CHAPTER > 07

Equilibrium

KEY NOTES

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

  It may be represented by

$$H_2O(l) \rightleftharpoons H_2O(\text{vap.})$$

- The mixture of reactants and products in the equilibrium state is called an **equilibrium mixture**.

  The concept of equilibrium is applicable for both physical and chemical processes.

Equilibrium in Physical Processes

A **physical equilibrium** is a state at which two phases of a compound can co-exist and an equilibrium is established between these two states.

Physical equilibrium may be obtained by the following **phase transformation processes**.

Solid-Liquid Equilibrium

$$\text{Ice}(s) \rightleftharpoons \text{Water}(l)$$

Rate of melting of ice = rate of freezing of water

Liquid-Vapour Equilibrium

$$H_2O(l) \rightleftharpoons H_2O\,(\text{vap.})$$

Rate of evaporation of water = rate of condensation of water vapours

Solid-Vapour Equilibrium

Certain solids on heating directly change from solid to vapour state (sublimation)

e.g., $I_2(s) \rightleftharpoons I_2\ (\text{vap.})$

Equilibrium Involving Dissolution of Solid or Gases in Liquids

- For dissolution of solid in liquids, the solubility is constant at a given temperature.

  e.g. Sugar (solution) $\rightleftharpoons$ Sugar (solid)

- For dissolution of gases in liquids, i.e.

$$CO_2(\text{gas}) \rightleftharpoons CO_2(\text{in solution})$$

  This is equilibrium is governed by **Henry's law**, which states that, mass of a gas dissolved in a given mass of a solvent at any temperature is proportional to the pressure of the gas above the solvent.

General Characteristics of Equilibria Involving Physical Processes

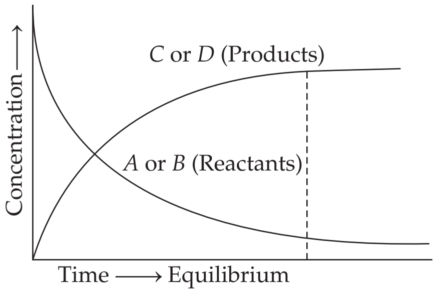
Some important characteristics of physical equilibrium are as follows :

- Equilibrium is possible only in a closed system at a given temperature.
- All the measurable properties remains constant.
- Both the opposing processes occur at the same rate and there is a dynamic but stable condition.
- The physical equilibrium is characterised by constant value of one of its parameter (such as melting point) at a given temperature.

Equilibria in Chemical Processes

The equilibrium that involves only chemical change is called **chemical equilibrium**. It is also called **dynamic equilibrium.**

The variation of concentration of reactants and products in a reversible reaction can be seen as ,



Attainment of chemical equilibrium

Note *Use of isotope (deuterium) in the formation of ammonia clearly indicates that, chemical reactions reach a state of dynamic equilibrium in which rates of forward and reverse reactions are equal and there is no net change in composition.*

Law of Chemical Equilibria and Equilibrium Constant

Law of chemical equilibrium states that, the value obtained by dividing the product of concentration of products raised to the respective stoichiometric coefficient in a balanced chemical equation by the product of concentration of reactants raised to their individual stoichiometric coefficients is constant. i.e.

For a reaction, $aA + bB \rightleftharpoons cC + dD$; $K_C = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}$

where, $[A]$, $[B]$, $[C]$ and $[D]$ are molar concentration of A, B, C and D at equilibrium and K_C is **equilibrium constant**. The unit of K_C is mol L^{-1}.

Note *The above equilibrium equation is also known as law of mass action.*

- The characteristics of equilibrium constant are as follows :
  - The value of equilibrium constant for a particular reaction is always constant and depends only upon the temperature of a reaction.
  - If the reaction is reversed, the value of equilibrium constant is reversed, i.e. $K'_C = \frac{1}{K_C}$
  - If an equation is divided by a factor of '*n*', the new equilibrium constant is the *n*th root of the previous value. i.e. $K'_C = (K_C)^{1/n}$
  - If the equation is multiplied by a factor of '*n*', the new equilibrium constant is *n*th root of the previous value. i.e. $K'_C = (K_C)^n$

Homogeneous and Heterogeneous Equilibria

- The equilibrium constants for the two types of equilibria *viz* homogeneous and heterogeneous equilibria are as follows :
  - For **homogeneous equilibria**, all the reactants and products are in the same phase.

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

    For a general reaction,

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

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

$$K_p = \frac{[C]^c\,[D]^d\,[RT]^{c+d}}{[A]^a\,[B]^b\,[RT]^{a+b}}$$

$$K_p = \frac{[C]^c\,[D]^d\,[RT]^{(c+d)-(a+b)}}{[A]^a\,[B]^b}$$

or $$K_p = \frac{[C]^c\,[D]^d}{[A]^a\,[B]^b}(RT)^{\Delta n} \quad \left[\because p = CRT; C = \frac{n}{V}\right]$$

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

where, Δn = (number of moles of gaseous products) − (number of moles of gaseous reactants).

The unit of K_p is expressed in bar.

  - Equilibrium in a system having more than one phase is called **heterogeneous equilibrium**.

    It involves pure solids or liquids.

    e.g. $CaCO_3(s) \rightleftharpoons CaO(s) + CO_2(g)$

$$K_C = \frac{[CaO(s)]\,[CO_2(g)]}{[CaCO_3(s)]}$$

$$\therefore \quad K_C = [CO_2(g)] \text{ and } K_P = p\,CO_2$$

Applications of Equilibrium Constant

The value of equilibrium constant is helpful in many ways :

- **Predicting the extent of reaction**

  If $K_C > 10^3$, products predominates over reactants and reaction proceeds completion.

  If $K_C < 10^{-3}$, then reactants predominates over products and reaction proceeds rarely.

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

- **Predicting the direction of a reaction**

  $Q = K_C$, reaction in equilibrium.

  $Q < K_C$, reaction proceeds in forward direction.

  $Q > K_C$, reaction proceeds in backward direction.

  Here, Q is reaction quotient.

Relationship between Equilibrium Constant (*K*), Reaction Quotient (*Q*) and Gibbs' Energy (*G*)

- Gibbs free energy and reaction quotient are related as

$$\Delta G = \Delta G^\circ + RT \ln Q$$

  where, ΔG° = Standard Gibbs energy

  At equilibrium, $\Delta G = 0$ and $Q_C = K_C$, therefore the equation becomes

$$\Delta G^\circ = -RT \ln K \quad \text{or} \quad \ln K = \frac{-\Delta G^\circ}{RT}$$

  Taking antilog on both sides, we get

$$K = e^{-\Delta G^\circ / RT}$$

- The equation, $K = e^{-\Delta G^\circ / RT}$ helps in predicting the spontaneity of the reaction as,
  - If $\Delta G^\circ < 0; e^{-\Delta G^\circ / RT} > 1 \Rightarrow K > 1$

    Therefore, forward reaction is spontaneous.
  - If $\Delta G^\circ > 0; e^{-\Delta G^\circ / RT} < 1 \Rightarrow K < 1$

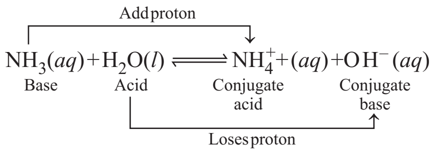
    Therefore, backward reaction is spontaneous.

Factors Affecting Equilibria (Le-Chatelier's Principle)

- According to Le-Chatelier's principle, if any of the factors that determine the equilibrium condition of a system is changed, the system will move in such a direction, so that effect of the change is reduced or nullified or opposed.
- Different factors affecting equilibrium are as follows :
  - **Effect of concentration change** Change in the concentration of either reactant (s) or product(s), shift the reaction in such a direction in which the effect of change is minimised or nullified.
  - **Effect of pressure change** Increase in pressure, shifts the equilibrium in that direction, where the number of moles of the gas or pressure decreases and *vice-versa*.
  - **Effect of temperature change** High temperature favours endothermic reaction and low temperature favours exothermic reaction.
  - **Effect of inert gas addition** At constant volume, there is no effect of addition of inert gas. While, at constant pressure, when inert gas is added, reaction goes in the direction in which there is an increase in the number of moles of the gases.
  - **Effect of catalyst** A catalyst increases the rate of forward reaction as well as the backward reaction, so it does not effect the equilibrium and equilibrium constant.

Ionic Equilibrium

- Equilibria that involve ions only are studied under different class called **ionic equilibrium**.
- Michael Faraday classified the substances into two categories based on the ability to conduct electricity. i.e. **electrolytes** and **non-electrolytes**.
- **Strong electrolytes** on dissolution in water are ionised almost completely, while the **weak electrolytes** are only partially dissociated.
- Different theories related to acids and bases are as follows :

Concept	Acids	Bases	Examples
Arrhenius concept	Furnish/release H^+ ions in their aqueous solution.	Furnish/release OH^- ions in their aqueous solution.	$\underset{\text{(Acid)}}{HCl} \rightleftharpoons H^+ + Cl^-$; $\underset{\text{(Base)}}{NaOH} \rightleftharpoons Na^+ + OH^-$ **Strong acids** $HClO_4$, HCl, HBr, HI, HNO_3 **Weak acids** HF, CH_3COOH **Strong bases** NaOH, KOH, $Ba(OH)_2$ **Weak bases** NH_4OH, $Al(OH)_3$
Lewis concept	Accept a pair of electrons, i.e. acids are electron deficient compounds.	Donate a pair of electrons to form coordinate bond, i.e. bases are electron rich compounds.	$\underset{\text{(Acid)}}{H^+} + \underset{\text{(Base)}}{OH^-} \longrightarrow H_2O$ **Acids** BF_3, $AlCl_3$, Fe^{3+}, Al^{3+}, Cu^{2+}, SF_6 (vacant *d*-orbitals) **Bases** $H_2\ddot{O}:$, $\ddot{N}H_3$, OH^-
Bronsted-Lowry	Acid is a proton donor.	Base is a proton acceptor.	 Add proton $\underset{\text{Base}}{NH_3(aq)} + \underset{\text{Acid}}{H_2O(l)} \rightleftharpoons \underset{\text{Conjugate acid}}{NH_4^+(aq)} + \underset{\text{Conjugate base}}{OH^-(aq)}$ Loses proton

Note
- *The acid-base pair which differ by a proton are said to form a conjugate* ***acid-base pair.***
- *If Bronsted acid is a strong acid, then its conjugate base is weak and vice-versa.*

Ionisation Constant and Ionic Product of Water

The ionisation constant of water and its ionic product is given as :

$$K_w = [\text{H}^+]\,[\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 298 \text{ K}$$

where, K_w is the ionic product of water.

pH scale

- In order to represent, the hydronium ion concentration more conveniently in terms of molarity, Sorensen introduced scale, called pH scale.

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

  If $\text{pH} < 7$, acidic solution, $\text{pH} = 7$ neutral, if $\text{pH} > 7$, basic solution.
- $\text{p}K_w$ is a very important quantity for aqueous solutions and controls the relative concentrations of hydrogen and hydroxyl ions as their product is a constant. i.e.

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

Ionisation of Acids and Bases

Ionisation Constants of Weak Acids

For a reaction,

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

Initial conc.	C	0	0
At equil	$C(1-\alpha)$	$C\alpha$	$C\alpha$

The ionisation or dissociation constant is given as,

$$K_a = \frac{[\text{H}^+][X^-]}{[\text{H}X]} = \frac{C\alpha^2}{1-\alpha}$$

If $\alpha << 1 \Rightarrow (1-\alpha) = 1$ and degree of ionisation is given as,

$$\alpha = \sqrt{\frac{K_a}{C}} \quad \text{or} \quad \propto \frac{1}{\sqrt{C}} \propto \sqrt{V} \quad \left(\because C \propto \frac{1}{V}\right)$$

K_a is a dimensionless quantity. The larger the value of K_a, stronger is the acid.

