Chemical Processes
- Law of Chemical Equilibrium
- Le-Chatelier's Principle
- Ionic Equilibrium
- Degree of Ionisation or Dissociation
- Acids and Bases
- Concept of pH
- Hydrolysis of Salt
- Solubility Product (K_{sp})
- Buffer Solutions

In a reversible reaction, the point at which there is no further change in concentration of reactants and products, is called **equilibrium state**. The mixture of reactants and products in the equilibrium state is called an **equilibrium mixture**.

Equilibrium in Physical and Chemical Processes

It can be established for both physical and chemical processes as discussed below:

- The equilibrium developing between different phases or physical properties of a substance is termed as **physical equilibria.**
  (i) Solid-liquid equilibrium, $H_2O(s) \rightleftharpoons H_2O(l)$
  (ii) Liquid-vapour equilibrium, $H_2O(l) \rightleftharpoons H_2O\text{ (vap)}$
  (iii) Solid-vapour equilibrium, $I_2(s) \rightleftharpoons I_2\text{(vap)}$
- In case of reversible reactions, when the concentration of reactants and products do not change with time, the reaction is called in a state of **chemical equilibrium**.
  (i) Homogeneous equilibrium,
  $$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$
  (ii) Heterogeneous equilibrium,
  $$MgCO_3(s) \rightleftharpoons MgO(s) + CO_2(g)\uparrow$$

Dynamic Nature of Equilibrium

It is always dynamic in nature, i.e. the reaction does not stop but goes on forward and backward directions with equal speed.

e.g. solid $\rightleftharpoons$ liquid (physical equilibria)

$H_2O\ (s) \rightleftharpoons H_2O(l)$ (273 K, 1 atm)

It indicates that at equilibrium, rate of conversion of ice into water = rate of conversion of water into ice

Law of Chemical Equilibrium

It states that "Rate of a reaction is directly proportional to the concentration of reactants with each concentration term raised to the power equal to the respective stoichiometric coefficient".

$$aA + bB \rightleftharpoons cC + dD$$

Rate of forward reaction $\propto [A]^a\,[B]^b = k_f\,[A]^a\,[B]^b$

Rate of backward reaction $\propto [C]^c\,[D]^d = k_b\,[C]^c\,[D]^d$

At equilibrium, $k_f\,[A]^a[B]^b = k_b[C]^c[D]^d$;

$$\frac{k_f}{k_b} = K_C = \frac{[C]^c[D]^d}{[A]^a[B]^b}$$

where, K_C = equilibrium constant
k_f = rate constant for forward reaction
k_b = rate constant for backward reaction

This expression is also known as law of chemical equilibrium

Equilibrium Constant

- It is the product of molar concentration of the products, each raised to the power equal to its stoichiometric coefficient divided by the product of the molar concentration of reactants, each raised to the power equal to its stoichiometric coefficient is constant at constant temperature.
- For a gaseous reaction, $K_p = \dfrac{p_C^c \cdot p_D^d}{p_A^a \cdot p_B^b}$

  where, K_p = equilibrium constant in terms of partial pressure
- The relation between K_p and K_C are given below:

$$K_p = K_C\,(RT)^{\Delta n_g}$$

R = gas constant, T = temperature in Kelvin
Δn_g = gaseous moles of products
– gaseous moles of reactants

Hence, If $\Delta n_g = 0,\ K_p = K_C$
If $\Delta n_g = +$ ve, $K_p > K_C$
If $\Delta n_g = -$ve, $K_p < K_C$

- Equilibrium constant in terms of mole fractions, K_χ

$$aA + bB \rightleftharpoons cC + dD$$

$$K_\chi = \frac{[\chi_C]^c\,[\chi_D]^d}{[\chi_A]^a\,[\chi_B]^b}$$

Similarly, $K_p = K_\chi\,(p)^{\Delta n_g}$

- Equilibrium constant in terms of activities,

$$K_a\,K_a = \frac{a_C^c \times a_D^d}{a_A^a \times a_B^b}$$

Activity = activity coefficient × molality (or molarity)
i.e. $a = \gamma \times m$

Some Facts Related to Equilibrium Constant

- Equilibrium constant (K_p or K_C) does not depend on pressure, volume, concentration and catalyst but depends only upon temperature.
- Equilibrium constant for a given reaction is independent of the reaction mechanism.
- Equilibrium constant depends on stoichiometric coefficient

e.g. $$H_2(g) + I_2(g) \overset{K_{C_1}}{\rightleftharpoons} 2HI(g)$$

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \overset{K_{C_2}}{\rightleftharpoons} HI(g),\ K_{C_2} = \sqrt{K_{C_1}}$$

$$HI\,(g) \overset{K_{C_3}}{\rightleftharpoons} \frac{1}{2}H_2(g) + \frac{1}{2}I_2(g),\ K_{C_3} = \frac{1}{K_{C_2}} = \frac{1}{\sqrt{K_{C_1}}}$$

- If a reaction is multiplied by n, the rate constant, K_c becomes $(K_C)^n$. n can be fraction also (+ve only).
- If K_1 be equilibrium constant for $P \rightleftharpoons Q$ and K_2 be equilibrium constant for $R \rightleftharpoons S$, is equilibrium constant for $P + R \rightleftharpoons Q + S$ is K_1K_2.
- Equilibrium constant depends on temperature

  For exothermic process $K_C \propto \dfrac{1}{T}$

  For endothermic process $K_C \propto T$

Units of K_C and K_p

(i) If $\Delta n_g = 0$, $K_p = K_C$, no units for both K_C and K_p.

(ii) If $\Delta n_g > 0$, unit of K_C is $(\text{mol L}^{-1})^{\Delta n_g}$ and that of K_p is $(\text{atm})^{\Delta n_g}$.

(iii) If $\Delta n_g < 0$, unit of K_C is $(\text{L mol}^{-1})^{\Delta n_g}$ and that of K_p is $(\text{atm})^{\Delta n_g}$.

Relation between K and ΔG°

Gibbs free energy change and equilibrium constant are related as :

$$\Delta G° = -2.303\ RT \log K_C \text{ or } \Delta G° = -2.303\ RT \log K_p$$

Significance of ΔG° are given below:

(i) If $\Delta G° < 0$, $\log K < 0 \Rightarrow K < 1$.
Therefore, forward reaction is spontaneous.

(ii) If $\Delta G° > 0$, $\log K < 0 \Rightarrow K < 1$.
Therefore, backward reaction is spontaneous.

(iii) If $\Delta G° = 0$, $\log K = 0$, $\Rightarrow K = 1$.
Therefore, reaction is at equilibrium.

Significance of K_C and K_p are given below :

(i) If $K_C > 10^3$, products predominate over reactants. In other words, if K_C is very large, the reaction proceeds almost in all the ways to completion.

(ii) If $K_C < 10^{-3}$, reactants predominate over products. In other words, if K_C is very small, the reaction proceeds hardly at all.

(iii) If K_C is in the range 10^{-3} to 10^3, appreciable concentration of both reactants and products are present.

Le-Chatelier's Principle

It states that change in any of the factors that determine the equilibrium conditions of a system, will cause the system to change in such a manner so as to reduce or to counteract the effect of the change.

Factors Affecting Equilibrium

Different factors affecting equilibrium are discussed below:

1. Effect of Concentration Change

The concentration stress of an added reactant or product is relieved by net reaction in the direction that consumes the added substance.

e.g. $A + B \rightleftharpoons C$

- If we increase the concentration of either A or B (reactants), the equilibrium goes in the direction that consumes A or B, i.e. forward side.
- If we increase the concentration of C (product), the equilibrium goes in the direction that consumes C, i.e. backward side.
- If we remove C (product), the equilibrium goes in the direction in which its concentration increases, i.e. forward side.
- If any of the species is in solid or in liquid state, its addition does not alter the original equilibrium.

NOTE Sweet substances cause tooth decay because on fermentation these produce H^+ ions which combine with OH^- ions and shift the equilibrium in forward direction

$$Ca_5(PO_4)_3OH\,(s) \underset{\text{Remineralisation}}{\overset{\text{Demineralisation}}{\rightleftharpoons}} 5Ca^{2+}(aq) + 3PO_4^{3-}(aq) + OH^-(aq)$$

2. Effect of Pressure

At high pressure, reaction goes from higher moles to lower moles or from higher volume to lower volume and *vice versa*.

- If $\Delta n_g = 0$, no effect on equilibrium due to pressure change.
- If $\Delta n_g > 0$, the increase in pressure favours backward reaction.
- If $\Delta n_g < 0$, the increase in pressure favours forward reaction. ($\Delta n_g =$ number of moles of gaseous products $-$ number of moles of gaseous reactants).
- Flash evaporation technique is used for concentrating some aqueous solutions which cannot be concentrated by normal boiling. Concentration of this type of solution is carried out under reduced pressure below 100°C.

3. Effect of Temperature

At high temperature, reaction goes to endothermic direction while at low temperature reaction goes to exothermic direction. The equilibrium constant for an endothermic reaction (positive ΔH) increases as the temperature increases.

$$K \propto T;\ \text{if } \Delta H^\circ = +\text{ve (endothermic)}$$

$$K \propto \frac{1}{T};\ \text{if } \Delta H^\circ = -\text{ve (exothermic)}$$

Freeze drying technique is used for drying heat sensitive substances. In this technique, water is made to sublime off at a temperature below 0°C.

4. Effect of Catalyst

A catalyst increases the rate of forward reaction as well as the rate of backward reaction, so it does not affect the equilibrium and equilibrium constant.

5. Effect of Inert Gas

At constant volume, there is no effect of addition of inert gas. At constant pressure, when inert gas is added, reaction goes from lower moles to higher moles.

Ionic Equilibrium

Existance of ions in equilibrium with its electrolytes is called ionic equilibrium. The species furnish ions can be a weak or strong electrolyte.

Weak and Strong Electrolytes

- Separation of an electrolyte into their ions either on fusion or dissolution is called **ionisation** or **dissociation**.

  $$NaCl + aq \longrightarrow Na^+(aq) + Cl^-(aq)$$

- **Weak electrolytes** is defined as a substance which dissociates partially into their ions in the solutions and such solutions are weak conductor of electricity.
  e.g. CH_3COOH, H_3PO_4, H_3BO_3, NH_4OH, HCN, etc.
- **Strong electrolytes** is defined as a substance which dissociates completely into their ions in solution and such solutions are very good conductor of electricity,
  e.g. HCl, H_2SO_4, NaOH, KOH, NaCl, KCl, etc.
- Ionic equilibrium can be defined as equilibrium which is established between the unionised molecules and the ions in the solution of weak electrolytes.
- The weak electrolytes are only partially ionised and a dynamic equilibrium is maintained after sometime between the ions and unionised molecules.
- **Ionisation of acids and bases** Acids and bases dissociate into the ions on ionisation. The acids which completely dissociates into their constituent ions in an aqueous medium are called as **strong acids**, e.g. HCl, HNO_3, H_2SO_4, etc. while the bases which are completely dissociated into ions in an aqueous medium are called **strong bases**, e.g. NaOH, $Ba(OH)_2$ etc.