Thus, the degree of dissociation is proportional to the square root of dilution for weak electrolytes. This is the statement of **Ostwald's law.**

Ionisation Constant of Weak Base

For a reaction,

$$MOH(aq) \rightleftharpoons M^+(aq) + \text{OH}^-(aq)$$

Initial conc.	C	0	0
At equil.	$C(1-\alpha)$	$C\alpha$	$C\alpha$

The base ionisation constant is represented by K_b and is given as :

$$K_b = \frac{[M^+][\text{OH}^-]}{[M\text{OH}]} = \frac{C\alpha^2}{1-\alpha}$$

and degree of ionisation is given as, $\alpha = \sqrt{\frac{K_b}{C}}$

Higher the value of K_b, more basic is the base.

Relation between K_a and K_b

- In case of a conjugate acid-base pair

  $$K_a \times K_b = K_w$$
- **The pK value of the conjugate acid and base** are related to each other by the equation :

  $$\text{p}K_a + \text{p}K_b = \text{p}K_w = 14 \text{ (at 298 K)}$$

  Here, $\text{p}K_a = -\log K_a$ and $\text{p}K_b = -\log K_b$

Polybasic Acids and Polyacidic Bases

- Acids having more than one ionisable proton per molecule of acids are known as **polybasic** or **polyprotic acids**. For **dibasic acids**, like H_2X have two ionisation constants and for **tribasic acids** like H_3PO_4, have three ionisation constants.
- It is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces.

  That's why, the higher order ionisation constants (K_{a_2}, K_{a_3}) are smaller than lower order ionisation constant (K_{a_1}).
- The extent of dissociation of an acid depends on the strength and polarity of the H — A bond.

  For example,

  $$-\xrightarrow{\text{Size increases}}$$
  $$\text{HF} << \text{HCl} << \text{HBr} << \text{HI}$$
  $$\xrightarrow[\text{Acidic strength increases}]{}$$

  $$-\xrightarrow{\text{Electronegativity increases}}$$
  $$\text{CH}_4 << \text{NH}_3 < \text{H}_2\text{O} < \text{HF}$$
  $$\xrightarrow[\text{Acidic strength increases}]{}$$

Note *The **equilibrium constant for a net reaction** obtained after adding two (or more) reactions equals the products of equilibrium constant for individual reactions, i.e.*

$$K_{\text{net}} = K_1 \times K_2 \times \ldots\ldots\ldots.$$

Salt Hydrolysis

- The salts formed by reaction between acids and bases get ionised in water and exist as hydrated ions. The reaction of ions with water is known as **hydrolysis** or **salt hydrolysis**.
- Depending upon the nature of acid and base from which a salt is obtained, the salts are categories into four types as tabulated below :

Salt of	Example	K_h (hydrolysis constant)	h (degree of hydrolysis)	pH of solution
weak acid and strong base	CH_3COONa	$\frac{K_w}{\mathrm{K}_a}$	$\sqrt{\frac{K_w}{K_a \cdot C}}$	$\frac{1}{2}\mathrm{p}K_w + \frac{1}{2}\mathrm{p}K_a + \frac{1}{2}\log C$
strong acid and weak base	NH_4Cl	$\frac{K_w}{\mathrm{K}_b}$	$\sqrt{\frac{K_w}{K_b \cdot C}}$	$\frac{1}{2}\mathrm{p}K_w - \frac{1}{2}\mathrm{p}K_b - \frac{1}{2}\log C$
weak acid and weak base	CH_3COONH_4	$\frac{K_w}{K_a \cdot K_b}$	$\sqrt{\frac{K_w}{K_a \cdot K_b}}$	$\frac{1}{2}\mathrm{p}K_w + \frac{1}{2}\mathrm{p}K_a - \frac{1}{2}\mathrm{p}K_b$
strong acid and strong base	NaCl	Does not undergo hydrolysis		

Buffer Solutions

- The solutions which resist change in their pH on dilution or an addition of small amounts of acid or alkali are called **buffer solutions**.
- The different types of buffer solutions are as follows :
  - A buffer solution having pH less than 7 is called as an **acidic buffer,** e.g. $CH_3COOH + CH_3COONa$.

    The pH of an acidic buffer is given by **Henderson-Hasselbalch equation** as

    $$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{Conjugate base, } A^-]}{[\text{Acid, H}A]}$$

    or, $$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$
  - A buffer solution having pH greater than 7 is called as **basic buffer,** e.g. $NH_4OH + NH_4Cl$. The pH of basic buffer is given by **Henderson-Hasselbalch equation** as,

    $$\mathrm{pOH} = \mathrm{p}K_b + \log\frac{[\text{Conjugate acid, } BH^+]}{[\text{Base, } B]}$$

    or $$\mathrm{pOH} = \mathrm{p}K_b + \log\frac{[\text{Salt}]}{[\text{Base}]}$$

    In terms of pH, it can be written as :

    $$\mathrm{pH} = \mathrm{p}K_a + \log\frac{[\text{Conjugate acid, } BH^+]}{[\text{Base, } B]}$$

Note *If molar concentration of base and its conjugate acid is same, then the pH of the buffer solution will be same as the* $\mathrm{p}K_a$ *value for the base.*

Solubility and Solubility Product

- Lattice enthalpy and solvation enthalpy play a key role in deciding the **solubility of salts** in a particular solvent.
- Depending upon the solubility, salts are categories into three groups.

Category I	Soluble	Solubility > 0.1M
Category II	Slightly soluble	0.01 M < Solubility < 0.1M
Category III	Sparingly soluble	Solubility < 0.01M

- A solid salt of the general formula, $M_x^{p+}X_y^{q-}$ with molar **solubility 'S'** in equilibrium with its saturated solution may be represented by the equation.

$$A_xB_y(s) \rightleftharpoons xA^{p+}(aq) + yB^{q-}(aq)$$

$$K_{\mathrm{sp}} = [A^{p+}]^x[B^{q-}]^y = (xS)^x(yS)^y = x^xy^yS^{(x+y)}$$

$$S^{(x+y)} = K_{\mathrm{sp}}/x^xy^y$$

$$S = (K_{\mathrm{sp}}/x^xy^y)^{1/x+y}$$

where, K_{sp} is called the solubility product.

Applications of K_{sp}

- The value of Q (ionic product) and K_{sp} (solubility) product are helpful for predicting, whether a precipitate is formed or not.

  In general,

  if $Q > K_{\mathrm{sp}}$, then precipitation takes place.

  if $Q < K_{\mathrm{sp}}$, then no precipitation takes place.

  if $Q = K_{\mathrm{sp}}$, the reaction is at equilibrium.
- The solubility of salts of weak acids like phosphates increases with decrease in pH as at lower pH, the anion gets protonated and, hence its concentration decreases.

Common Ion Effect

The decrease in the ionisation of a weak electrolyte by the presence of a common ion from a strong electrolyte is called common ion effect. e.g. Ionisation of a weak acid (HA) decreases in the presence of a strong acid such as HCl because H^+ as common ion combines with A^- to form HA. It is used in (a) purification of common salt (b) in qualitative analysis (c) salting out of soap.

Mastering NCERT

MULTIPLE CHOICE QUESTIONS

TOPIC 1 ~ Equilibrium in Physical and Chemical Process alongwith Dynamic Equilibrium

1 Which of the following is the example of a reversible reaction?

(a) $Pb(NO_3)_2(aq) + 2NaI(aq) \longrightarrow PbI_2(s) + 2NaNO_3(aq)$

(b) $2Na(s) + 2H_2O(l) \longrightarrow 2NaOH(aq) + H_2(g)$

(c) $AgNO_3(aq) + HCl(aq) \longrightarrow AgCl(s) + HNO_3(aq)$

(d) $KNO_3(aq) + NaCl(aq) \longrightarrow KCl(aq) + NaNO_3(aq)$

2 In an experiment, if we expose three watch glasses containing separately 1 mL each of acetone, ethyl alcohol and water to atmosphere and repeat the experiment with different volumes of the liquids in a warmer room. It is observed that, in all such cases the liquid eventually disappears and the time taken for complete evaporation depends on

(a) the nature of the liquid (b) the amount of the liquid

(c) the temperature (d) All of these

3 The partial pressure of ethane over a solution containing 6.56×10^{-3} g of ethane is 1 bar. If the solution contains 5.00×10^{-2} g of ethane, then what will be the partial pressure of gas?

(a) 6.2 bar (b) 5.6 bar (c) 7.6 bar (d) 7.3 bar

4 When the two reactions occur at the same rate, the system reaches

(a) a state of completion

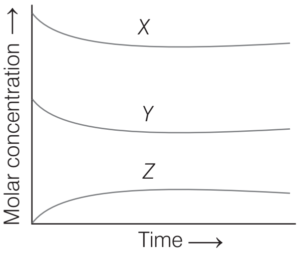
(b) a state of equilibrium

(c) 90% completion

(d) 50% completion

5 The method of preparation of ammonia can be represented graphically as

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



In the above graph, X, Y and Z respectively are

(a) N_2, H_2 and NH_3

(b) NH_3,H_2 and N_2

(c) H_2, N_2 and NH_3

(d) N_2, NH_3 and H_2

6 In the chemical reaction,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

at equilibrium point,

(a) equal volumes of N_2 and H_2 are reacting

(b) equal masses of N_2 and H_2 are reacting

(c) the reaction has stopped

(d) the same amount of ammonia is formed, as it is decomposed into N_2 and H_2

TOPIC 2 ~ Law of Chemical Equilibrium and Equilibrium Constant

7 The active mass of 64 g of HI in a 2L flask would be

(a) 0.25 mol/L (b) 0.50 mol/L

(c) 0.025 mol/L (d) 32.0 mol/L

8 Given that, equilibrium constant for the reaction,

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

has a value 278 at a particular temperature. What is the value of the equilibrium constant for the following reaction at the same temperature?

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

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(a) 1.8×10^{-3} (b) 3.6×10^{-3} (c) 6×10^{-2} (d) 1.3×10^{-5}

9 Given the reaction between two gases represented by A_2 and B_2 to give the compound $AB(g)$ as

$$A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$$

At equilibrium, the concentration of $A_2 = 3.0 \times 10^{-3}$ M, of $B_2 = 4.2 \times 10^{-3}$ M and of $AB = 2.8 \times 10^{-3}$ M. If the reaction takes place in a sealed vessel at 527°C, then the value of K_C will be

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(a) 2.0 (b) 1.9 (c) 0.62 (d) 4.5

10 The equilibrium,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

is established in a reaction vessel of 2.5L capacity. The amount of N_2 and O_2 taken at the start were respectively 2 moles and 4 moles. Half a mole of nitrogen has been used at equilibrium. The molar concentration of nitric oxide is

(a) 0.2 (b) 0.4 (c) 0.6 (d) 0.1

11 The equilibrium constant for the reaction,

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

is 1.80 at 1000°C. If 1.0 mole of H_2 and 0.1 mole of CO_2 are placed in 1 L flask, the final equilibrium concentration of CO at 1000°C is

(a) 0.573 M (b) 0.385 M

(c) 5.73 M (d) 0.295 M

12 For the reaction,

$$I_2(g) \rightleftharpoons 2I(g);\ K_C = 37.6 \times 10^{-6}$$

at 1000 K. If 1.0 mole of I_2 is introduced into a 1.0 L flask at 1000 K, at equilibrium

(a) $[I_2] > [I]$ (b) $[I_2] = [I]$

(c) $[I_2] < [I]$ (d) Unpredictable

13 1.1 mole of A is mixed with 2.2 mole of B and the mixture is kept in a 1 L flask till the equilibrium, $A + 2B \rightleftharpoons 2C + D$ is reached. At equilibrium, 0.2 mole of C is formed. The equilibrium constant would be

(a) 0.002 (b) 0.004

(c) 0.001 (d) 0.003

14 When 3 moles of ethyl alcohol are mixed with 3 moles of acetic acid, 2 moles of ester are formed at equilibrium. According to the equation,

$$CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$$

The value of the equilibrium constant for the reaction is

(a) 4 (b) 2/9

(c) 2 (d) 4/9

15 Two moles of HI were heated in a sealed tube at 440°C till the equilibrium was reached. HI was found to be 22% decomposed. The equilibrium constant for dissociation is

(a) 0.282 (b) 0.0796

(c) 0.0199 (d) 1.99

16 In the equilibrium, $AB \rightleftharpoons A + B$, if the equilibrium concentration of A is double, then equilibrium concentration of B will be

(a) half (b) twice

(c) $\frac{1}{4}$ th (d) $\frac{1}{8}$ th

17 For the reaction,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g),$$

the equilibrium constant is K_1. The equilibrium constant is K_2 for the reaction,

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g).$$

What is K for the reaction :

$$NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g)$$

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(a) $\frac{1}{(K_1K_2)}$ (b) $\frac{1}{(2K_1K_2)}$

(c) $\frac{1}{(4K_1K_2)}$ (d) $\left[\frac{1}{K_1K_2}\right]^{1/2}$

18 Consider the following reversible chemical reactions,

$$A_2(g) + B_2(g) \xrightleftharpoons{K_1} 2AB(g) \qquad \ldots\text{(i)}$$

$$6AB(g) \xrightleftharpoons{K_2} 3A_2(g) + 3B_2(g) \qquad \ldots\text{(ii)}$$

The relation between K_1 and K_2 is ***JEE Main 2019***

(a) $K_2 = K_1^3$ (b) $K_1K_2 = 3$

(c) $K_2 = K_1^{-3}$ (d) $K_1K_2 = \frac{1}{3}$

19 The equilibrium constants for the reaction,

$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$ and

$Cu(s) + 2Ag^{+}(aq) \rightleftharpoons Cu^{2+}(aq) + 2Ag(s)$

are K_1 and K_2 respectively. The equilibrium constant for the combined reaction is

(a) $K_1 \times K_2$ (b) $K_1 + K_2$

(c) $K_1 - K_2$ (d) K_1/K_2

TOPIC 3~ Homogeneous and Heterogeneous Equilibria with its Applications

20 For reaction in equilibrium,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

Choose the correct option.

(a) $K_C = \dfrac{[HI(g)]^2}{[H_2(g)]\,[I_2(g)]}$

(b) $K_p = \dfrac{[HI(g)]^2\,[RT]^2}{[H_2(g)]RT \cdot [I_2(g)]RT}$

(c) In this reaction, $K_p = K_C$, i.e. both equilibrium constants are equal

(d) All of the above

21 For the reaction,

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

if $K_p = K_C(RT)^x$ where the symbols have usual meaning, then the value of x is (assuming ideality).

JEE Main 2014

(a) -1 (b) $-\dfrac{1}{2}$ (c) $\dfrac{1}{2}$ (d) 1

22 For the equilibrium,

$2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$, the value of the equilibrium constant, K_C is 3.75×10^{-6} at 1069 K. The value of K_p for the reaction at this temperature will be

(a) 0.133 (b) 1.242 (c) 0.033 (d) 0.00033

23 Consider the reaction,

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

The equilibrium constant of the above reaction is K_p. If pure ammonia is left to dissociate,the partial pressure of ammonia at equilibrium is given by (Assume that $p_{NH_3} << p_{\text{total}}$ at equilibrium)

JEE Main 2019

(a) $\dfrac{3^{3/2}K_p^{1/2}P^2}{4}$ (b) $\dfrac{3^{3/2}K_p^{1/2}P^2}{16}$ (c) $\dfrac{K_p^{1/2}P^2}{16}$ (d) $\dfrac{K_p^{1/2}P^2}{4}$

24 At a certain temperature and total pressure of 10^5 Pa, iodine vapour contains 40% by volume of I-atoms.

$$I_2(g) \rightleftharpoons 2I(g)$$

The value of K_p for the equilibrium is

(a) 2.67×10^4 Pa (b) 7.2×10^5 Pa

(c) 3.67×10^5 Pa (d) 4.66×10^7 Pa

25 At 450 K, $K_p = 2.0 \times 10^{10}$/bar for the given reaction at equilibrium,

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

The value of K_C at this temperature will be

(a) 6.4×10^{12} L mol^{-1} (b) 7.479×10^{11} L mol^{-1}

(c) 7.00×10^{-11} L mol^{-1} (d) 5.66×10^6 L mol^{-1}

26 5.1 g NH_4SH is introduced in 3.0 L evacuated flask at 327°C. 30% of the solid NH_4SH decomposed to NH_3 and H_2S as gases. The K_p of the reaction at 327°C is ($R = 0.082$ atm mol^{-1} K^{-1}, molar mass of $S = 32$ g mol^{-1} molar mass of N = 14 g mol^{-1})

JEE Main 2019

(a) 0.242×10^{-4} atm^2 (b) 0.242 atm^2

(c) 4.9×10^{-3} atm^2 (d) 1×10^{-4} atm^2

27 If 0.2 mole of $H_2(g)$ and 2.0 moles of $S(s)$ are mixed in a 1m^3 vessel at 90°C, the partial pressure of $H_2S(g)$ formed according to the reaction,

$$H_2(g) + S(s) \rightleftharpoons H_2S(g),$$

($K_p = 6.8 \times 10^{-2}$) would be

(a) 0.072 atm (b) 0.610 atm (c) 0.38 atm (d) 0.423 atm

28 The partial pressure of carbon monoxide from the following data will be

$$CaCO_3(s) \overset{\Delta}{\rightleftharpoons} CaO(s) + CO_2\uparrow; K_{p_1} = 8 \times 10^{-2}$$

$$CO_2(g) + C(s) \rightleftharpoons 2CO(g); K_{p_2} = 2$$

(a) 0.2 atm (b) 0.6 atm (c) 0.8 atm (d) 0.4 atm

29 For the following equilibrium,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

K_p is found to be equal to K_C. This is attained when

(a) $T = 1$ K (b) $T = 273$ K

(c) $T = 12.18$ K (d) $T = 17.15$ K

30 At equilibrium, the concentration of

$N_2 = 3.0 \times 10^{-3}$ M

$O_2 = 4.2 \times 10^{-3}$ M and $NO = 2.8 \times 10^{-3}$ M

in a sealed vessel at 800 K and 1 atm pressure. What will be K_p for the given reaction?

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

(a) 0.328 atm (b) 0.622 atm (c) 0.483 atm (d) 0.712 atm

31 The values of K_p / K_C for the following reactions at 300 K are, respectively (At 300 K, $RT = 24.62$ dm^3 atm mol^{-1})

JEE Main 2019

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

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

(a) 1, 24.62 dm^3 atm mol^{-1}, 606.0 dm^6 atm^2 mol^{-2}
(b) 1, 24.62 dm^3 atm mol^{-1}, 1.65×10^{-3} dm^{-6} atm^{-2} mol^2
(c) 24.62 dm^3 atm mol^{-1}, 606.0 dm^6 atm^{-2} mol^2, 1.65×10^{-3} dm^{-6} atm^{-2} mol^2
(d) 1, 4.1×10^{-2} dm^{-3} atm^{-1} mol, 606 dm^6 atm^2 mol^{-2}

32 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

33 For the reaction,
$H_2(g) + I_2(g) \rightleftharpoons 2HI(g); K_C = 57.0$ at 700 K.
The molar concentration of $[H_2] = 0.10$ M, $[I_2] = 0.20$ M and $[HI] = 0.40$ M.
The reaction quotient, Q_C of the reaction is
(a) 10.0
(b) 7.0
(c) 8.0
(d) 12.0

34 The value of K_C for the reaction, $2A \rightleftharpoons B + C$ is 2×10^{-3}. At a given time, the composition of reaction mixture is $[A] = [B] = [C] = 3 \times 10^{-4}$ M. **JIPMER 2018**
In which direction, the reaction will proceed?
(a) Forward direction
(b) Reverse direction
(c) At equilibrium
(d) None of the above

35 3.00 moles of PCl_5 kept in 1L closed reaction vessel was allowed to attain equilibrium at 380 K. The composition of the mixture at equilibrium will be, (Given $K_C = 1.80$)
(a) $[PCl_5] = 1.59$ M, $[PCl_3] = [Cl_2] = 1.41$ M
(b) $[PCl_5] = 1.41$ M, $[PCl_3] = [Cl_2] = 1.59$ M
(c) $[PCl_5] = 1.81$ M, $[PCl_3] = [Cl_2] = 1.75$ M
(d) $[PCl_5] = 1.75$ M, $[PCl_3] = [Cl_2] = 1.81$ M

TOPIC 4 ~ *Equilibrium Constant (K), Reaction Quotient (Q) and Gibbs' Energy (G) with Factors Affecting Equilibria*

36 The correct equation of equilibrium constant in terms of Gibbs energy is
(a) $K = e^{-\Delta G^\circ/RT}$
(b) $K = e^{-\Delta G/RT}$
(c) $K = e^{\Delta G^\circ/RT}$
(d) $K = e^{\Delta G/RT}$

37 Using the equation ($K = e^{-\Delta G^\circ/RT}$), the reaction spontaneity can be interpreted in terms of the value of ΔG° as
(a) If $\Delta G^\circ < 0$, the reaction proceeds in the forward direction to such an extent that the products are present predominantly.
(b) If $\Delta G^\circ > 0$, the reaction proceeds in the forward direction to such a small extent that only a very minute quantity of product is formed.
(c) Both (a) and (b)
(d) None of the above

38 The value of ΔG° for the phosphorylation of glucose in glycolysis is 13.8 kJ/mol. The value of K_C at 298 K is
(a) 7.72×10^{-4}
(b) 5.62×10^{-4}
(c) 4.81×10^{-3}
(d) 3.81×10^{-3}

39 Hydrolysis of sucrose gives,
Sucrose + $H_2O \rightleftharpoons$ Glucose + Fructose
Equilibrium constant (K_C) for the reaction is 2×10^{13} at 300 K. The value of ΔG° at 300 K is
(a) 3.52×10^5 J mol^{-1}
(b) 5.12×10^5 J mol^{-1}
(c) 7.64×10^4 J mol^{-1}
(d) -7.64×10^4 J mol^{-1}

40 The standard Gibbs energy change at 300 K, for the reaction, $2A \rightleftharpoons B + C$ is 2494.2J. At a given time, the composition of the reaction mixture is $[A] = 1/2$, $[B] = 2$ and $[C] = 1/2$. The reaction proceeds in the ($R = 8.314$ J/K mol, $e = 2.718$) **JEE Main 2014**
(a) forward direction because $Q > K_C$
(b) reverse direction because $Q > K_C$
(c) forward direction because $Q < K_C$
(d) reverse direction because $Q < K_C$

41 Which one of the following informations can be obtained on the basis of Le-Chatelier's principle?
(a) Dissociation constant of a weak acid
(b) Entropy change in a reaction
(c) Equilibrium constant of a chemical reaction
(d) All of the above

42 A pressure change obtained by changing the volume can affect the yield of products in case of a gaseous reaction, where

(a) the total number of moles of gaseous reactants and total number of moles of gaseous products are different
(b) the total number of moles of gaseous reactants and total number of moles of gaseous products are same
(c) number of moles of reactants > number of moles of products
(d) number of moles of reactants < number of moles of products

43 Production of ammonia according to the reaction,

$$N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g); \quad \Delta H = -92.38 \text{ kJ mol}^{-1}$$

is an exothermic process. At low temperature, the reaction shifts in

(a) forward direction
(b) backward direction
(c) either forward or backward direction
(d) None of the above

44 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 concentrations of $N_2(g)$ and $H_2(g)$
(d) by increasing pressure and decreasing temperature

45 Ostwald's process for the manufacture of nitric acid involves the reaction,

$$4NH_3(g) + 5O_2(g) \rightleftharpoons 4NO(g) + 6H_2O(l); \quad \Delta H = +Q\text{kJ}$$

Which of the following factors will not affect the concentration of NH_3 at equilibrium?