  (Usually the term dissociation is used for weak electrolyte and ionisation for strong electrolyte).

Degree of Ionisation or Dissociation

- It is the fraction of total number of moles undergoing ionisation and is denoted by (α).

  Alternately, the fraction of the amount of an electrolyte present in the solution as free ions is called degree of ionisation (α).

$$\alpha = \frac{\text{number of moles of electrolyte dissociated as ions}}{\text{total number of moles of electrolyte dissolved}}$$

$$\text{or } \alpha = \frac{\text{amount of electrolyte dissociated}}{\text{initial amount}}$$

- **Degree of dissociation** (α) of a gaseous compound is related to its vapour density by $\alpha = \dfrac{D-d}{d(y-1)}$

  Here, D = molar density before dissociation/initial density

  d = density after dissociation/density of the gaseous mixture

  y = number of moles of products

  $$\text{Density of gas} = \frac{\text{Molecular weight}}{2}$$

  Molecular weight = Density of gas × 2

  $$M_O = D \times 2 \text{ or } M_C = d \times 2$$

  Here, M_O = Observed molecular weight (Abnormal)

  M_C = Calculated molecular weight (Theoretical)

Ostwald's Dilution Law

- It states that degree of dissociation of weak electrolyte is inversely proportional to the square root of concentration.

  $$\alpha \propto \frac{1}{\sqrt{C}}, \; \alpha = \sqrt{\frac{K}{C}} = \sqrt{KV}$$

  where, α = degree of dissociation

  V = volume containing 1 mole of weak electrolyte

  K = dissociation constant.
- This law is used to calculate the degree of dissociation, α for weak acids and bases from the known value of K.

Limitations of Ostwald's Law

Ostwald's law has following limitations :

- This law holds good only in case of weak electrolytes. Even weak electrolytes do not obey this law in concentrated solutions.
- The value of K can be calculated only in dilute solutions of weak electrolytes.

Factors Influencing Degree of Ionisation/Dissociation

Ionisation or dissociation is influenced by the following factors:

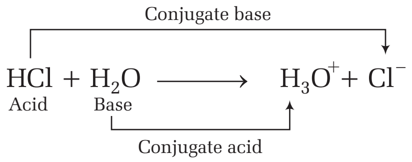
- For strong electrolyte, $\alpha = 1$ at normal dilution, while for most of the polar covalent compounds, i.e. weak electrolytes, $\alpha <<< 1$.
- Degree of ionisation of an electrolyte increases with polarity of the solvent.
- The degree of ionisation of an electrolyte decreases with increase in concentration of the electrolyte.
- The degree of ionisation rises with raise in temperature of the solution.
- The addition of species possessing a common ion to that of weak electrolyte causes a decrease in the degree of dissociation of weak electrolyte.

Acids and Bases

An acid is that whose aqueous solution tastes sour, turns blue litmus red, neutralises bases and so on. On the other hand, the aqueous solution of a base tastes bitter, turns red litmus blue, neutralises acid and so on.

Various concepts of acids and bases are given below:

- According to **Arrhenius concept**, the substances which release H^+ ions on dissolving in water are called acids and which release OH^- ions on dissolving in water are called bases.
- According to **Bronsted-Lowry concept**, acids are proton donors, while bases are proton acceptors.



- According to **Lewis concept**, acids are the substances which accept a pair of electrons to form a coordinate bond, e.g., BF_3 $AlCl_3$, etc. and bases are the substances which donate a pair of electrons to form coordinate bond. e.g., NH_3, CN^-, OH^-, I^- etc.
  - (i) **Acid strength** The extent to which the acidic property is shown by an acid is a measure of its strength.
  - (ii) The strength of an acidic solution does not depend upon its concentration but depend upon the number of H^+ ions present.
  - (iii) To measure the relative strength of the two acids, the measurements of their H^+ ions concentration, i.e. the degree of dissociation of their equinormal solutions is used.

    $$\frac{\text{Strength of acid I}}{\text{Strength of acid II}} = \frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_1/C}{K_2/C}} = \sqrt{\frac{K_1}{K_2}}$$

    where, K_1 and K_2 are the dissociation constants of two acids at the same concentration C.

    α_1 and α_2 are their degree of dissociation.

Ionisation of Polybasic Acids

- The acids which have more than one ionisable proton per molecule of acids are known as polybasic or polyprotic acids, e.g. oxalic acid (HOOC—COOH), H_2SO_4 and H_3PO_4.
- The ionisation reactions for a dibasic acid, H_2X are represented as

  $$H_2X(aq) \rightleftharpoons H^{\oplus}(aq) + HX^{\ominus}(aq)$$

  $$HX^{\ominus}(aq) \rightleftharpoons H^{\oplus}(aq) + X^{2-}(aq)$$

  The corresponding equilibrium constants are as:

  $$K_{a_1} = \frac{[H^{\oplus}][HX^{\ominus}]}{[H_2X]} \text{ and } K_{a_2} = \frac{[H^{\oplus}][X^{2-}]}{[HX^{\ominus}]}$$

  (K_{a_1} and K_{a_2} are called first and second ionisation constants, respectively, of the acid H_2X).

- Similarly, for tribasic acids such as H_3PO_4, there are three ionisation constants.
- It is found that K_{a_1} of polyprotic acid is greater than K_{a_2} or K_{a_3} (i.e. $K_{a_1} > K_{a_2} > K_{a_3}$), because it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces.
- Similarly, it is more difficult to remove a proton from a doubly charged anion as compared to single charged anion. The primary reaction involves the dissociation of H_2X and $H_3O^{\oplus}$ in the solution comes mainly from the first dissociation step.

Ionic Product of Water (K_w)

- Pure water is a weak electrolyte and is ionised according to following equation.

$$H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$$

At 25°C, for pure water

$$[H_3O^+] = [OH^-] = 10^{-7} \text{ mol/L}$$

$$K_w = [H_3O^+][OH^-] = 10^{-14} \text{ and } K = \frac{K_w}{55.55}$$

where, K_w = ionic product of water,

K = ionisation constant.

- Value of K_w depends upon temperature. If temperature increases, value of K_w also increases.

Concept of pH

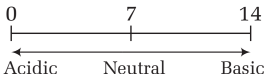
It is used to express and compare the acidic and basic strength of a solution.

- It is defined as the negative logarithm of H_3O^+ ion concentration (in moles per litre) present in it.

Thus, $pH = -\log [H_3O^+]$

Similarly, $pOH = -\log [OH^-] \Rightarrow pH + pOH = 14$

- Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as **pH scale**.
- **pH scale range** is 0 to 14 and it depends upon the value of K_w. As temperature increases, value of pH decreases at 25°C. pH scale range will be



(i) pH of very dilute ($\sim 10^{-8}$ M or lower) acids or bases is nearly 7 but not 7 (i.e. not simply $-\log$ [acid or base]) due to ionisation of water.

(ii) pH of strong acids with concentration > 1 M is never negative, it is zero only.

pH of Mixtures of Acids and Bases

The rules for determining the pH of mixtures of acids and bases are as follows:

(i) If strong acid or strong base remains unused, calculate the concentration or molarity of $H^{\oplus}$ ions and $\overset{\ominus}{O}H$ ions left in the solution and then calculate the pH or pOH accordingly.

(ii) If weak acid or weak base is left behind or remains unused, a buffer (acidic or basic) is formed. Calculate the concentration of salt formed (mmoles of salt formed/volume of solution) and the concentration of weak acid or weak base left behind. Use the buffer equation to calculate the pH of the solution.

(iii) If acids or bases are completely neutralised, then salt is formed. Calculate the concentration of the salt formed and use the hydrolysis equation to calculate the pH of the solution.

Hydrolysis of Salt

- The process of salt hydrolysis is actually the reverse process of neutralisation.
- The reaction of an anion or cation of the salt with water accompanied by cleavage of O—H bond, is called **hydrolysis of salt.**
- Salt hydrolysis affects the pH of the solution. On the basis of relative strengths of acid and base, the salts are divided into four categories:

  (i) Salts of strong acids and strong bases (i.e. neutral salts) do not undergo hydrolysis, e.g. NaCl, $CaSO_4$ etc. If such salt is dissolved in water, pH of the solution remains 7.

  (ii) Salt of a strong acid and weak base, e.g. NH_4Cl are called **acidic salts**. Such salts undergo cationic hydrolysis.

  pH of acidic salt solution will be less than 7.

  For such salts, $[H_3O^+] = \sqrt{K_h \times C}$

$$K_h = \frac{K_w}{K_b} \text{ or } pH = 7 - \frac{1}{2}[pK_b + \log C]$$

  where, K_h = hydrolysis constant

  K_b = ionisation constant for weak base

  C = molar concentration of salt.

(iii) Salt of strong base and weak acid, e.g. $NaNO_2$, NaCN, CH_3COONa are termed as **basic salts**. Such salts undergo anionic hydrolysis.

pH of basic salt solution will be more than 7.

For basic salts, $[OH^-] = \sqrt{K_h \times C}$ or $K_h = \frac{K_w}{K_a}$

$$pH = 7 + \frac{1}{2}[pK_a + \log C]$$

(iv) The salts other than halides, sulphates, nitrates of metals fall into this category. e.g. CH_3COONH_4 etc.

For such salts,

$$K_h = \frac{K_w}{K_a \times K_b}, \; pH = 7 + \frac{1}{2}[pK_a - pK_b]$$

$$BaSO_4(s) \underset{\text{in water}}{\xrightleftharpoons{\text{Saturated solution}}} \underset{S}{Ba^{2+}}(aq) + \underset{S}{SO_4^{-}}(aq)$$

There is no effect of dilution on the hydrolysis of salts of weak acid and weak base because h, pH and K_h are all independent of concentration, C.

Solubility Product (K_{sp})

It is defined as the product of molar concentration of its ions in a saturated solution, each concentration terms raised to the power equal to the number of ions produced on dissociation of one molecule of electrolyte.