(a) Addition of catalyst
(b) Decrease of temperature
(c) Increase of pressure
(d) Increase of volume

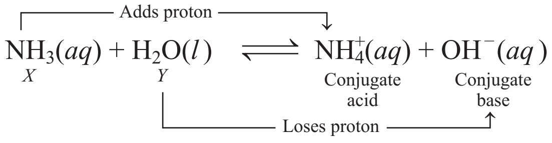
TOPIC 5 ~ *Ionic Equilibrium with Concept of Acids, Bases and Salts*

46 While, comparing the ionisation of hydrochloric acid with that of acetic acid in water we find that though both of them are polar covalent molecules, former is completely ionised into its constituent ions, while the latter is only partially ionised (< 5%).

The reason is that,

(a) ionisation depends upon the strength of the bond and the extent of solvation of ions produced
(b) ionisation depends upon the strength of the bond only
(c) extent of solvation of ions produced
(d) hydrochloric acid is stronger than acetic acid

47 In the reaction,



$$\underset{X}{NH_3(aq)} + \underset{Y}{H_2O(l)} \rightleftharpoons \underset{\text{Conjugate acid}}{NH_4^+(aq)} + \underset{\text{Conjugate base}}{OH^-(aq)}$$

X and Y respectively are

(a) neutral and acid (b) acid and base
(c) base and acid (d) base and neutral

48 Conjugate base for Bronsted acids H_2O and HF are

NEET 2019

(a) H_3O^+ and F^-, respectively
(b) OH^- and F^-, respectively
(c) H_3O^+ and H_2F^+, respectively
(d) OH^- and H_2F^+, respectively

48 Which of the following cannot act both as Bronsted acid and as Bronsted base? **NEET (Odhisa) 2019**

(a) HCO_3^-
(b) NH_3
(c) HCl
(d) HSO_4^-

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

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

51 Which one of the following is the weakest acid?

(a) HCl
(b) HF
(c) H_2SO_4
(d) HNO_3

52 Which equilibrium can be described as an acid-base reaction using the Lewis acid-base definition, but not using Bronsted-Lowry definition?

(a) $NH_3 + CH_3COOH \rightleftharpoons CH_3COO^- + NH_4^+$
(b) $H_2O + CH_3COOH \rightleftharpoons H_3O^+ + CH_3COO^-$
(c) $4NH_3 + [Cu(H_2O)_4]^{2+} \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4H_2O$
(d) $2NH_3 + H_2SO_4 \rightleftharpoons 2NH_4^+ + SO_4^{2-}$

TOPIC 6 ~ *Ionisation of Acids and Bases*

53 In the following reaction,

$$\underset{\text{Acid}}{H_2O(l)} + \underset{X}{H_2O(l)} \rightleftharpoons \underset{\text{Conjugate acid}}{H_3O^+(aq)} + \underset{Y}{OH^-(aq)}$$

X and Y respectively are

(a) base and conjugate acid (b) acid and conjugate base
(c) base and conjugate base (d) acid and conjugate acid

54 The correct order of increasing $[H_3O^+]$ in the aqueous solution is

(a) $0.01\,M\,H_2S < 0.01\,M\,H_2SO_4 < 0.01\,M\,NaCl < 0.01\,M\,NaNO_2$
(b) $0.01\,M\,NaCl < 0.01\,M\,NaNO_2 < 0.01\,M\,H_2S < 0.01\,M\,H_2SO_4$
(c) $0.01\,M\,NaNO_2 < 0.01\,M\,NaCl < 0.01\,M\,H_2S < 0.01\,M\,H_2SO_4$
(d) $0.01\,M\,H_2S < 0.01\,M\,NaNO_2 < 0.01\,M\,NaCl < 0.01\,M\,H_2SO_4$

55 The decreasing order of strength of the bases OH^-, NH_2^-, $H—C\equiv C^-$ and $CH_3—CH_2^-$ is

(a) $CH_3—CH_2^- > NH_2^- > H—C\equiv C^- > OH^-$
(b) $H—C\equiv C^- > CH_3—CH_2 > NH_2 > OH^-$
(c) $OH^- > NH_2^- > H—C\equiv C^- > CH_3—CH_2^-$
(d) $NH_2^- > H—C\equiv C^- > OH—CH_3—CH_2^-$

56 Which of the following salts is the most basic in aqueous solution? ***JEE Main 2018***

(a) $Al(CN)_3$ (b) CH_3COOK
(c) $FeCl_3$ (d) $Pb(CH_3COO)_2$

57 The concentration of hydrogen ion in a sample of soft drink is 3.8×10^{-3} M. The value of its pH is

(a) 4.32 (b) 5.12 (c) 3.31 (d) 2.42

58 If the ionisation constant of acetic acid is 1.8×10^{-5}, at what concentration will it be dissociated to 2%?

(a) 1 M (b) 0.018 M
(c) 0.18 M (d) 0.045 M

59 The dissociation constant of acetic acid at a given temperature is 1.69×10^{-5}. The degree of dissociation of 0.01 M acetic acid in the presence of 0.01 M HCl is equal to

(a) 0.41×10^{-2} (b) 0.18×10^{-7}
(c) 0.169×10^{-2} (d) 0.013×10^{-4}

60 A 0.2 molar solution of formic acid is 3.2% ionised. Its ionisation constant is

(a) 9.6×10^{-3} (b) 2.1×10^{-4}
(c) 1.25×10^{-6} (d) 4.8×10^{-5}

61 For a reaction,

$$CH_3COOH(aq) \rightleftharpoons H^+(aq) + CH_3COO^-(aq)$$

or $$HAc(aq) \rightleftharpoons H^+(aq) + Ac^-(aq)$$

The value of pH of the solution resulting on addition of 0.05 M acetate ion to 0.05 M acetic acid solution is $(K_a = 1.8 \times 10^{-5})$.

(a) 5.72 (b) 3.87
(c) 4.24 (d) 4.74

62 The pH of 0.10 N acetic acid having $K_a = 1.8 \times 10^{-5}$ is

(a) 2.9 (b) 5.6
(c) 6.8 (d) 3.4

63 A 0.01 M ammonia solution is 5% ionised. The concentration of OH^- ion is

(a) 0.005 M (b) 0.0001 M
(c) 0.0005 M (d) 0.05 M

64 2g of NaOH is dissolved in water to make 1L solution. The pH of solution is

(a) 10.25 (b) 8.256
(c) 12.70 (d) 10.89

65 The pH of 0.01 M NaOH (*aq*) solution will be

(a) 7.01 (b) 2
(c) 12 (d) 9

66 The pH of a mixture when a 50 mL solution of $pH = 1$ is mixed with a 50 mL of $pH = 2$ is

(a) 0.56 (b) 1.26
(c) 1.76 (d) 2.06

67 Assuming complete ionisation, the pH of 0.1 M HCl is 1. The molarity of H_2SO_4 with the same pH is

(a) 0.01 (b) 0.2 (c) 0.05 (d) 2.0

68 How many litres of water must be added to 1 L of an aqueous solution with a pH of 1 to create an aqueous solution of pH of 2? ***JEE Main 2013***

(a) 49 L (b) 9 L
(c) 79 L (d) 59 L

69 If 50 mL of 0.1 HBr is mixed with 50 mL 0.2 M NaOH, find pH of resulting mixture ***JIPMER 2019***

(a) 2.7 (b) 12.7
(c) 10.7 (d) 1.3

70 A weak base BOH is titrated with a strong acid HA. When 10 mL of HA is added, pH is found to be 9.00 and when 25 mL is added, pH is 8.00. The volume of the acid required to reach the equivalence point is

(a) 55 mL (b) 40 mL
(c) 30 mL (d) 50 mL

71 Following solutions were prepared by mixing different volumes of NaOH and HCl of different concentrations : ***NEET 2019***

I. $60\text{ mL}\,\frac{M}{10}\,\text{HCl} + 40\text{ mL}\,\frac{M}{10}\,\text{NaOH}$

II. $55\text{ mL}\,\frac{M}{10}\,\text{HCl} + 45\text{ mL}\,\frac{M}{10}\,\text{NaOH}$

III. $75\text{ mL}\,\frac{M}{5}\,\text{HCl} + 25\text{ mL}\,\frac{M}{5}\,\text{NaOH}$

IV. $100\text{ mL}\,\frac{M}{10}\,\text{HCl} + 100\text{ mL}\,\frac{M}{10}\,\text{NaOH}$

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

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

72 The pK_b for fluoride ion at 25°C is 10.83, the ionisation constant of hydrofluoric acid at this temperature is

(a) 2.72×10^{-5}
(b) 3.52×10^{-3}
(c) 6.76×10^{-4}
(d) 5.38×10^{-2}

73 The pH 0.005 M codeine ($C_{18}H_{21}NO_3$) solution is 9.95. Its pK_b value is

(a) 8.92
(b) 5.80
(c) 3.76
(d) 4.29

74 The extent of dissociation of an acid depends on

(a) polarity
(b) strength and polarity
(c) dipole moment
(d) None of the above

75 The degree of ionisation of a compound depends on

(a) size of solute molecules
(b) nature of solute molecules
(c) nature of vessel used
(d) quantity of electricity passed

76 In the following observation.

Acid	K_{a_1}	K_{a_2}	(X)
Oxalic acid	5.9×10^{-2}	6.4×10^{-5}	
Ascorbic acid	7.4×10^{-4}	1.6×10^{-12}	
Sulphurous acid	1.7×10^{-2}	6.4×10^{-8}	
(Y)	Very large	1.2×10^{-2}	
Carbonic acid	4.3×10^{-7}	(Z)	
Citric acid	7.4×10^{-4}	1.7×10^{-5}	4.0×10^{-7}
Phosphoric acid	7.5×10^{-3}	6.2×10^{-8}	4.2×10^{-13}

X, Y and Z respectively are

(a) $K = K_{a_1} \times K_{a_2}$, phosphorous acid, 6.5×10^{-11}
(b) K_{a_3}, phosphorous acid, 6.5×10^{-11}
(c) $K = K_{a_1} \times K_{a_2}$, sulphuric acid, 5.6×10^{-11}
(d) K_{a_3}, sulphuric acid, 5.6×10^{-11}

77 The process of interaction between water and cations/anions or both of salts is called

(a) hydration
(b) hydrolysis
(c) dehydration
(d) Both (a) and (b)

78 The pK_a of acetic acid and pK_b of ammonium hydroxide are 4.76 and 4.75 respectively. Calculate the pH of ammonium acetate solution. ***JEE Main 2017***

(a) 4.765
(b) 5.012
(c) 7.005
(d) 6.098

79 pH of a salt solution of weak acid ($pK_a = 4$) and weak base ($pK_b = 5$) at 25°C is ***AIIMS 2019***

(a) 6.5
(b) 6
(c) 7
(d) 7.5

80 A 100 mL, 0.1 M solution of ammonium acetate is diluted by adding 100 mL of water. The pH of the resulting solution will be

(pK_a of acetic acid is nearly equal to pK_b of NH_4OH) ***CBSE AIPMT 2012***

(a) 4.9
(b) 5.9
(c) 7.0
(d) 10.0

TOPIC 7 ~ *Buffer Solutions*

81 A mixture of acetic acid and sodium acetate acts as buffer solution around pH P and a mixture of ammonium chloride and ammonium hydroxide acts as a buffer around pH Q. P and Q respectively are

(a) 9.25 and 4.75
(b) 4.75 and 9.25
(c) 8.74 and 3.87
(d) 3.87 and 8.74

82 100 mL of a solution contains 0.1 M NH_4OH and 0.1 M NH_4Cl. The pH of the solution will not change on adding.

(a) 20 mL of 0.1 M NH_4OH solution
(b) 20 mL of 0.1 M NH_4Cl solution
(c) 10 mL of 0.1 M NaOH solution
(d) 10 mL of distilled water

83 Which of the following combinations of $CH_3COOH + NaOH$ would result in the formation of acidic buffer?

(a) 1 : 1 mol ratio (b) 2 : 1 mol ratio
(c) 1 : 2 mol ratio (d) Both (a) and (c)

84 The pH of a buffer solution will be equal to the pK_a of acid, only if

(a) molar concentration of acid is greater than molar concentration of conjugate base.
(b) molar concentration of acid is smaller than molar concentration of conjugate base.
(c) molar concentration of acid is equal to the molar concentration of conjugate base.
(d) molar concentration of acid is almost negligible.

85 pH of the buffer solution formed by mixing acetic acid and sodium acetate taken in equimolar concentration will be

[Given : pK_a value for $CH_3COOH = 4.76$]

(a) > 4.76 (b) < 4.76
(c) $= 4.76$ (d) $<< 4.76$

86 pH of a buffer prepared by adding 10 mL of 0.10 M acetic acid to 20 mL of 0.1M sodium acetate is equal to (pK_a of $CH_3COOH = 4.74$)

(a) 4.74 (b) 5.6 (c) 5.04 (d) 6.02

87 50 mL of 0.1 M NaOH is added to 75 mL of 0.1M NH_4Cl to make a basic buffer. If pK_a of NH_4^+ is 9.26, then the pH of solution is

(a) 4.44 (b) 9.56 (c) 4.74 (d) 5.76

88 The pK_a of HCN is 9.30. The pH of a solution prepared by mixing 2.5 moles of KCN and 2.5 moles of HCN in water and making up the total volume of 500 mL is

(a) 9.30 (b) 7.30 (c) 10.30 (d) 8.30

89 A buffer solution is prepared in which the conc. 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 equals 1.8×10^{-5}, what is the pH of this solution? ***CBSE AIPMT 2011***

(a) 8.73 (b) 9.08 (c) 9.44 (d) 11.72

90 One litre of a buffer solution containing 0.01 M NH_4Cl and 0.1 M NH_4OH having pK_b of 5 has pH of

(a) 9 (b) 10 (c) 6 (d) 7

91 Which of the following will make basic buffer ?

(a) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1 M NaOH
(b) 100 mL of 0.1 M HCl + 200 mL of 0.1 M NH_4OH
(c) 100 mL of 0.1 M HCl + 100 mL of 0.1 M NaOH
(d) 50 mL of 0.1 M NaOH + 25 mL of 0.1 M CH_3COOH

TOPIC 8 ~ *Solubility Equilibria of Sparingly Soluble Salts*

92 What will be the molar solubility S of a solid salt with general formula $M_x^{p+} X_y^{q-}$?

(a) $\left(\frac{K_{sp}}{x^y \cdot y^x}\right)^{1/x+y}$ (b) $\left(\frac{K_{sp}}{x^x \cdot y^y}\right)^{x+y}$
(c) $\left(\frac{K_{sp}}{x^x \cdot y^y}\right)^{1/x+y}$ (d) $\left(\frac{K_{sp}}{x^y \cdot y^x}\right)^{x+y}$

93 The solubility product (K_{sp}) of solid barium sulphate at 298 K is 1.1×10^{-10}. The molar solubility, (S) of $[Ba^{2+}]$ and $[SO_4^{2-}]$ are

(a) 1.05×10^{-7} mol L^{-1} (b) 1.05×10^{-10} mol L^{-1}
(c) 1.05×10^{-6} mol L^{-1} (d) 1.05×10^{-5} mol L^{-1}

94 The K_{sp} of Ag_2CrO_4, AgCl, AgBr and AgI are respectively, $1.1 \times 10^{-12}, 1.8 \times 10^{-10}, 5.0 \times 10^{-23}$, 8.3×10^{-17}. Which one solution is added to the solution containing equal moles of NaCl, NaI and Na_2CrO_4? ***CBSE AIPMT 2015***

(a) Ag I (b) AgCl (c) AgBr (d) Ag_2CrO_4

95 Calculate the molar solubility (S) of a salt like zirconium phosphate of molecular formula. $(Zr^{4+})_3(PO_4^{3-})_4$.

(a) $\left(\frac{K_{sp}}{9612}\right)^{1/8}$ (b) $\left(\frac{K_{sp}}{6912}\right)^{1/7}$
(c) $\left(\frac{K_{sp}}{5348}\right)^{1/6}$ (d) $\left(\frac{K_{sp}}{8435}\right)^{1/7}$

96 Calculate the solubility of A_2X_3 in pure water, assuming that neither kind of ion reacts with water. (Given, the solubility product of A_2X_3, $K_{sp} = 1.1 \times 10^{-23}$.)

(a) 2.0×10^{-5} mol L^{-1} (b) 5.0×10^{-5} mol L^{-1}
(c) 1.0×10^{-5} mol L^{-1} (d) 4.0×10^{-3} mol L^{-1}

97 The molar solubility of CaF_2 ($K_{sp} = 5.3 \times 10^{-11}$) in 0.1 M solution of NaF will be ***NEET (Odhisa) 2019***

(a) 5.3×10^{11} mol L^{-1} (b) 5.3×10^{-8} mol L^{-1}
(c) 5.3×10^{-9} mol L^{-1} (d) 5.3×10^{-10} mol L^{-1}

98 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, ***NEET 2018***

(Given, molar mass of $BaSO_4 = 233$ g mol^{-1})

(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}

99 Concentration of the Ag^+ ions in a saturated solution of $Ag_2C_2O_4$ is 2.2×10^{-4} mol^{-1}. The 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}

100 The solubility product of sparingly soluble salt AX_2 is 3.2×10^{-11}. Its solubility (in mol/L) is ***AIIMS 2018***

(a) 5.6×10^{-6} (b) 3.1×10^{-4}
(c) 2×10^{-4} (d) 4×10^{-4}

101 The solubility product (K_{sp}) of the sparingly soluble salt Ag_2CrO_4 is 4×10^{-12}. The molar solubility of the salt is

(a) 1.0×10^{-4} mol L^{-1} (b) 2×10^{-6} mol L^{-1}
(c) 1.0×10^{-5} mol L^{-1} (d) 2×10^{-12} mol L^{-1}

102 Calculate the volume of water required to dissolve 0.1g lead (II) chloride to get a saturated solution. (K_{sp} of $PbCl_2 = 3.2\times10^{-8}$ and atomic mass of Pb = 207 u)

(a) 100 mL (b) 180 mL
(c) 120 mL (d) 150 mL

103 The solubility product of $Cr(OH)_3$ at 298 K is 6.0×10^{-31}. The concentration of hydroxide ions in a saturated solution of $Cr(OH)_3$ will be

(a) $(2.22\times10^{-31})^{1/4}$ (b) $(18\times10^{-31})^{1/4}$
(c) $(4.86\times10^{-29})^{1/4}$ (d) $(18\times10^{-31})^{1/2}$

104 If the maximum concentration of $PbCl_2$ in water is 0.01 M at 25°C, its maximum concentration in 0.1 M NaCl will be

(a) 2×10^{-3} M (b) 1×10^{-4} M
(c) 1.6×10^{-2} M (d) 4×10^{-4} M

105 At 20°C, the Ag^+ ion concentration in a saturated solution of Ag_2CrO_4 is 1.5×10^{-4} mol/L. At 20°C, the solubility product of Ag_2CrO_4 will be

(a) 3.3750×10^{-12} (b) 1.6875×10^{-10}
(c) 1.6875×10^{-12} (d) 1.6875×10^{11}

106 Solubility of calcium phosphate (molecular mass, M) in water is W g per 100 mL at 25°C. Its solubility product at 25°C will be approximately.

(a) $10^7\left(\frac{W}{M}\right)^3$ (b) $10^7\left(\frac{W}{M}\right)^5$
(c) $10^5\left(\frac{W}{M}\right)^5$ (d) $10^3\left(\frac{W}{M}\right)^5$

107 If S_1, S_2, S_3 and S_4 are the solubilities of AgCl in water, in 0.01 M $CaCl_2$, in 0.01 M NaCl and in 0.05 M $AgNO_3$ respectively at a certain temperature, the correct order of solubilities is,

(a) $S_1 > S_2 > S_3 > S_4$
(b) $S_1 > S_3 > S_2 > S_4$
(c) $S_1 > S_2 = S_3 > S_4$
(d) $S_1 > S_3 > S_4 > S_2$

108 Three sparingly soluble salt that have same solubility products are given below.

I. A_2X II. AX III. AX_3

Their solubilities order in a saturated solution will be

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

109 Given, $Ag(NH_3)_2^+ \rightleftharpoons Ag^+ + 2NH_3$; $K_C = 6.2\times10^{-8}$ and K_{sp} of AgCl is 1.8×10^{-10} at 298 K. Calculate concentration of the complex in 1 M aqueous ammonia, if ammonia is added to a water solution containing excess of AgCl(s) only.

(a) 0.539 M (b) 0.0539 M
(c) 0.641 M (d) 0.0641 M

110 Using the Gibbs energy change, $\Delta G° = +63.3$ kJ for the following reaction,

$$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$$

the K_{sp} of $Ag_2CO_3(s)$ in water at 25°C is, ($R = 8.314$ JK^{-1} mol^{-1}) ***CBSE AIPMT 2014***

(a) 3.2×10^{-26}
(b) 8.0×10^{-12}
(c) 2.9×10^{-3}
(d) 7.9×10^{-2}

111 pH of saturated solution of $Ba(OH)_2$ is 12. The value of solubility product of K_{sp} of $Ba(OH)_2$ is ***CBSE AIPMT 2012***

(a) 3.3×10^{-7} (b) 5.0×10^{-7}
(c) 4.0×10^{-4} (d) 5.0×10^{6}

112 The values of K_{sp} of two sparingly soluble salts $Ni(OH)_2$ and AgCN are 2.0×10^{-15} and 6×10^{-17} respectively. Which salt is more soluble?

(a) $Ni(OH)_2$ is more soluble than AgCN
(b) AgCN is more soluble than $Ni(OH)_2$
(c) Both $Ni(OH)_2$ and AgCN soluble to same extent
(d) $Ni(OH)_2$ is soluble but AgCN is insoluble

113 The value of molar solubility of $Ni(OH)_2$ in 0.10 M NaOH. If is; then the ionic product of $Ni(OH)_2$ is 2.0×10^{-15}.