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

$$\therefore \quad K_{sp} = [A^+]^x\,[B^-]^y$$

e.g. $$\mathrm{BaSO_4} \rightleftharpoons \underset{S}{\mathrm{Ba^{2+}}} + \underset{S}{\mathrm{SO_4^{2-}}}$$

$$K_{sp} = [\mathrm{Ba^{2+}}][\mathrm{SO_4^{2-}}]$$

$$\therefore \quad K_{sp} = S^2 \text{ or } S = \sqrt{K_{sp}}$$

where, S = solubility, K_{sp} = solubility product

e.g. $$A_2X_3 \longrightarrow \underset{2S}{2A^{3+}} + \underset{3S}{3X^{2-}}$$

$$K_{sp} = [A^{3+}]^2[X^{2-}]^3$$

$$\Rightarrow \quad K_{sp} = (2S)^2(3S)^3$$

$$\therefore \quad K_{sp} = 108S^5$$

Ionic Product (Q)

(At any stage of reaction)

It is the product of ions and give the direction of reaction.

If $Q > K_{sp}$, precipitate will be formed.

If $Q < K_{sp}$, precipitate does not form.

If $Q = K_{sp}$, reaction is at equilibrium.

Buffer Solutions

It is the solution, which maintains its pH constant or reserve acidic or basic nature even upon addition of small amounts of acid or base. The ability of buffer solution to resist changes in pH on addition of acid or base is called buffer action.

Types of buffer solutions
- Acidic buffer [pH<7]
- Basic buffer [pH>7]

Henderson's Equation

- A buffer solution pH of which is less than 7 is called **acidic buffer**. Weak acid + salt of the acid with strong base

  e.g. $\mathrm{CH_3COOH + CH_3COONa}$; $\mathrm{HCN + NaCN}$
- A buffer solution having pH more than 7 is called **basic buffer**. Weak base + salt of the base with strong acid

  e.g. $\mathrm{NH_4OH + NH_4Cl}$, $\mathrm{C_6H_5NH_2 + C_6H_5NH_3^+Cl^-}$
- A buffer solution should exhibit following characteristics:
  - (i) Buffer solutions possess a definite pH value.
  - (ii) Their pH value remains constant on keeping long or on dilution.
  - (iii) The pH value is not changed on the addition of a strong acid in acidic buffer and a strong base in basic buffer.

(i) For acidic buffer; $\mathrm{pH} = \mathrm{p}K_a + \log\dfrac{[\text{salt}]}{[\text{acid}]}$

(ii) For basic buffer; $\mathrm{pOH} = \mathrm{p}K_b + \log\dfrac{[\text{salt}]}{[\text{base}]}$

$$\mathrm{pH} + \mathrm{pOH} = 14$$

Buffer Capacity

The quantitatively defined as the number of moles of acid or base added to 1 L in of butter solution to change the pH by unity.

Buffer capacity

$$= \frac{\text{number of moles of acid / base added to 1 L of buffer}}{\text{change in pH}}$$

Buffer capacity is maximum when

(a) $[\text{salt}] = [\text{acid}]$, $\mathrm{pH} = \mathrm{p}K_a$ for acidic buffer

(b) $[\text{salt}] = [\text{base}]$, $\mathrm{pH} = \mathrm{p}K_b$ for basic buffer

Greater the buffer capacity, larger is its capacity to resist the change in pH value.

Common-Ion Effect

- It can be defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium.

  e.g. $$\mathrm{NH_4OH \rightleftharpoons NH_4^+ + OH^-}$$
- If $\mathrm{NH_4Cl}$ or NaOH is added to $\mathrm{NH_4OH}$ solution, the above equilibrium will shift to the left due to high concentration of common ion and therefore, the ionisation of $\mathrm{NH_4OH}$ is further suppressed.

DAY PRACTICE SESSION 1

FOUNDATION QUESTIONS EXERCISE

1 4 moles of *A* are mixed with 4 moles of *B*. At equilibrium for the reaction, $A + B \rightleftharpoons C + D$, 2 moles of *C* and *D* are formed. The equilibrium constant for the reaction will be

(a) 1 (b) 1/2 (c) 4 (d) 1/4

2 If the value of an equilibrium constant for a particular reaction is 1.6×10^{12} then at equilibrium the system will contain **→ CBSE-AIPMT 2015**

(a) all reactants
(b) mostly reactants
(c) mostly products
(d) similar amounts of reactants and products

3 The following equilibria are given

I. $N_2 + 3H_2 \rightleftharpoons 2NH_3$; K_1
II. $N_2 + O_2 \rightleftharpoons 2NO$; K_2
III. $H_2 + \frac{1}{2} O_2 \rightleftharpoons H_2O$; K_3

The equilibrium constant for the reaction,

$$2NH_3 + \frac{5}{2}O_2 \rightleftharpoons 2NO + 3H_2O$$

in terms of K_1, K_2 and K_3 will be **→ NEET 2017**

(a) $K_1K_3^2/K_2$ (b) $K_2K_3^3/K_1$ (c) $\frac{K_2K_3}{K_1}$ (d) $\frac{K_2^3K_3}{K_1}$

4 One mole of a compound *AB* reacts with one mole of a compound *CD* according to the equation $AB + CD \rightleftharpoons AD + CB$. When equilibrium had been established it was found that 3/4 mole each of reactants *AB* and *CD* had been converted to *AD* and *CB*. There is no change in volume. The equilibrium constant for the reaction is

(a) $\frac{9}{16}$ (b) $\frac{1}{9}$ (c) $\frac{16}{19}$ (d) 9

5 A mixture of 0.3 moles of H_2 and 0.3 mole of I_2 is allowed to react in a 10 L evacuated flask at 500°C. The reaction is $H_2 + I_2 \rightleftharpoons 2HI$, the *K* is found to be 64. The amount of unreacted I_2 at equilibrium is

(a) 0.03 mol (b) 0.06 mol
(c) 0.09 mol (d) 3.6 mol

6 For the reaction,

$$H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(g);$$

If initial concentration of $[H_2] = [CO_2]$ and *x* mol/L of hydrogen is consumed at equilibrium, the correct expression of K_p is

(a) $\frac{x^2}{(1-x)^2}$ (b) $\frac{x^2}{(2+x)^2}$ (c) $\frac{x^2}{1-x^3}$ (d) $\frac{(1+x)^2}{(1-x)^2}$

7 At 3000 K, the equilibrium pressure of CO_2, CO and O_2 are 0.6, 0.4 and 0.2 atm respectively. K_p for the reaction, $2CO_2 \rightleftharpoons 2CO + O_2$ is

(a) 0.089 (b) 0.098
(c) 0.189 (d) 0.198

8 In which of the following equilibrium K_c and K_p are not equal? **→ CBSE-AIPMT 2010**

(a) $2C(s) + O_2(g) \rightleftharpoons 2CO_2(g)$
(b) $SO_2(g) + NO_2(g) \rightleftharpoons SO_3(g) + NO(g)$
(c) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$
(d) $2NO(g) \rightleftharpoons N_2(g) + O_2(g)$

9 For the reaction,

$$CH_4(g) + 2O_2(g) \rightleftharpoons CO_2(g) + 2H_2O(l);$$
$$\Delta_r H = -170.8 \text{ kJ mol}^{-1}$$

Which of the following statements is not true?

(a) At equilibrium, the concentration of $CO_2(g)$ and $H_2O(l)$ are not equal
(b) The equilibrium constant for the reaction is given by

$$K_p = \frac{[CO_2]}{[CH_4][O_2]}$$

(c) Addition of $CH_4(g)$ or $O_2(g)$ at equilibrium will cause a shift to the right
(d) The reaction is exothermic

10 $K_p = 0.04$ atm at 899 K for the equilibrium shown below. The equilibrium concentration of C_2H_6 when it placed in a flask at 4.0 atm pressure and allowed to come to equilibrium is

$$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

(a) 0.30 (b) 3.6 (c) 4.0 (d) 2.8

11 The value of K_p for the following reaction $2H_2S(g) \rightleftharpoons 2H_2(g) + S_2(g)$; is 1.2×10^{-2} at 106.5°C. The value of K_c for this reaction is

(a) $= 1.2 \times 10^{-2}$ (b) $< 1.2 \times 10^{-2}$
(c) $> 1.2 \times 10^{-2}$ (d) None of these

12 Which of the following statement is correct for a reversible process in a state of equilibrium? **→ CBSE-AIPMT 2015**

(a) $\Delta G = -2.30RT \log K$ (b) $\Delta G = 2.30RT \log K$
(c) $\Delta G^\circ = -2.30RT \log K$ (d) $\Delta G^\circ = 2.30RT \log K$

13 What is the effect of increasing pressure on the dissociation of PCl_5, according to the equation?

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) - x$ cal

(a) Dissociation decreases
(b) Dissociation increases
(c) Dissociation does not change
(d) None of the above

14 Of the following which change will shift the equilibrium towards the product?

$$I_2(g) \rightleftharpoons 2I(g);\ \Delta H_r{}^\circ(298) = +150 \text{ kJ}$$

(a) Increase in temperature
(b) Increase in total pressure
(c) Increase in concentration of I
(d) Decrease in concentration of I_2

15 For the reaction, $PCl_3(g) + Cl_2(g) \rightleftharpoons PCl_5(g)$, the position of equilibrium can be shifted to the right by

(a) doubling the volume
(b) increasing the temperature
(c) addition of Cl_2 at constant volume
(d) addition of equimolar quantities of PCl_3 and PCl_5

16 For the reversible reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g) + \text{Heat}$$

The equilibrium shifts in forward direction

→ CBSE-AIPMT 2014

(a) By increasing the concentration of $NH_3(g)$
(b) By decreasing the pressure
(c) By decreasing the concentration of $N_2(g)$ and $H_2(g)$
(d) By increasing the pressure and decreasing temperature

17 The value of ΔH for the reaction,
$X_2(g) + 4Y_2(g) \rightleftharpoons 2XY_4(g)$ is less than zero. Formation of $XY_4(g)$ will be favoured at **→ CBSE-AIPMT 2011**

(a) low pressure and low temperature
(b) high temperature and low pressure
(c) high pressure and low temperature
(d) high temperature and high pressure

18 The degree of dissociation of 1.0 M weak acid, HA is 0.5%. If 2 mL of 1.0 M HA solution is diluted to 32 mL, the degree of dissociation of the acid and H_3O^+ ion concentration in the resulting solution will be respectively?