(a) 6.0×10^{-12} M (b) 8.0×10^{-13} M
(c) 2.0×10^{-13} M (d) 5.0×10^{-12} M

114 Dissolution of sodium sulphate is an exothermic process. If a saturated solution of sodium sulphate containing extra undissolved sodium sulphate is heated, then

(a) more of sodium sulphate will dissolve
(b) some sodium sulphate will be precipitated out
(c) concentration of the solution will not change
(d) the solution will become supersaturated

115 The addition of NaCl to AgCl decreases the solubility of AgCl because

(a) solubility product decreases
(b) solubility product remains constant
(c) solution becomes unsaturated
(d) solution becomes supersaturated

116 The solubility product (K_{sp}) of AgCl is 1.8×10^{-10}. Precipitation of AgCl will occur only when equal volumes of solutions of

(a) 10^{-4} M Ag^+ and 10^{-4} M Cl^- are mixed
(b) 10^{-7} M Ag^+ and 10^{-7} M Cl^- are mixed
(c) 10^{-5} M Ag^+ and 10^{-5} M Cl^- are mixed
(d) 10^{-10} M Ag^+ and 10^{-10} M Cl^- are mixed

117 What is the minimum pH of a solution having concentration 0.10 M of Mg^{2+}, from which $Mg(OH)_2$ will not precipitate? $K_{sp} Mg(OH)_2 = 1.2 \times 10^{-11}$

(a) 6.04 (b) 4.96
(c) 9.04 (d) 5.07

SPECIAL TYPES QUESTIONS

I. Statement Based Questions

118 Which of the following statements is incorrect regarding equilibrium state ?

(a) The value of ΔG at equilibrium is zero
(b) The reaction ceases at equilibrium
(c) Equilibrium constant is independent of initial concentrations of reactants
(d) Catalysts have no effect on equilibrium state

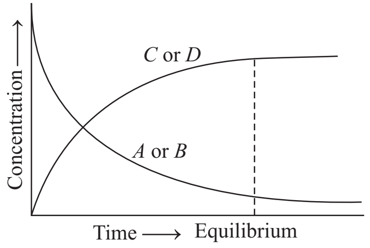
119 Which of the following statements is correct?

(a) Boiling point of the liquid depends on the atmospheric pressure
(b) Boiling point depends on the altitude of the place
(c) At high altitude the boiling point decreases
(d) All of the above

120 Which one of the following statements is incorrect about chemical equilibrium?

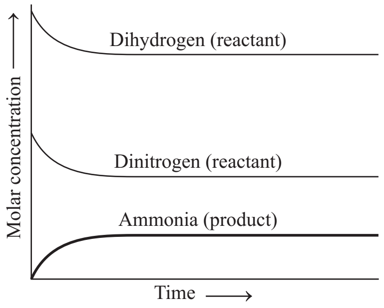
(a) Chemical equilibrium is attained whether we start with reactants or products
(b) Chemical equilibrium is dynamic in nature
(c) Chemical equilibrium, $CaCO_3(s) \rightleftharpoons CaO(s) + O_2(g)$ is attained, when $CaCO_3(s)$ is heated in an open vessel
(d) At equilibrium, the concentration of each of the reactants and products becomes constant.

121 Consider the graph given below and choose the incorrect statement regarding it.



(a) The given graph represents the attainment of equilibrium for a reversible reaction, $A + B \rightleftharpoons C + D$
(b) The rate of forward reaction decreases and that of reverse reaction increases.
(c) The two reactions occur at the same rate.
(d) The reaction can reach the state of equilibrium only if it starts with A and B.

122 Consider the following statements about the graph given below,



I. After a certain time, the composition of the mixture remains same.

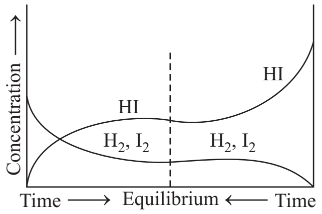
II. The reaction mixture starting with either H_2 or D_2 reach equilibrium with same composition.

III. The constancy in composition indicates that the reaction has reached equilibrium.

Choose the correct statements.

(a) Only I (b) Only II
(c) I and III (d) I, II & III

123 Consider the following graph and choose the incorrect statements.



(a) If total number of H and I atoms are same in a given volume, then same equilibrium mixture is obtained.

(b) Chemical equilibrium in the reaction $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ can attained from reactant side only.

(c) The concentration of $H_2$and I_2 decreases while that of HI increases with time.

(d) The reaction can proceed in the reverse directing by starting with HI alone.

124 For the reaction,

$$2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g),$$
$$\Delta H = -57.2 \text{ kJ mol}^{-1} \text{ and } K_c = 1.7 \times 10^{16}.$$

Which of the following statement is incorrect?

JEE Main 2019

(a) The equilibrium constant decreases as the temperature increases.

(b) The addition of inert gas at constant volume will not affect the equilibrium constant.

(c) The equilibrium will shift in forward direction as the pressure increases.

(d) The equilibrium constant is large suggestive of reaction going to completion and so no catalyst is required.

125 Consider the following equilibrium in a closed container, $N_2O_4(g) \rightleftharpoons 2NO_2(g)$. At a fixed temperature, the volume of the reaction container is halved. For this change, which of the following statements hold true regarding the equilibrium constant (K_p) and degree of dissociation (α)?

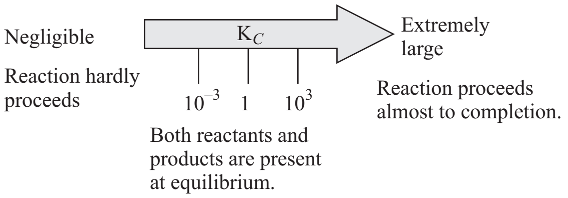
(a) K_p does not change, but α changes

(b) K_p changes, but α does not change

(c) Both K_p and α change

(d) Neither K_p nor α changes

126 Consider the following figure which shows dependence of extent of reaction on K_C.



Point out of the correct statement(s) for the above graph.

(a) If $K_C > 10^3$, products predominate over reactants, i.e. if K_C is very large, the reaction proceeds nearly to completion.

(b) If $K_C < 10^{-3}$, reactants predominate over products, i.e. if K_C is very small, the reaction proceeds rarely.

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

(d) All of the above

127 Which of the following statement is incorrect regarding the formation of salt NaCl?

(a) It exist in solid state as a cluster of positively charged chloride ions and negatively charged sodium ions.

(b) Sodium and chloride ions are held together due to electrostatic interactions between oppositely charged species.

(c) When sodium chloride is dissolved in water, the electrostatic interactions are reduced by a factor of 80.

(d) Ions of NaCl in water are free to move in the solution.

128 Carboxylic acids readily dissolve in aqueous sodium bicarbonate, liberating carbon dioxide. Which one of the following statement is correct?

(a) The free carboxylic acid and its conjugate base are of comparable stability

(b) The free carboxylic acid is more stable than its conjugate base

(c) The conjugate base of the carboxylic acid is more stable than the free carboxylic acid

(d) The conjugate acid of the carboxylic acid is more stable than the free carboxylic acid

129 Which one of the following statements is incorrect?

(a) The degree of ionisation of a weak electrolyte increases with dilution

(b) Strong electrolytes are ionised completely at all concentrations

(c) Addition of NH_4Cl to NH_4OH increases the ionisation of the latter

(d) Increase of temperature increases the ionisation

130 Which of the following statement is correct?

(a) Acidic buffer consist of a strong acid and its salt with weak base in a fixed proportion.

(b) pH of the buffer solution changes by dilution.

(c) Natural buffer are the solution of salts of weak acid and weak base.

(d) Glycine + glycine hydrochloride is an example of acidic buffer.

131 Consider the following statements regarding physical processes.

I. Equilibrium is possible only in a closed system at a given temperature.

II. Both the opposing processes occur at the same rate and there is a dynamic but stable condition.

III. All measurable properties of the system remain constant.

IV. When equilibrium is attained for a physical process, it is characterised by constant value of one of its parameters at a given temperature.

V. The magnitude of such quantities at any stage indicates the extent to which the physical process has proceeded before reaching equilibrium.

Which of the following statements is correct?

(a) I, III and V (b) I, III and IV

(c) III, IV and V (d) All of these

132 Consider the following statements about an experiment in which two 100 mL measuring cylinders (marked as *A* and *B*) and two glass tubes each of 40 cm length is taken cylinder *A* is filled nearly half with coloured water and cylinder *B* is kept empty.

I. On intertransferring coloured solution between the cylinders, there will no further change in the levels of colloured water in both the cylinders.

II. This experiment indicates the dynamic nature of the process .

Select the correct statement and choose the correct option.

(a) Only I (b) Only II

(c) Both I and II (d) None of these

133 Consider the following statements regarding the equilibrium constants.

I. Expression for the equilibrium constant is not applicable when concentrations of the reactants and products have attained constant value at equilibrium state.

II. The value of equilibrium constant is dependent on initial concentration of the reactants and products.

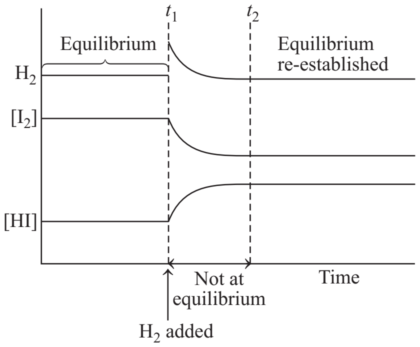
III. Equilibrium constant is temperature dependent having one unique value for a particular reaction represented by a balanced equation at a given temperature.

IV. The equilibrium constant for the reverse reaction is directly proportional to the equilibrium constant for the forward reaction.

The correct statement(s) is/are

(a) I and II (b) II and III (c) Only III (d) All of these

134 Consider the following statements about the figure given below



I. On addition of $H_2(g)$ to the reaction mixture at equilibrium, the equilibrium of the reaction is disturbed.

II. To restore equilibrium, the reaction proceeds in the backward direction.

III. This is in accordance with the Le-Chateliers principle

IV. Change in the concentration of either reactants or products shift the reaction in the direction in which the effect of change is minimised or nullified .

Select the correct statements and choose the correct option.

(a) Only I (b) I and II

(c) II and III (d) I, III and IV

135 Consider the following statements for a given reaction,

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

I. The equilibrium constant,

$$K_C = \frac{[Fe(SCN)^{2+}(aq)]}{[Fe^{3+}(aq)][SCN^-(aq)]}$$

II. A reddish colour appears on adding two drops of 0.002 M potassium thiocyanate solution to 1 mL of 0.2 M iron (III) nitrate solution due to the formation of $[Fe(SCN)]^{2+}$. The intensity of the red colour becomes constant on attaining equilibrium.

III. The equilibrium can be shifted in either forward or reverse directions depending on our choice of adding a reactant or a product.

IV. The equilibrium can be shifted in the opposite direction by adding reagents that remove Fe^{3+} or SCN^- ions.

Choose the correct statement(s).

(a) Only I (b) I, III and IV
(c) I and II (d) All of these

136 Consider the following statements.

I. In general, the temperature dependence of the equilibrium constant depends on the sign of ΔH for the reaction.

II. The equilibrium constant for an exothermic reaction (negative, ΔH) decreases as the temperature increases.

III. The equilibrium constant for an endothermic reaction (positive, ΔH) increases as the temperature increases.

IV. Temperature changes affect the equilibrium constant and rates of reactions.

Choose the correct statements.

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

137 Consider the following statement about the equilibrium,

$$2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g); \Delta H^\circ = -198 \text{ kJ}$$

I. On decreasing the temperature as well as pressure equilibrium shifts in forward direction.

II. On increasing temperature and pressure equilibrium shifts in forward direction.

III. On decreasing the temperature and increasing the pressure, equilibrium will shift in forward direction.

Choose the correct statement.

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

138 Consider the following statements.

I. The pH of a mixture containing 400 mL of 0.1 M H_2SO_4 and 400 mL of 0.1 M NaOH will be approximately 1.3.

II. Ionic product of water is temperature dependent.

III. A monobasic acid with $K_a = 10^{-5}$ has a pH = 5. The degree of dissociation of this acid is 50%.

IV. The Le-Chatelier's principle is not applicable to common-ion effect.

The correct statements are ***JEE Main 2019***

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

139 Based on the extent to which the reactions proceed to reach the state of chemical equilibrium, the reactions may be classified as

I. The reactions that proceed nearly to completion and only negligible concentrations of the reactants are left.

II. The reactions in which only small amounts of products are formed and most of the reactants remain unchanged at equilibrium stage.

III. The reactions in which the concentrations of the reactants and products are comparable, when the system is in equilibrium.

Which of the following is a correct option?

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

II. Assertion and Reason

■ **Directions** (Q. Nos. 140-149) *In the following questions a statement of Assertion* (A) *followed by a statement of Reason* (R) *is given. Choose the correct answer out of the following choices.*

(a) Both A and R are correct; R is the correct explanation of A
(b) Both A and R are correct; R is not the correct explanation of A
(c) A is correct; R is incorrect
(d) A is incorrect; R is correct

140 **Assertion** (A) For dissolution of gases in liquids, on increasing the temperature or decreasing the pressure the amount of gas dissolved decreases.

Reason (R) For dissolution of gases in liquids, the concentration of a gas in liquid is inversely proportional to the pressure (concentration) of the gas over the liquid.

141 **Assertion** (A) There is an equilibrium between the gaseous molecules and dissolved molecules of the gas under pressure.

Reason (R) Such equilibrium is governed by Henry's law.

142 **Assertion** (A) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$ is the example of homogeneous equilibria.

Reason (R) For this reaction, K_C has unit L/mol and K_p has unit bar.

143 **Assertion** (A) In the dissociation of PCl_5 at constant pressure and temperature, addition of helium at equilibrium increases the dissociation PCl_5.

Reason (R) Helium removes Cl_2 from the field of action.

144 **Assertion** (A) A solution of $FeCl_3$ in water produces brown precipitate on standing.

Reason (R) Hydrolysis of $FeCl_3$ in water produces brown precipitate of $Fe(OH)_3$.

145 **Assertion** (A) If a volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed.

Reason (R) It is because, the addition of an inert gas at constant volume does not change the partial pressure or the molar concentrations of the substance involved in the reaction.

146 **Assertion** (A) Michael Faraday classified the substances into two categories based on their ability to conduct electricity.

Reason (R) One category of substances conduct electricity in their aqueous solutions and are called electrolytes, while the other do not and are, thus referred to as non-electrolytes.

147 **Assertion** (A) Higher order ionisation constant (K_{a_2}, K_{a_3}) are smaller than the lower order ionisation constant (K_{a_1}) of a polyprotic acid.

Reason (R) It is more difficult to remove a positively charged proton from a negative ion due to Coulombic forces.

148 **Assertion** (A) Common ion effect is defined as a shift in equilibrium on adding a substance that provides more of an ionic species already present in the dissociation equilibrium.

Reason (R) Common ion effect is a phenomenon based on the Le-Chatelier's principle.

149 **Assertion** (A) Buffer system of carbonic acid and sodium bicarbonate is used for the precipitation of hydrolysis of third group elements.

Reason (R) It maintains the pH to a constant value about 7.4.

III. Matching Type Questions

150 Match the Column I with Column II and choose the correct option from the codes given below.

Column I (Process)	**Column II** (Conclusion)
A. Liquid $\rightleftharpoons$ vapour	1. Concentration of solute in solution is constant at a given temperature.
B. Solid $\rightleftharpoons$ liquid	2. [Gas (*aq*)]/ [gas (*g*)] is constant at a given temperature.
C. Solute (*s*) $\rightleftharpoons$ solute (solution)	3. p_{H_2O} constant at given temperature.
D. Gas (*g*) $\rightleftharpoons$ Gas (*aq*)	4. Melting point is fixed at given temperature.

Codes

	A	B	C	D
(a)	2	3	4	1
(b)	1	2	3	4
(c)	4	3	2	1
(d)	3	4	1	2

151 Match the Column I with Column II and choose the correct option from the codes given below.

Column I (Name of the fluid)	**Column II** (pH)
A. Human blood	1. 2.2
B. Milk	2. 4.2
C. Human saliva	3. 7.4
D. Lemon juice	4. 6.8
E. Gastric juice	5. 6.4

Codes

	A	B	C	D	E
(a)	2	5	3	4	1
(b)	1	2	3	4	5
(c)	3	4	5	1	2
(d)	1	3	5	4	2

152 Match the Column I with Column II and choose the correct option from the codes given below.

Column I (Hydrolysis of the salts)	**Column II** (Example)
A. Weak acid and strong base	1. NH_4Cl
B. Strong acid and weak base	2. CH_3COONH_4
C. Weak acid and weak base	3. CH_3COONa

Codes

	A	B	C
(a)	3	2	1
(b)	1	2	3
(c)	2	3	1
(d)	3	1	2

NCERT & NCERT Exemplar

MULTIPLE CHOICE QUESTIONS

NCERT

153 When hydrochloric acid is added to cobalt nitrate solution at room temperature, the following reaction takes place and the reaction mixture becomes blue. On cooling the mixture it becomes pink. On the basis of this information mark the correct answer.

$$\underset{\text{(Pink)}}{[Co(H_2O_6)]^{3+}}(aq) + 4Cl^-(aq) \rightleftharpoons \underset{\text{(Blue)}}{[CoCl_4]^{2-}}(aq) + 6H_2O\ (l)$$

(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 ΔH cannot be predicted on the basis of this information

154 For the reaction, $H_2(g) + I_2(g) \rightleftharpoons 2HI\ (g)$, the standard free energy is $\Delta G^\circ > 0$. The equilibrium constant (K_C) would be

(a) $K = 0$ (b) $K > 1$ (c) $K = 1$ (d) $K < 1$

155 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 order of pH of $0.1\ \text{mol dm}^{-3}$ 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

NCERT Exemplar

156 Which of the following is not a general characteristic of equilibria involving physical process?

(a) Equilibrium is possible only in a closed system at a given temperature

(b) All measurable properties of the system remain constant

(c) All the physical process stop at equilibrium

(d) The opposing processes occur at the same rate and there is dynamic but stable condition.

157 Which of the following statements is incorrect?

(a) In equilibrium mixture of ice and water kept in perfectly insulated flask, mass of ice and water does not change with time

(b) The intensity of red colour increases when oxalic acid is added to a solution containing iron (III) nitrate and potassium thiocyanate

(c) On addition of catalyst, the equilibrium constant value is not affected

(d) Equilibrium constant for a reaction with negative ΔH value decreases as the temperature increases

158 PCl_5, PCl_3, and Cl_2 are at equilibrium at 500 K in a closed container and their concentrations are 0.8×10^{-3} mol L^{-1}, 1.2×10^{-3} mol L^{-1} and 1.2×10^{-3} mol L^{-1}, respectively. The value of K_C for the reaction.

$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g)$ will be

(a) 1.8×10^3 mol L^{-1} (b) 1.8×10^{-3} mol L^{-1}

(c) 1.8×10^{-3} mol^1 L (d) 0.55×10^4 mol L^{-1}

159 We know that, relationship between K_c and K_p is

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

What would be the value of Δn for the reaction $NH_4Cl(s) \rightleftharpoons NH_3(g) + HI(g)$?

(a) 1 (b) 0.5 (c) 1.5 (d) 2

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

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

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

(a) $K_{a_3} = K_{a_1} \times K_{a_2}$ (b) $K_{a_3} = K_{a_1} + K_{a_2}$

(c) $K_{a_3} = K_{a_1} - K_{a_2}$ (d) $K_{a_3} = K_{a_1} / K_{a_2}$

161 On increasing the pressure, in which direction will the gas phase reaction proceed to re-establish equilibrium, is predicted by applying the Le-Chatelier's principle.

Consider the reaction,

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

Which of the following statement is correct, if the total pressure at which the equilibrium is established is increased without changing the temperature?

(a) K will remain same

(b) K will decrease

(c) K will increase

(d) K will increase initially and decrease when pressure is very high

162 In which of the following reactions, the equilibrium remains unaffected on addition of small amount of argon at constant volume?

(a) $H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$

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

(c) $N_2(g) + 3H_2(g) \rightleftharpoons NH_3(g)$

(d) The equilibrium will remain unaffected in all the three cases

163 What will be the correct order of vapour pressure of water, acetone and ether at 30°C? Given that among these compounds, water has maximum boiling point and ether has minimum boiling point?

(a) Water < ether < acetone

(b) Water < acetone < ether

(c) Ether < acetone < water

(d) Acetone < ether < water

164 At 500 K, equilibrium constant, K_C, for the following reaction is 5.

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

What would be the equilibrium constant K_C for the reaction?

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

(a) 0.04

(b) 0.4

(c) 25

(d) 2.5

165 K_a for CH_3COOH is 1.8×10^{-5} and K_b for NH_4OH is 1.8×10^{-5}. The pH of ammonium acetate will be

(a) 7.005

(b) 4.75

(c) 7.0

(d) Between 6 and 7

166 Which of the following options will be correct for the stage of half-completion of the reaction $A \rightleftharpoons B$?

(a) $\Delta G^s = 0$

(b) $\Delta G^s > 0$

(c) $\Delta G^s < 0$

(d) $\Delta G^s = -RT \ln K$

167 Acidity of BF_3 can be explained on the basis of which of the following concepts?

(a) Arrhenius concept

(b) Bronsted Lowry concept

(c) Lewis concept

(d) Bronsted Lowry as well as Lewis concept

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

(a) 0.1 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl

(b) 0.05 mol dm^{-3} NH_4OH and 0.1 mol dm^{-3} HCl

(c) 0.1 mol dm^{-3} NH_4OH and 0.05 mol dm^{-3} HCl

(d) 0.1 mol dm^{-3} CH_4COONa and 0.1 mol dm^{-3} NaOH

169 In which of the following solvents, silver chloride is 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

170 The pH of neutral water at 25° C is 7.0. As the temperature increases, ionisation of water increases, however the concentration of H^+ ions and OH^- ions are equal. What will be the pH of pure water at 60°C?

(a) Equal to 7.0

(b) Greater than 7.0

(c) Less than 7.0

(d) Equal to zero

171 What will be the value of pH of 0.01 mol dm^{-3} CH_3COOH $(K_a = 1.74 \times 10^{-5})$?

(a) 3.4

(b) 3.6

(c) 3.9

(d) 3.0

■ **Directions** (Q. No. 172-176) *In the following questions a statement of Assertion* (A) *followed by a statement of Reason* (R) *is given. Choose the correct option out of the choices given below in each question.*

(a) Both A and R are correct R is the correct explanation of A

(b) Both A and R are correct but R is not the correct explanation of A

(c) A is correct but R is incorrect

(d) Both A and R are incorrect

172 **Assertion** (A) Aqueous solution of ammonium carbonate is basic.