(a) 0.02 and 8.2×10^{-12}
(b) 0.02 and 3.125×10^{-4}
(c) 0.02 and 1.25×10^{-3}
(d) 1.25×10^{-3} and 0.02

19 The percentage of pyridine (C_5H_5N) that forms pyridinium ion $(C_5H_5N^+H)$ in a 0.10 M aqueous pyridine solution $(K_b$ for $C_5H_5N = 1.7 \times 10^{-9})$ is **→ NEET 2016, Phase II**

(a) 0.0060%
(b) 0.013%
(c) 0.77%
(d) 1.6%

20 The dissociation equilibrium of a gas AB_2 can be represented as

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

The degree of dissociation is x and is small compared to 1. The expression relating the degree of dissociation (x) with equilibrium constant K_p and total pressure p is

→ CBSE-AIPMT 2008

(a) $(2K_p/p)$
(b) $(2K_p/p)^{1/3}$
(c) $(2K_p/p)^{1/2}$
(d) (K_p/p)

21 The conjugate base of $H_2PO_4^-$ is

(a) PO_4^{3-}
(b) P_2O_5
(c) H_3PO_4
(d) HPO_4^{2-}

22 Which of the following is least likely to behave as Lewis base? **→ CBSE-AIPMT 2011**

(a) NH_3
(b) BF_3
(c) OH^-
(d) H_2O

23 Ammonium ion is

(a) neither an acid nor a base
(b) both an acid and a base
(c) a conjugate acid
(d) a conjugate base

24 Which of the following fluoro-compounds is most likely to behave as a Lewis base? **→ NEET 2016, Phase II**

(a) BF_3
(b) PF_3
(c) CF_4
(d) SiF_4

25 Which of the following is electron deficient?

(a) $(CH_3)_2$
(b) $(SiH_3)_2$
(c) $(BH_3)_2$
(d) PH_3

26 K_{a_1}, K_{a_2} and K_{a_3} are the respective ionisation constant for the following reactions.

$$H_2S \rightleftharpoons H^+ + HS^-$$
$$HS^- \rightleftharpoons H^+ + S^{2-}$$
$$H_2S \rightleftharpoons 2H^+ + S^{2-}$$

The correct relationship between K_{a_1}, K_{a_2} and K_{a_3} is

(a) $K_{a_3} = K_{a_1} \times K_{a_2}$
(b) $K_{a_3} = K_{a_1} \times K_{a_2}$
(c) $K_{a_3} = K_{a_1} - K_{a_2}$
(d) $K_{a_3} = K_{a_1} / K_{a_2}$

27 What is the pH of 0.01 M glycine solution? For glycine $K_{a_1} = 4.5 \times 10^{-3}$ and $K_{a_2} = 1.7 \times 10^{-10}$ at 298 K?

(a) 3.0
(b) 10.0
(c) 6.1
(d) 7.1

28 Given pH of a solution A is 3 and it is mixed with another solution B having pH 2. If both mixed then resultant pH of the solution will be

(a) 3.2
(b) 1.9
(c) 3.4
(d) 3.5

29 Hydrogen ion concentration in mol/L in a solution of pH = 5.4 will be

(a) 3.98×10^{-6}
(b) 3.68×10^{-6}
(c) 3.88×10^{6}
(d) 3.98×10^{8}

30 pH of 0.08 mol dm^{-3} HOCl solution is 2.85. Calculate its ionisation constant.

(a) 24.9×10^{-6}
(b) 28.6×10^{-5}
(c) 2.5×10^{-6}
(d) 24.9×10^{-5}

31 Following solutions were prepared by mixing different volumes of NaOH and HCl of different concentrations:

I. 60 mL $\frac{M}{10}$ HCl + 40 mL $\frac{M}{10}$ NaOH
II. 55 mL $\frac{M}{10}$ HCl + 45mL $\frac{M}{10}$ NaOH
III. 75 mL $\frac{M}{10}$ HCl + 25 mL $\frac{M}{5}$ NaOH
IV. 100 mL $\frac{M}{10}$ HCl + 100 mL $\frac{M}{10}$ NaOH **→ NEET-2018**

pH of which one of them will be equal to 1?

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

32 By adding 20 mL of 0.1 N HCl to 20 mL 0.001 N KOH, the pH of the obtained solution will be

(a) 2 (b) 1.3 (c) 0 (d) 7

33 Equimolar solutions of the following substances were prepared separately. Which one of these will record the highest pH value? **→ CBSE-AIPMT 2012**

(a) $BaCl_2$ (b) $AlCl_3$ (c) LiCl (d) $BeCl_2$

34 The ionisation constant of ammonium hydroxide is 1.77×10^{-5} at 298 K. Hydrolysis constant of ammonium chloride is **→ CBSE-AIPMT 2009**

(a) 5.65×10^{-10} (b) 6.50×10^{-12}
(c) 5.65×10^{-13} (d) 5.65×10^{-12}

35 Concentration of the Ag^+ ions in a saturated solution of $Ag_2C_2O_4$ is 2.2×10^{-4} mol^{-1} solubility product of $Ag_2C_2O_4$ is **→ NEET 2017**

(a) 2.42×10^{-8} (b) 2.66×10^{-12}
(c) 4.5×10^{-11} (d) 5.3×10^{-12}

36 The solubility of $BaSO_4$ in water is 2.42×10^{-3} gL^{-1} at 298 K. The value of its solubility product (K_{sp}) will be (Given molar mass of $BaSO_4$ = 233 g mol^{-1}) **→ NEET 2018**

(a) 1.08×10^{-14} mol^{2}L^{-2} (b) 1.08×10^{-12} mol^{2}L^{-2}
(c) 1.08×10^{-10} mol^{2}L^{-2} (d) 1.08×10^{-8} mol^{2}L^{-2}

37 MY and NY_3, two nearly insoluble salts, have the same K_{sp} values of 6.2×10^{-13} at room temperature. Which statement would be true in regard to MY and NY_3?

→ NEET 2016, Phase I

(a) The molar solubility of MY in water is less than that of NY_3
(b) The salts MY and NY_3 are more soluble in 0.5M KY than in pure water
(c) The addition of the salt of KY to solution of MY and NY_3 will have no effect on their solubilities
(d) The molar solubilities of MY and NY_3 in water are identical.

38 The solubility of AgCl(s) with solubility product 1.6×10^{-10} in 0.1 M NaCl solution would be **→ NEET 2016, Phase II**

(a) 1.26×10^{-5} M (b) 1.6×10^{-9} M
(c) 1.6×10^{-11} M (d) zero

39 If pH of a saturated solution of Ba $(OH)_2$ is 12, the value of its K_{sp} is **→ CBSE-AIPMT 2010**

(a) $4.00 \times 10^{-6}M^3$ (b) $4.00 \times 10^{-7}M^3$
(c) $5.00 \times 10^{-7}M^3$ (d) $5.00 \times 10^{-6}M^3$

40 In which of the following solvents is silver chloride most soluble?

(a) 0.1 mol dm^{-3} $AgNO_3$ solution
(b) 0.1 mol dm^{-3} HCl solution
(c) H_2O
(d) Aqueous ammonia

41 A buffer solution is used in

(a) preparation of potash alum
(b) the removal of PO_4^{3-} ions
(c) increasing the pH value of a solution
(d) precipitation of $Cr(OH)_3$ from $CrCl_3$

42 An aqueous solution of 1 M NaCl and 1 M HCl is

(a) not a buffer but pH < 7 (b) not a buffer but pH = 7
(c) a buffer with pH < 7 (d) a buffer with pH > 7

43 0.1 mole of $CH_3NH_2(K_b = 5 \times 10^{-4})$ is mixed with 0.08 moles of HCl and diluted to one litre. What will be the H^+ concentration in the solution?

(a) 8×10^{-2} M (b) 8×10^{-11}M
(c) 1.6×10^{-11} M (d) 8×10^{-5} M

44 Which one of the following pairs of solution is not an acidic buffer? **→ CBSE-AIPMT 2015**

(a) $HClO_4$ and $NaClO_4$
(b) CH_3COOH and CH_3COONa
(c) H_2CO_3 and Na_2CO_3
(d) H_3PO_4 and Na_3PO_4

45 A physician wishes to prepare a buffer solution at pH = 3.58 that efficiently resist changes in pH yet contains only small concentration of the buffering agents. Which one of the following weak acid together with its sodium salt would be best to use?

(a) *m*-chlorobenzoic acid (pK_a = 3.98)
(b) *p*-chlorocinnamic acid (pK_a = 4.41)
(c) 2,5-dihydroxy benzoic acid (pK_a = 2.97)
(d) Acetoacetic acid (pK_a = 3.58)

46 Buffer solutions have constant acidity and alkalinity because **→ CBSE-AIPMT 2012**

(a) these give unionised acid or base on reaction with added acid or alkali
(b) acids and alkalies in these solutions are shielded from attack by other ions
(c) they have large excess of H^+ or OH^- ions
(d) they have fixed value of pH

47 A buffer solution is prepared in which the concentration of NH_3 is 0.30 M and the concentration of NH_4^+ is 0.20 M. If the equilibrium constant, K_b for NH_3 is to equal 1.8×10^{-5}, what is the pH of this solution? (log 2.7 = 0.43)
→ CBSE-AIPMT 2011

(a) 9.43 (b) 11.72
(c) 8.73 (d) 9.08

48 What is $[H^+]$ in mol/L of a solution that is 0.20 M in CH_3COONa and 0.10 M in CH_3COOH ?
(K_a for $CH_3COOH = 1.8\times 10^{-5}$) **→ CBSE-AIPMT 2010**

(a) 3.5×10^{-4} (b) 1.1×10^{-5}
(c) 1.8×10^{-5} (d) 9.0×10^{-6}

49 In a buffer solution containing equal concentration of B^- and HB, the K_b for B^- is 10^{-10}. The pH of buffer solution is
→ CBSE-AIPMT 2010

(a) 10 (b) 7
(c) 6 (d) 4

50 In which of the following, dissociations of NH_4OH will be minimum? **→ CBSE-AIPMT 2010**

(a) NaOH (b) H_2O
(c) NH_4Cl (d) NaCl

DAY PRACTICE SESSION 2

PROGRESSIVE QUESTIONS EXERCISE

1 A buffer solution with pH 9 is to be prepared by mixing NH_4Cl and NH_4OH. Calculate the number of moles of NH_4Cl that should be added to one litre of 1.0 M NH_4OH. $[K_b = 1.8 \times 10^{-5}]$

(a) 3.4 (b) 2.6
(c) 1.5 (d) 1.99

2 For a reaction,

(i) $CaCO_3\ (s) \rightarrow CaO\ (s) + CO_2(g),\ p_{CO_2} = 2\,\text{atm}$

(ii) $CO_2\ (l) + C(s) \rightarrow 2CO(g); K = 6\,\text{atm}$

Hence, equilibrium constant for the reaction

$CaCO_3\ (s) + C(s) \rightleftharpoons CaO(s) + 2CO(g)$ is

(a) 8 atm (b) 4 atm
(c) 12 atm (d) 3 atm

3 At constant temperature, the equilibrium constant (K_p) for the decomposition reaction. $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is expressed by $K_p = \dfrac{(4x^2p)}{(1-x^2)}$; where, p = pressure, x = extent of decomposition, which one of the following statements is true?

(a) K_p increases with increase of p
(b) K_p remains constant with change in p and x
(c) K_p increases with increase of x
(d) None of the above

4 An amount of solid NH_4HS is placed in a flask already containing ammonia gas at a certain temperature and 0.50 atm pressure. Ammonium hydrogen sulphide decomposes to yield NH_3 and H_2S gases in the flask.
When the decomposition reaction reaches at equilibrium, the total pressure in the flask rises to 0.84 atm.
The equilibrium constant for NH_4HS decomposition at this temperature is

(a) 0.11 (b) 0.22 (c) 0.33 (d) 0.44

5 pH of a buffer solution decreases by 0.02 units when 0.12 g of acetic acid is added to 250 mL of a buffer solution of acetic acid and potassium acetate at 27°C. The buffer capacity of the solution is

(a) 0.1 (b) 10 (c) 1 (d) 0.4

6 At a given temperature, equilibrium is attained when 50% of each reactant is converted into the products

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

If amount (in mol) of $B(g)$ is doubled, percentage of B converted into products will be

(a) 100% (b) 50%
(c) 66.67% (d) 33.33%

7 Which of the following, on the addition will cause deep red colour to disappear?

$$\underset{\text{(Pale yellow)}}{Fe^{3+}(aq)} + \underset{\text{(Colourless)}}{SCN^-} \rightleftharpoons \underset{\text{(Deep red)}}{Fe(SCN)^{2+}(aq)}$$

I : $AgNO_3$; II: $HgCl_2$
III: $H_2C_2O_4$ (oxalic acid)

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

8 The rapid change of pH near the stoichiometric point of an acid-base titration is the basis of indicator detection. pH of the solution is related to ratio of the concentration of the conjugate acid (HIn) and base (In^-) forms of the indicator given by the expression

(a) $\log \dfrac{[In^-]}{[HIn]} = pK_{In} - pH$

(b) $\log \dfrac{[HIn]}{[In^-]} = pK_{In} - pH$

(c) $\log \dfrac{[HIn]}{[In^-]} = pH - pK_{In}$

(d) $\log \dfrac{[In^-]}{[HIn]} = pH - pK_{In}$

9 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 1.74×10^{-5}, 3.0×10^{-8} and 1.8×10^{-4} respectively. Which of the following orders of 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

10 For the following equilibrium, $N_2O_4 \rightleftharpoons 2NO_2$ in gaseous phase, NO_2 is 50% of the total volume when equilibrium is setup. Hence, per cent of dissociation of N_2O_4 is

(a) 50% (b) 25% (c) 66.66% (d) 33.33%

11 For the following reaction,

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

The equilibria relation between K_C and K_x is

(a) $K_C = K_x (RT)^{-1}$ (b) $K_C = K_x (RT)$
(c) $K_C = K_x \left(\dfrac{1}{V}\right)$ (d) $K_C = K_x (V)$

12 A weak acid HX has the dissociation constant 1×10^{-5} M. It forms a salt NaX on reaction with alkali. The degree of hydrolysis of 0.1 M solution of NaX is

(a) 0.0001% (b) 0.01% (c) 0.1% (d) 0.15%

13 For the following equilibrium: (omitting charges)

I. $M + \text{Cl} \longrightarrow M\text{Cl}$ $\quad K_{\text{eq}} = \beta_1$

II. $M\text{Cl} + \text{Cl} \longrightarrow M\text{Cl}_2$ $\quad K_{\text{eq}} = \beta_2$

III. $M\text{Cl}_2 + \text{Cl} \longrightarrow M\text{Cl}_3$ $\quad K_{\text{eq}} = \beta_3$

IV. $M + 3\text{Cl} \longrightarrow M\text{Cl}_3$ $\quad K_{\text{eq}} = K$

then relation between K, β_1, β_2 and β_3 is

(a) $p_K = p_{\beta_1} + p_{\beta_2} + p_{\beta_3}$
(b) $K = \beta_1\beta_2\beta_3$
(c) $\log K = \log \beta_1 + \log\beta_2 + \log \beta_3$
(d) All of the above

14 When NH_3 is heated in a 0.50 L flask at 700 K and 100 atm pressure, it decomposes into N_2 and H_2 and their equilibrium moles are given below :

$$\underset{0.30}{2NH_3(g)} \rightleftharpoons \underset{0.30}{N_2(g)} + \underset{0.90}{3H_2(g)}$$

Which of the pairs given represents correct value?

Initial moles of NH_3	**K_C for NH_3 formation**
(a) 0.80	9.72
(b) 0.90	9.72
(c) 0.80	0.103
(d) 0.90	0.103

15 If x moles of lead acetate and 0.1 mole of acetic acid in 1 L solution make a solution of pH = 5.04. Then, find the value of x, If pK_a of CH_3COOH is 4.74

(a) 0.2 mol (b) 0.05 mol
(c) 0.1 mol (d) 0.02 mol

16 A solution which is 10^{-3} M each in Mn^{2+}, Fe^{2+}, Zn^{2+} and Hg^{2+} is treated with 10^{-16} M sulphide ion. If K_{sp} of MnS, FeS, ZnS and HgS are $10^{-15}, 10^{-23}, 10^{-20}$ and 10^{-54} respectively, which one will precipitate first?

(a) FeS (b) MgS
(c) HgS (d) ZnS

17 HCOOH and CH_3COOH solution have equal pH. If K_1 / K_2 (ratio of acid ionisation constant) is 4, their molar concentration ratio will be

(a) 2 (b) 0.5 (c) 4 (d) 0.25

18 pK_b of NH_3 A^- is 4.74 and pK_b of, B^- and C^- are 4, 5 and 6, respectively. Aqueous solution of 0.01 M has pH in the increasing order

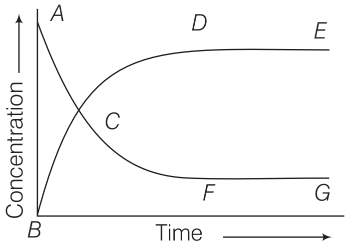
(a) $NH_4 A < NH_4 B < NH_4 C$
(b) $NH_4 C < NH_4 B < NH_4 A$
(c) $NH_4 C < NH_4 A < NH_4 B = 7$
(d) All have equal pH being salt of weak acid and weak base

19 $N_2O_4 \rightleftharpoons 2NO_2, K_C = 4$. This reversible reaction is studied graphically as shown in the given figure. Select the correct statements out of I, II and III.

I. Reaction quotient has maximum value at point A.

II. Reaction proceeds left to right at a point when $[N_2O_4] = [NO_2] = 0.1$ M

III. $K_c = Q$ when point D or F is reached.



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

20 1 mole each of CO (g), $H_2O(g)$, $H_2(g)$, and $CO_2(g)$ are place in 1 L flask at 25°C. When following equilibrium is setup

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

$K_p = 9$. Hence, CO_2 present at equilibrium is

(a) 0.5 mol (b) 1.5 mol (c) 0.25 mol (d) 3.0 mol

ANSWERS

SESSION 1	**1** (a)	**2** (c)	**3** (b)	**4** (d)	**5** (b)	**6** (a)	**7** (a)	**8** (a)	**9** (b)	**10** (b)
	11 (b)	**12** (c)	**13** (a)	**14** (a)	**15** (c)	**16** (d)	**17** (c)	**18** (c)	**19** (b)	**20** (b)
	21 (d)	**22** (b)	**23** (c)	**24** (b)	**25** (c)	**26** (b)	**27** (d)	**28** (b)	**29** (a)	**30** (a)
	31 (d)	**32** (b)	**33** (a)	**34** (a)	**35** (d)	**36** (c)	**37** (a)	**38** (b)	**39** (c)	**40** (d)
	41 (b)	**42** (a)	**43** (b)	**44** (a)	**45** (d)	**46** (a)	**47** (a)	**48** (d)	**49** (d)	**50** (c)
SESSION 2	**1** (d)	**2** (c)	**3** (b)	**4** (a)	**5** (d)	**6** (d)	**7** (d)	**8** (d)	**9** (b)	**10** (d)
	11 (d)	**12** (b)	**13** (d)	**14** (d)	**15** (c)	**16** (c)	**17** (d)	**18** (b)	**19** (b)	**20** (b)

Hints and Explanations

SESSION 1

1 $$A + B \rightleftharpoons C + D$$

Initial conc. $\quad 4 \quad 4 \quad 0 \quad 0$

Conc. at eq. $\quad (4-2) \quad (4-2) \quad 2 \quad 2$

Eq. constant $K_C = \dfrac{[C][D]}{[A][B]} = \dfrac{2 \times 2}{2 \times 2} = 1$

2 For a reaction,

$$A \rightleftharpoons B$$

Reactant $\quad$ Product

$$K = \frac{[B]_{eq}}{[A]_{eq}}$$

$$1.6 \times 10^{12} = \frac{[B]_{eq}}{[A]_{eq}}$$

$\therefore \quad [B]_{eq} >> [A]_{eq}$

So, mostly the product will be present in the equilibrium mixture.

3 From given equations,

We have, $K_1 = \dfrac{[NH_3]^2}{[N_2][H_2]^3}$

$$K_2 = \frac{[NO]^2}{[N_2][O_2]}$$

$$K_3 = \frac{[H_2O]}{[H_2][O_2]^{1/2}}$$

For the given reaction,

$$K = \frac{[NO]^2 [H_2O]^3}{[NH_3]^2 [O_2]^{5/2}}$$

$$\frac{K_2 K_3^3}{K_1} = \frac{[NO]^2 [H_2O]^3}{[NH_3]^2 [O_2]^{5/2}}, \; K = \frac{K_2 K_3^3}{K_1}$$

4 $$AB + CD \longrightarrow AD + CB$$

Initial conc. $\quad 1 \quad 1 \quad 0 \quad 0$

Conc. at equi. $\left(1 - \dfrac{3}{4}\right)\left(1 - \dfrac{3}{4}\right) \quad \dfrac{3}{4} \quad \dfrac{3}{4}$

$$K_C = \frac{[AD][CB]}{[AB][CD]} = \frac{\left\{\frac{3}{4}\right\}\left\{\frac{3}{4}\right\}}{\left\{\frac{1}{4}\right\}\left\{\frac{1}{4}\right\}} = 9$$

5 $$K_C = \frac{[HI]^2}{[H_2][I_2]}$$

$$64 = \frac{x^2}{0.03 \times 0.03}$$

$$x^2 = 64 \times 9 \times 10^{-4}$$

$$x = 8 \times 3 \times 10^{-2} = 0.24$$

x is the amount of HI at equilibrium,

$\therefore$ Amount of I_2 at equilibrium

$= 0.30 - 0.24 = 0.06$

6 $H_2(g) + CO_2(g) \rightleftharpoons CO(g) + H_2O(l)$

Initial conc. $\quad 1 \quad 1 \quad 0 \quad 0$

Conc. at equi. $(1-x) \quad (1-x) \quad x \quad x$

$$K_p = \frac{p_{CO} \cdot p_{H_2O}}{p_{H_2} \cdot p_{CO_2}} = \frac{x \cdot x}{(1-x)(1-x)}$$

$$= \frac{x^2}{(1-x)^2}$$

7. $$K_p = \frac{[p_{CO}]^2 [p_{O_2}]}{[p_{CO_2}]}$$

$$= \frac{[0.4]^2 \times [0.2]}{[0.6]^2} = 0.0888 \approx 0.089$$

8 The reaction for which the number of moles of gaseous products (n_p) is not equal to the number of moles of gaseous reactants (n_R), has different value of K_C and K_p.

(a) $n_p \neq n_R$, thus, $K_p \neq K_C$

(b) $n_p = n_R = 2$, thus, $K_p = K_C$

(c) $n_p = n_R = 2$, thus, $K_p = K_C$

(d) $n_p = 2, n_R = 2$ thus, $K_p = K_C$

9 This is an example of heterogeneous chemical equilibrium

$$K_C = \frac{[CO_2]}{[CH_4][O_2]^2}$$

and $\quad K_p = \dfrac{p_{CO_2}}{p_{CH_4} \times p_{O_2}^2}$

(according to partial pressure)

Thus, concentration of $CO_2(g)$ and $H_2O\ (l)$ are not equal to equilibrium.

$K_p = \dfrac{[CO_2]}{[CH_4]\,[O_2]}$ is not correct expression.

10 $$C_2H_6(g) \rightleftharpoons C_2H_4(g) + H_2(g)$$

Initial pres. $\quad 4.0$ atm $\quad 0 \quad 0$

Equili. pres. $\quad (4.0 - p)$ atm $\quad p \quad p$

$$K_p = \frac{p_{C_2H_4} \cdot p_{H_2}}{p_{C_2H_6}} = \frac{p \cdot p}{4.0 - p}$$

$$0.04 = \frac{p^2}{4.0 - p}$$

or $\quad 0.16 - 0.04p = p^2$

$$a = 1, b = 0.04, c = -0.16$$

We know that,

$$p = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$p = \frac{0.04 \pm \sqrt{0.0016 - 4(-0.16)}}{2}$$

$$p = \frac{-0.04 \pm 0.80}{2}$$

$p = 0.38 \quad$ (by taking positive value)

Hence, $p_{C_2H_6} = 4.0 - 0.38 = 3.62$ atm

11 $K_p = K_C (RT)^{\Delta n}$

Here, $\quad \Delta n = 1$

Thus, K_C will be less than K_p.

12 Mathematical expression of the thermodynamic equilibrium is

$\Delta G = \Delta G° + 2.303\ RT \log Q$

At equilibrium, when $\Delta G = 0$

and $Q = K$, then

$\Delta G = \Delta G° + 2.303\ RT \log K = 0$

$\Delta G° = -2.303\ RT \log K$

13 $PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$

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

Value of Δn is positive, so the dissociation of PCl_5 take forward by decrease in the pressure and by increase in the pressure the dissociation of PCl_5 decreases.

14 ΔH is positive, so it will shift towards the products by increase in temperature.

15 According to Le-Chatelier's principle, when concentration of reactant increases, the equilibrium shift in favour of forward reaction.

16 According to Le-Chatelier's principle :

By increasing the pressure and decreasing temperature the equilibrium shifts in forward direction.

17 $X_2(g) + 4Y_2 \rightleftharpoons 2XY_4\ (g)$;

$\Delta H < 0$ and $\Delta n < 0$

$\therefore$ The forward reaction is favoured at high pressure and low temperature. (According to Le-Chatelier's principle).

18 $\alpha_1 = 0.005 = \sqrt{K_a} \quad (\because C_1 = 1\ \text{mol L}^{-1})$

Molarity of the diluted solution,

$$C_2 = \frac{2}{32} = \frac{1}{16} \text{mol L}^{-1}$$

$$\because \quad \alpha_2 = \sqrt{\frac{K_a}{C_2}} = \sqrt{\frac{K_a}{C_2}}$$

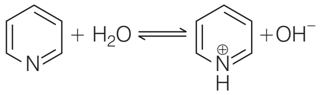
$$= 0.005 \times \sqrt{16} = 0.02$$

Again $[H_3O^+] = C_2\alpha_2$

$$= \frac{1 \times 0.002}{16}$$

$$= 1.25 \times 10^{-3} \text{M}$$

19 The percentage of pyridine can be equal to the percentage of dissociation of pyridinium ion and pyridine solution as shown below:



As pyridinium is a weak base, so degree of dissociation is given as :

$$\alpha = \sqrt{\frac{K_b}{C}} = \sqrt{\frac{1.7\times10^{-9}}{0.10}}$$

$$= \sqrt{1.7\times10^{-8}} = 1.3\times10^{-4}$$

or, percentage of dissociation

$$= (\alpha\times100)\%$$

$$= (1.3\times10^{-4})\times100 = 0.013\%$$

20

	$2\,AB_2(g) \rightleftharpoons$	$2\,AB(g)\,+$	$B_2(g)$
Initial moles	1	0	0
At equil.	$2(1-x)$	$2x$	x

where, x = degree of dissociation

Total moles at equilibrium

$$= 2 - 2x + 2x + x = (2+x)$$

So, $p_{AB_2} = \dfrac{2(1-x)p}{(2+x)}$, $\quad p_{AB} = \dfrac{2x\,p}{(2+x)}$

$$p_{B_2} = \frac{x\,p}{(2+x)}$$

$$K_p = \frac{(p_{AB})^2(p_{B_2})}{(p_{AB_2})^2}$$

$$= \frac{\left(\dfrac{2x\,p}{2+x}\right)^2\left[\left(\dfrac{x}{2+x}\right)p\right]}{\left[\left(\dfrac{2(1-x)}{(2+x)}\right)p\right]^2}$$

$$= \frac{4x^3p^3}{(2+x)^3}\times\frac{(2+x)^2}{p^2\,4(1-x)^2}$$

$$= \frac{x^3p}{(2+x)(1-x)^2}$$

$$= \frac{x^2p}{2} \quad [\because\ x <<< 1 \text{ and } 2]$$

$$x = \left(\frac{2K_p}{p}\right)^{1/3}$$

so, $(1-x)\approx1$ and $(2+x)\approx2$

21 H_3PO_4 is a tribasic acid, thus ionise in three steps.

I : $H_3PO_4 \rightleftharpoons H^+ + H_2PO_4^-$

II : $H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-}$

III : $HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$

Conjugate base is formed when an acid loses its proton. Thus, HPO_4^{2-} is the conjugate base of $H_2PO_4^-$ (which is an acid in step II, but is the conjugate base of H_3PO_4 in step I).

22 BF_3 is an electron deficient species, thus behaves like a Lewis acid.

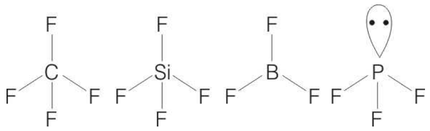
23 Ammonium ion is a conjugate acid. Water behaves both as an acid as well as a base. It is amphoteric solvent. In reaction like

$$H_2O + NH_3 \rightleftharpoons \underset{\text{Conjugate acid}}{NH_4^+} + OH^-$$

It behaves like an acid.

24 The molecule with lone pair at centre atom, will behave as Lewis base.

In the given molecules, only PF_3 has lone pair at P as shown below:



Thus, PF_3 acts as a Lewis base (electron-pair donor) due to presence of lone pair on P-atom.

25 Boron is an element of 13 group and contains three electrons in its valence shell. When its compound BH_3 dimerises, each boron atom carry only 6 electrons that is their octet is incomplete. Hence, $(BH_3)_2$ is an electron deficient compound.

In all other given molecules, octet of central atom is complete.

26 $K_{a_1} = \dfrac{[H^+][HS^-]}{[H_2S]}$,

$$K_{a_2} = \frac{[H^+][S^{2-}]}{[HS^-]}$$

$$K_{a_3} = \frac{[H^+]^2[S^{2-}]}{[H_2S]},$$

$$K_{a_3} = K_{a_1}\times K_{a_2}$$

27 $K = K_{a_1}\times K_{a_2}$

$$= 4.5\times10^{-3}\times1.7\times10^{-10}$$

$$= 7.65\times10^{-13}$$

$$[H^+] = \sqrt{K_C} = \sqrt{7.65\times10^{-13}\times0.01}$$

$$= 8.7\times10^{-8}$$

$$pH = -\log[H^+] = -\log 8.7\times10^{-8}$$

$$= -(\log10^{-8} + \log8.7) = 8 - 0.93$$

$= 7.07$ (Answer is nearer to *d*)

28 pH of the solution $A = 3$

$$[H^+]_A = 10^{-3}\text{ M}$$

pH of the solution $B = 2$

$$[H^+]_B = 10^{-2}\text{ M}$$

$$[H^+] = 10^{-3} + 10^{-2} = 11\times10^{-3}$$

$$pH = -\log(11\times10^{-3}) = 3 - \log 11$$

$$= 3 - 1.04 = 1.9$$

29 pH = 5.4,

$\therefore \quad [H^+] = 10^{-5.4} = 10^{-6}\cdot10^{0.6}$

Antilog of 0.6 is ≈ 3.98

$$[H^+] = 3.98\times10^{-6}\text{ M}$$

30 pH of HOCl = 2.85

But, $\quad -pH = \log[H^+]$

$\therefore -2.85 = \log[H^+] \Rightarrow 3.15 = \log[H^+]$

$\Rightarrow \quad [H^+] = 1.413\times10^{-3}$

For weak monobasic acid,

$$[H^+] = \sqrt{K_a\times C}$$

$\Rightarrow \quad K_a = \dfrac{[H^+]^2}{C} = \dfrac{(1.413\times10^{-3})^2}{0.08}$

$$= 24.957\times10^{-6}$$

$$= 2.4957\times10^{-5}$$

31 $75\text{ mL } \dfrac{M}{5}\text{ HCl} + 25\text{ mL } \dfrac{M}{5}\text{ NaOH}$

Milliequivalent of HCl = 75 mL of $\dfrac{M}{5}$ HCl

$$= \frac{1}{5}\times75 = 15$$

Milliequivalent of NaOH

$= 25\text{ mL of } \dfrac{M}{5}\text{ NaOH} = \dfrac{1}{5}\times25 = 5$

$\therefore$ Milliequivalent of HCl left unused

$$= 15 - 5 = 10$$

Volume of solution = 100 mL

$\therefore$ Molarity of $[H^+]$ in the resulting mixture

$$= \frac{10}{100} = \frac{1}{10}$$

$$pH = \log\frac{1}{[H^+]} = \log(10) = 1$$

32 20 mL of 0.1 NHCl $= \dfrac{0.1}{1000}\times20$ g eq

$$= 2\times10^{-3}\text{ g eq}$$

20 mL of 0.001 N KOH

$$= \frac{0.001}{1000}\times20\text{ g eq}$$

$$= 2\times10^{-5}\text{ g eq}$$

$\therefore$ HCl left unneutralised

$$= 2\ (10^{-3} - 10^{-5})$$
$$= 2 \times 10^{-3}\ (1 - 0.01)$$
$$= 2 \times 0.99 \times 10^{-3}$$
$$= 1.98 \times 10^{-3} \text{ g eq}$$

Volume of solution = 40 mL

$$[\text{HCl}] = \frac{1.98 \times 10^{-3}}{40} \times 1000 \text{ M}$$
$$= 4.95 \times 10^{-2}$$
$$\text{pH} = 2 - \log 4.95 = 2 - 0.7 = 1.3$$

33 $BaCl_2$ is a salt of strong acid HCl and strong base $Ba(OH)_2$. So, its aqueous solution is neutral with pH 7. All other salts give acidic solution due to cationic hydrolysis, so their pH is less than 7. Thus, pH value is highest for the solution of $BaCl_2$.

34 Given, $K_a\ (NH_4OH) = 1.77 \times 10^{-5}$

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$
$$K_a = \frac{[NH_4^+][OH^-]}{[NH_4OH]} = 1.77 \times 10^{-5} \quad \ldots(i)$$

Hydrolysis of NH_4Cl takes place as,

$$NH_4Cl + H_2O \longrightarrow NH_4OH + HCl$$

or $NH_4^+ + H_2O \longrightarrow NH_4OH + H^+$

Hydrolysis constant,

$$K_h = \frac{[NH_4OH][H^+]}{[NH_4^+]} \quad \ldots(ii)$$

or $K_h = \dfrac{[NH_4OH][H^+][OH^-]}{[NH_4^+][OH^-]} \quad \ldots(iii)$

From Eqs. (i), (ii) and (iii)

$$K_h = \frac{K_w}{K_a} \quad [\because [H^+][OH^-] = K_w]$$
$$= \frac{10^{-14}}{1.77 \times 10^{-5}} = 5.65 \times 10^{-10}$$

35 For a sparingly soluble salt, if S is the molar solubility,

$$A_xB_y(s) + H_2O \rightleftharpoons xA^{y+} + yB^{x-}$$

At saturation,

$K[A_xB_y] = [A^{y+}]^x \times [B^{x-}]^y = [xS]^x\ [yS]^y$

or $K_{sp} = x^y \cdot y^y\ S^{x+y}$

Where, the constant K_{sp} is called solubility product.

$$\underset{}{Ag_2C_2O_4(s)} \rightleftharpoons \underset{2S}{2Ag^+} + \underset{S}{C_2O_4^{2-}}$$

$K_{sp} = [Ag^+]^2\ [C_2O_4^{2-}] = [2S]^2\ [S]$

Given, $2S = 2.2 \times 10^{-4}$

or $S = 1.1 \times 10^{-4}$ M

$\therefore$ $K_{sp} = [2.2 \times 10^{-4}]^2\ [1.1 \times 10^{-4}]$

$$= 5.3 \times 10^{-12}$$

36 For a general reaction,

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

Solubility product $(K_{sp} = [A^{y+}]^x [B^{x-}]^y)$

For $BaSO_4$ (binary solute giving two ions)

$$BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$$

$\therefore$ $K_{sp} = [Ba^{2+}][SO_4^{2-}] = (S)(S) = S^2$

...(i) [where, S = solubility]

Given, $S = 2.42 \times 10^{-3}\ \text{gL}^{-1}$

Molar mass of $BaSO_4 = 233 \text{ g mol}^{-1}$

$\therefore$ Solubility of $BaSO_4$

$$(S) = \frac{2.42 \times 10^{-3}}{233} \text{ mol L}^{-1}$$
$$= 1.04 \times 10^{-5} \text{ mol L}^{-1}$$

On substituting the value of S in Eq. (i), we get

$$K_{sp} = (1.04 \times 10^{-5} \text{ mol L}^{-1})^2$$
$$= 1.08 \times 10^{-10} \text{ mol}^2 \text{ L}^{-2}$$

37 (a) For MY, $\underset{0}{MY} \rightleftharpoons \underset{S}{M^+} + \underset{S}{Y^-}$

where, S = solubility

and K_{sp} = solubility product.

$\therefore$ $K_{sp} = [M^+][Y^-]$

$K_{sp} = S^2$

$$S = \sqrt{K_{sp}} = \sqrt{6.2 \times 10^{-13}}$$
$$= 7.874 \times 10^{-7}$$

Similarly, for NY_3,

$$\underset{0}{NY_3} \rightleftharpoons \underset{S}{N^+} + \underset{3S}{3Y^-}$$

$\therefore$ $K_{sp} = [N^+]\ [Y^-]^3 = S \times (3S)^3$

$K_{sp} = 27S^4$

$\therefore$ $S = \sqrt[4]{\dfrac{K_{sp}}{27}} = \sqrt[4]{\dfrac{6.2 \times 10^{-13}}{27}}$

$$= 3.89 \times 10^{-4}$$

Therefore, molar solubility of MY in water is less than that of NY_3.

38 As solubility of AgCl(s) is asked in 0.1 M NaCl solution, so in the calculation, solubility of Cl^- (from NaCl) must be added to the solubility of Cl^- (from AgCl).

Let, S be the solubility of Ag^+ and Cl^- in AgCl before the addition of NaCl.

$$\underset{\substack{0.1\text{ M}\\0}}{NaCl(aq)} \longrightarrow \underset{\substack{0\\0.1\text{M}}}{Na^+(aq)} + \underset{\substack{0\\0.1+S}}{Cl^-(aq)}$$

$$AgCl(s) \rightleftharpoons \underset{S}{Ag^+(aq)} + \underset{S+0.1}{Cl^-(aq)}$$

Given, $K_{sp} = 1.6 \times 10^{-10} = [Ag^+][Cl^-]$

or $1.6 \times 10^{-10} = S(0.1 + S) = 0.1S + S^2$

$\because K_{sp}$ is small, so S is very less in comparison with 0.1. Hence, S^2 can be neglected.

Thus, $1.6 \times 10^{-10} = 0.1S$

or $S = 1.6 \times 10^{-9}$ M

39 Given, pH of $Ba(OH)_2 = 12$

So, pOH = 2

$\therefore$ $[H^+] = [1 \times 10^{-12}]$

$$K_w = (H^+)\ (OH^-)$$
$$K_w = 1 \times 10^{-14}$$
$$OH^- = \frac{K_W}{H^+}$$

and $[OH^-] = \dfrac{1 \times 10^{-14}}{1 \times 10^{-12}}$

$[\because [H^+]\ [OH^-] = 1 \times 10^{-14}]$

$$= 1 \times 10^{-2} \text{ mol/L}$$

$$Ba(OH)_2 \longrightarrow \underset{S}{Ba^{2+}} + \underset{2S}{2\ OH^-}$$

$$K_{sp} = [Ba^{2+}][OH^-]^2 = [S][2S]^2$$
$$= \left[\frac{1 \times 10^{-2}}{2}\right](1 \times 10^{-2})^2$$
$$= 0.5 \times 10^{-6} = 5.0 \times 10^{-7} \text{ M}^3$$

40 Among the given, AgCl is most soluble in aqueous ammonia solution, because it forms soluble complex with it.

41 A buffer solution is used in the removal of PO_4^{3-} ions.

42 NaCl is salt of strong acid and strong base. Its not the case of buffer.

$$NaCl + H_2O \rightleftharpoons NaOH + HCl$$

Aqueous NaCl, itself exact neutral solution.

$$HCl + H_2O \rightleftharpoons H_3O^+ + Cl^-$$

makes solution acidic.

43 $\underset{\substack{0.1\\0.02}}{CH_3NH_2} + \underset{\substack{0.08\\0}}{HCl} \longrightarrow \underset{\substack{0\\0.08}}{CH_3NH_3Cl}$

Basic buffer solution

$$\text{pOH} = pK_b + \log\frac{0.08}{0.02} = pK_b + 0.602$$
$$= 3.30 + 0.602 = 3.902$$

pH = 10.00

$[H^+] = 7.99 \times 10^{-11} = 8 \times 10^{-11}$ M

44 Strong acid with its salt cannot form buffer solution. Hence, $HClO_4$ and $NaClO_4$ is not an acidic buffer.

45 By the use of Henderson's equation

$$\text{pH} = \text{p}K_a + \log_{10}\frac{[\text{salt}]}{[\text{acid}]}$$

When, $[\text{salt}] = [\text{acid}]$

$\therefore \quad \text{pH} = \text{p}K_a$

$\because \text{p}K_a = 3.58$, thus at this state

$\text{pH} = 3.58$

So, acetoacetic acid $(\text{p}K_a = 3.58)$ is best to use.

46 If small amount of an acid or alkali is added to a buffer solution, it converts them into unionised acid or base. Thus, its pH remains unaffected or in other words its acidity/ alkalinity remains constant, e.g.

$$H_3O^+ + A^- \rightleftharpoons H_2O + HA$$

$$^-OH + HA \longrightarrow H_2O + A^-$$

If acid is added, it reacts with A^- to form undissociated HA. Similarly, if base/alkali is added, OH^- combines with HA to give H_2O and A^- and thus, maintains the acidity/alkalinity of buffer solution.

47 $\text{pOH} = \text{p}K_b + \log\frac{[\text{salt}]}{[\text{base}]}$

$$= -\log K_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

$$= -\log 1.8 \times 10^{-5} + \log\frac{0.20}{0.30}$$

$$= 5 - 0.25 + (-0.176)$$

$$= 4.75 - 0.176 = 4.57$$

$\therefore \text{pH} = 14 - 4.57 = 9.43$

48 (d) CH_3COOH (weak acid) and CH_3COONa (conjugated salt) form acidic buffer and for acidic buffer,

$$\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

and $\quad [H^+] = -\text{antilog pH}$

$$\text{pH} = -\log K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

$[\because \text{p}K_a = -\log K_a]$

$$= -\log(1.8 \times 10^{-5}) + \log\frac{(0.20)}{(0.10)}$$

$$= 4.74 + \log 2$$

$$= 4.74 + 0.3010 = 5.041$$

Now, $[H^+] = \text{antilog}(-5.045)$

$= 9.0 \times 10^{-6}$ mol/L

49 (d) (i) For basic buffer,

$$\text{pOH} = \text{p}K_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

(ii) $\text{pH} + \text{pOH} = 14$

Given, $\quad K_b = 1 \times 10^{-10}$, $[\text{salt}] = [\text{base}]$

$$\text{pOH} = -\log K_b + \log\frac{[\text{salt}]}{[\text{base}]}$$

$\therefore \quad \text{pOH} = -\log(1 \times 10^{-10}) + \log 1 = 10$

$\text{pH} + \text{pOH} = 14$

$[\because$ concentration of $[B^-] = [HB]$

$\text{pH} = 14 - 10 = 4$

50 When we add NH_4OH in NH_4Cl solution, ionisation of NH_4OH is decreased due to common ion effect.

SESSION 2

1 $\text{pOH} = -\log K_b + \log\left(\frac{\text{salt}}{\text{base}}\right)$

$$\text{pOH} = -\log[1.8 \times 10^{-5}] + \log\left[\frac{\text{salt}}{1.0}\right]$$

$$5 = 4.7 + \log\left[\frac{\text{salt}}{1.0}\right]$$

$$\log\left(\frac{\text{salt}}{1.0}\right) = 5 - 4.7 = 0.3$$

$$\left(\frac{\text{salt}}{1.0}\right) = \text{antilog } 0.3$$

$$\left(\frac{\text{salt}}{1.0}\right) = 1.995$$

$$[\text{salt}] = 1.99$$

2 (i) $(K_p)_{\text{I}} = p_{CO_2} = 2$ (ii) $(K_p)_{\text{II}} = \frac{p^2_{CO}}{p_{CO_2}} = 6$

$$CaCO_3(s) + C(s) \rightleftharpoons CaO(s) + 2CO(g)$$

$$(K_p)_{\text{III}} + p^2_{CO} = (K_p)_1 (K_p)_2 = 12$$

(Only gaseous species are taken in the expression of K_p).

3 K_p is independent of pressure and concentration.

4 $\quad NH_4HS(s) \rightleftharpoons NH_3(g) + H_2S(g)$

Initial at $\quad a \quad\quad 0.5$ atm $\quad 0$

Equili. at $(a - x) \quad\quad 0.5 + x \quad x$

Total pressure $= 0.5 + 2x = 0.84$

$x = 0.17$

$K_p = p_{NH_3} \cdot p_{H_2S} = 0.67 \times 0.17 = 0.1139$

5 Buffer capacity, $\beta = \frac{dC_{HA}}{d_{\text{pH}}}$

where, dC_{HA}

$= $ moles of acid added per litre

$d_{\text{pH}} = $ change in pH

$$dC_{HA} = \frac{\text{moles of acetic acid}}{\text{volume}}$$

$$= \frac{0.12/60}{250/1000} = \frac{1}{125}$$

$$\therefore \quad b = \frac{1/125}{0.02} = \frac{1}{2.5} = 0.4$$

6 $\quad A(g) + B(g) \rightleftharpoons C(g) + D(g)$

At $t = 0 \quad 1 \quad\quad 1 \quad\quad 0 \quad\quad 0$

At equi. $(1 - x) \quad (1 - x) \quad x \quad x$

$x = 0.5$

$$K_C = \frac{[C][D]}{[A][B]} = 1$$

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

$1 \quad 2 \quad\quad 0 \quad 0$

$(1\text{-}y) \quad (2 - y) \quad y \quad y$

$$K_C = 1 = \frac{y^2}{(1 - y)(2 - y)}$$

$$y = 2/3$$

7 The following reactions will disappear the red colour:

(i) $\quad Ag^+ + SCN^- \longrightarrow AgCNS\downarrow$

(ii) $\quad Hg^2 + SCN^- \longrightarrow Hg(CNS)_2\downarrow$

(iii) $Fe^{3+} + 3C_2O_4^{2-} \longrightarrow \underset{\text{Soluble}}{[Fe(C_2O_4)_3]^{3-}}$

8 Acid indicators are generally weak acid. The dissociation of indicator HIn takes place as follows :

$$HIn \rightleftharpoons H^+ + In^-$$

$$K_{In} = \frac{[H^+][In^-]}{[HIn]} \quad [H^+] = K_{In} \cdot \frac{[HIn]}{[In^-]}$$

$$\text{pH} = -\log[H^+] = -\log\left(K_{In} \cdot \frac{[HIn]}{[In^{-1}]}\right)$$

$$= -\log K_{In} + \log\frac{[In^-]}{[HIn]}$$

$$= \text{p}K_{In} + \log\frac{[In^{-1}]}{[HIn]} = \log\frac{[In^-]}{[HIn]}$$

$$= \text{pH} - \text{p}K_{In}$$

9 As the acidity or K_a value increases, pH decreases, thus the order of pH value of the acids is

Hypochlorous acid > acetic acid >

$(3.0 \times 10^{-8}) \quad\quad (1.74 \times 10^{-5})$

formic acid

(1.8×10^{-4})

$\left[\text{Note } K_a \propto \frac{1}{\text{pH}}\right]$

10 $N_2O_4 \rightleftharpoons 2NO_2$

$1 \quad\quad 0$

$(1 - x) \quad 2x$

Number of moles and volume

(since, $pV = nRT \therefore V \propto n$)

Total moles $= (1 + x)$

$\therefore$ % of NO_2 by volume

$$= \frac{2x}{1 + x} \times 100 = 50$$

$$x = \frac{1}{3} = 0.33$$

11 $K_p = K_C (RT)^{\Delta n}$

$K_p = K_x (p)^{\Delta n}$

$\therefore \quad K_C (RT)^{\Delta n} = K_x (p)^{\Delta n}$

$$K_C = K_x \left(\frac{p}{RT}\right)^{\Delta n}$$

$$= K_x \left(\frac{1}{V}\right)^{\Delta n}$$

$$= K_x \left(\frac{1}{V}\right)^{-1}$$

$$= K_x (V)$$

12 $X^- + H_2O \rightleftharpoons HX + OH^-$

$$K_h = \frac{10^{-14}}{10^{-5}} = 10^{-9}$$

$$x = \sqrt{\frac{K_h}{C}} = \sqrt{\frac{10^{-9}}{10^{-1}}} = 10^{-4}$$

$100 \times 10^{-4} = 10^{-2} = 0.01\%$

13 On adding I, II and III and we get IV

$\therefore \quad K = \beta_1 \beta_2 \beta_3$

or $\quad \log K = \log\beta_1 + \log\beta_2 + \log\beta_3$

or $\quad -\log K = -\log\beta_1 - \log\beta_2 - \log\beta_3$

$$p_K = p_{\beta_1} + p_{\beta_2} + p_{\beta_3}$$

Where, $\quad p_x = -\log x$

14 $\quad 2NH_3 \rightleftharpoons N_2(g) + 3H_2(g)$

Initial	a	0	0
Equil.	$(a-2x)$	x	$3x$

$x = 0.30$

$a - 2x = 0.30$

$\therefore \quad a = 0.90$

Thus, initial moles of NH_3 – 0.90 mol

$$K_C = \frac{[N_2][H_2]^3}{[NH_3]^2}$$

$$= \frac{\left(\frac{0.30}{0.50}\right)\left(\frac{0.90}{0.50}\right)^3}{\left(\frac{0.30}{0.50}\right)^2}$$

$= 9.72$

Thus, K_C for NH_3 formation

$$= \frac{1}{9.72} = 0.103$$

15 x mol $(CH_3COOH)_2Pb$

$= 2x$ mol CH_3COO^-

$[CH_3COOH] = 0.1\,M$

$[CH_3COO^-] = 2x\,M$

$$\therefore \text{pH} = \text{p}K_a + \log\frac{[CH_3COO^-]}{[CH_3COOH]}$$

$5.04 = 4.74 + \log 20x$

$0.30 = \log 20x$

$x = 0.1$ mol

16 Which has least solubility, i.e. $\sqrt{K_{sp}}$ option c is correct, as its solubility is 10^{-54} (least one).

17 Equal pH means

$[H^+]_1 = [H^+]_2$

$\sqrt{K_1C_1} = \sqrt{K_2C_2}$

(by Ostwald's dilution law)

or $\quad K_1C_1 = K_2C_2$

$$\therefore \quad \frac{C_1}{C_2} = \frac{K_2}{K_1} = \frac{1}{4} = 0.25$$

18 Salts (NH_4A, NH_4B, NH_4C) are of weak acid and weak base.

$$\text{pH} = 7 + \frac{\text{p}K_a}{2} - \frac{\text{p}K_b}{2}$$

Thus, greater the value of $\text{p}K_a$ of HA, greater the pH.

$$\text{p}K_b(A^-, B^-, C^-) = \underset{4}{A^-} < \underset{5}{B^-} < \underset{6}{C^-}$$

$$\text{p}K_a(HA, HB, HC) = \underset{8}{HC} < \underset{9}{HB} < \underset{10}{HA}$$

Greater the $\text{p}K_a$

Greater the pH

Thus, pH

$$NH_4C < NH_4B < NH_4A$$

19 I. $Q = \dfrac{[NO_2]^2}{[N_2O_4]}$

Since, $[NO_2]$ is maximum and $[N_2O_4]$ is minimum at point A, hence Q is minimum at this point. Thus, false.

II. $Q = \dfrac{(0.1)^2}{(0.1)} = (0.1) < K_C$

Thus, reaction proceeds-left to right.

Thus, true

III. $K_c = Q$ when equilibrium is reached at point D or F. Thus, true.

20 $\quad CO(g) + H_2O(g) \rightleftharpoons CO_2(g) + H_2(g)$

Initial	1	1	1	1
Equil.	$(1-x)$	$(1-x)$	$(1-x)$	$(1+x)$

$$K_C = \frac{[CO_2][H_2]}{[CO][H_2O]}$$

$$9 = \frac{(1+x)^2}{(1-x)^2}$$

$$\therefore \quad \frac{1+x}{1-x} = 3$$

$x = 0.5$

$\therefore \quad [CO_2] = 1 + x = 1 + 0.5 = 1.5$ mol