Reason (R) Acidic/basic nature of a salt solution depends on K_a and K_b value of the acid and the base forming it.

173 **Assertion** (A) The ionisation of hydrogen sulphide in water is low in the presence of hydrochloric acid.

Reason (R) Hydrogen sulphide is a weak acid.

174 **Assertion** (A) An aqueous solution of ammonium acetate can act as a buffer.

Reason (R) Acetic acid is a weak acid and NH_4OH is a weak base.

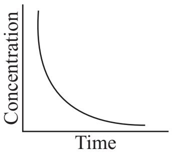
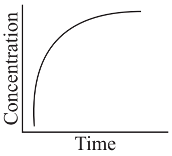
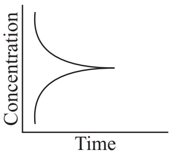
175 **Assertion** (A) Increasing order of acidity of hydrogen halides is HF < HCl < HBr < HI.

Reason (R) While comparing acids formed by the elements belonging to the same group of the periodic table, H—*A* bond strength is a more important factor in determining acidity of an acid than the polar nature of the bond.

176 **Assertion** (A) A solution containing a mixture of acetic acid and sodium acetate maintains a constant value of pH on addition of small amount of acid or alkali.

Reason (R) A solution containing a mixture of acetic acid and sodium acetate acts as a buffer solution of around pH 4.75.

177 Match the following graphical variation with their description.

Column I	Column II
A. 	1. Variation in product concentration with time
B. 	2. Reaction at equillibrium
C. 	3. Variation in reactant concentration with time

Choose the correct option

	A	B	C
(a)	1	3	2
(b)	2	3	1
(c)	3	1	2
(d)	1	2	3

Answers

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1 (d)	2 (d)	3 (c)	4 (b)	5 (c)	6 (d)	7 (a)	8 (c)	9 (c)	10 (b)
11 (a)	12 (a)	13 (c)	14 (a)	15 (c)	16 (a)	17 (d)	18 (c)	19 (a)	20 (d)
21 (b)	22 (d)	23 (b)	24 (a)	25 (b)	26 (b)	27 (c)	28 (d)	29 (c)	30 (b)
31 (b)	32 (c)	33 (c)	34 (b)	35 (b)	36 (a)	37 (c)	38 (d)	39 (d)	40 (b)
41 (c)	42 (a)	43 (a)	44 (d)	45 (a)	46 (a)	47 (c)	48 (b)	49 (c)	50 (d)
51 (b)	52 (c)	53 (c)	54 (c)	55 (a)	56 (b)	57 (d)	58 (d)	59 (c)	60 (b)
61 (d)	62 (a)	63 (c)	64 (c)	65 (c)	66 (b)	67 (c)	68 (b)	69 (b)	70 (c)
71 (d)	72 (c)	73 (b)	74 (b)	75 (b)	76 (d)	77 (b)	78 (c)	79 (a)	80 (c)
81 (b)	82 (d)	83 (b)	84 (c)	85 (c)	86 (c)	87 (b)	88 (a)	89 (c)	90 (b)
91 (b)	92 (c)	93 (d)	94 (d)	95 (b)	96 (c)	97 (c)	98 (c)	99 (d)	100 (c)
101 (a)	102 (b)	103 (c)	104 (d)	105 (c)	106 (b)	107 (b)	108 (a)	109 (b)	110 (b)
111 (b)	112 (a)	113 (c)	114 (b)	115 (b)	116 (a)	117 (c)			

Special Types Questions

118 (b)	119 (d)	120 (c)	121 (d)	122 (d)	123 (b)	124 (d)	125 (a)	126 (d)	127 (a)
128 (c)	129 (c)	130 (c)	131 (d)	132 (c)	133 (c)	134 (d)	135 (d)	136 (d)	137 (c)
138 (d)	139 (d)	140 (c)	141 (a)	142 (c)	143 (c)	144 (a)	145 (a)	146 (a)	147 (c)
148 (a)	149 (d)	150 (d)	151 (c)	152 (d)					

NCERT & NCERT Exemplar Questions

153 (a)	154 (d)	155 (b)	156 (c)	157 (b)	158 (b)	159 (d)	160 (a)	161 (a)	162 (d)
163 (b)	164 (a)	165 (c)	166 (a)	167 (c)	168 (c)	169 (d)	170 (c)	171 (a)	172 (a)
173 (b)	174 (b)	175 (a)	176 (a)	177 (c)					

Hints & Explanations

1 (*d*) In the reaction given in option (d), all reactants and products are strong electrolytes which are ionised completely in aqueous solution, i.e. ions are in equilibrium.

$$KNO_3(aq) + NaCl(aq) \longrightarrow KCl(aq) + NaNO_3(aq)$$

Thus, this reaction is an example of reversible reaction.

3 (*c*) According to Henry's law,

Mass of gas (m) dissolved in solution $\propto$ partial pressure (p) [at constant temperature]

$$\therefore \quad (6.56 \times 10^{-3}\ \text{g}) \propto 1\,\text{bar} = (5.00 \times 10^{-2}\ \text{g}) \propto p$$

$$\text{or} \quad p = \frac{(5.0 \times 10^{-2}\ \text{g})}{(6.56 \times 10^{-3}\ \text{g})} \times (1\ \text{bar}) = 7.6\,\text{bar}$$

6 (*d*) Since, at equilibrium,

rate of forward reaction = rate of backward reaction.

Therefore, in the chemical reaction,

$$N_2 + 3H_2 \rightleftharpoons 2NH_3$$

the same amount of ammonia is formed, as it is decomposed into N_2 and H_2.

7 (*a*) As we know that,

Moles of HI = 64/ 128

(Molar mass of HI = 1 + 127 = 128 g mol^{-1})

$$\therefore \text{Active mass of HI, i.e. } [\text{HI}] = \frac{64/128}{2} = 0.25\,\text{mol/L}$$

8 (*c*) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$

Equilibrium constant for this reaction,

$$K_C = \frac{[SO_3]^2}{[SO_2]^2\,[O_2]} \qquad \ldots\text{(i)}$$

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

Equilibrium constant for this reaction is

$$K' = \frac{[SO_2]\,[O_2]^{1/2}}{[SO_3]} \qquad \ldots\text{(ii)}$$

On squarring both sides in Eq. (ii), we have

$$(K')^2 = \frac{[SO_2]^2\,[O_2]}{[SO_3]^2}$$

$$= \frac{1}{K} = \frac{1}{278} \qquad (\text{as } K = 278)$$

$$\therefore \quad K' = \sqrt{\frac{1}{278}} = \sqrt{0.003597} = 5.99 \times 10^{-2}$$

$$\text{or} \quad \approx 6.0 \times 10^{-2}$$

9 (*c*) $A_2(g) + B_2(g) \rightleftharpoons 2AB(g)$

The equilibrium constant is given by,

$$K_C = \frac{[AB]^2}{[A_2][B_2]}$$

Given,

$$[AB] = 2.8 \times 10^{-3}$$

$$[A_2] = 3 \times 10^{-3}$$

$$[B_2] = 4.2 \times 10^{-3}$$

$$\therefore \quad K_C = \frac{(2.8 \times 10^{-3})^2}{(3 \times 10^{-3})\,(4.2 \times 10^{-3})}$$

$$K_C = \frac{7.84}{12.6} = 0.62$$

10 (*b*)

	$N_2(g)$ +	$O_2(g)$ $\rightleftharpoons$	$2NO(g)$
Initial	2 mol	4 mol	0
At equil.	$2 - \frac{1}{2}$	$4 - \frac{1}{2}$	$2 \times \frac{1}{2} = 1$ mol

$$\therefore \text{ Molar concentration of NO at equilibrium} = \frac{1}{2.5} = 0.4$$

$$[\because \text{given}, V = 2.5\ \text{L}]$$

11 (*a*)

	$H_2(g)$ +	$CO_2(g)$ $\rightleftharpoons$	$H_2O(g)$ +	$CO(g)$
Initial	1	0.1	0	0
At equil.	$1 - x$	$1 - x$	x	x

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

$$\Rightarrow \quad \sqrt{K} = \frac{x}{1-x} = \sqrt{1.80} = \frac{x}{1-x}$$

$$\Rightarrow \quad 1.34 = \frac{x}{1-x}$$

This gives $\quad x = 0.573\,\text{M}$

12 (*a*) As K_C is very low and $K_C = \dfrac{[\text{I}]^2}{[\text{I}_2]}$

For the reaction, $I_2(g) \rightleftharpoons 2I(g)$

$$\therefore \quad [I_2] > [I]$$

13 (*c*)

	A +	$2B$ $\rightleftharpoons$	$2C$ +	D
Initial moles	1.1	2.2	0	0
Moles at equil.	1.0	2.0	0.2	0.1

$$\text{Equilibrium constant for the reaction} = \frac{[C]^2\,[D]}{[A]\,[B]^2}$$

$$\therefore \quad K = \frac{[0.2/V]^2\,[0.1/V]}{[1/V][2/V]^2} = 0.001$$

14 (*a*) $CH_3COOH(l) + C_2H_5OH(l) \rightleftharpoons CH_3COOC_2H_5(l) + H_2O(l)$

Initial	3 mol	3 mol	0	0
At equil.	1	1	2	2

$$\therefore \qquad K = \frac{2\times 2}{1\times 1} = 4$$

15 (*c*) $2HI \rightleftharpoons H_2 + I_2$

Initial	2 mol	0	0
At equil.	$2 - \frac{22}{100}\times 2$	0.22	0.22

$$= 2 - 0.44 = 1.56$$

$$\therefore \qquad K = \frac{[H_2][I_2]}{[HI]^2} = \frac{0.22\times 0.22}{(1.56)^2} = 0.0199$$

16 (*a*) $AB \rightleftharpoons A + B$

$$\text{or} \qquad K = \frac{[A][B]}{[AB]}$$

If concentration of A is doubled, the equilibrium concentration of B becomes half to maintain K constant.

17 (*d*) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g), K_1$

$$2NO(g) + O_2(g) \rightleftharpoons 2NO_2(g), K_2$$

$$N_2(g) + 2O_2(g) \rightleftharpoons 2NO_2(g), K = K_1 \times K_2$$

$$\therefore \qquad \text{For } NO_2(g) \rightleftharpoons \frac{1}{2}N_2(g) + O_2(g),$$

$$K' = \left[\frac{1}{K_1K_2}\right]^{1/2}$$

18 (*c*) (i) $A_2(g) + B_2(g) \rightleftharpoons 2AB(g); K_1 = \frac{[AB]^2}{[A_2][B_2]}$

(ii) $6AB(g) \rightleftharpoons 3A_2(g) + 3B_2(g)$;

$$K_2 = \frac{[A_2]^3[B_2]^3}{[AB]^6} = \frac{1}{\left(\frac{[AB]^2}{[A_2][B_2]}\right)^3} = \frac{1}{K_1^3},$$

19 (*a*) The equilibrium constant for combined reaction is $K_1 \times K_2$. This is because, when two reaction are added, their equilibrium constants are multipled.

20 (*d*) For reaction in equilibrium,

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$$

we can write either

$$K_C = \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} \quad \text{or} \quad K_C = \frac{[p_{HI}]^2}{[p_{H_2}][p_{I_2}]}$$

Further, since $p_{HI} = [HI(g)]RT$

$$p_{I_2} = [I_2(g)]RT$$

$$p_{H_2} = [H_2(g)]RT$$

$$\text{Therefore, } K_p = \frac{[p_{HI}]^2}{[p_{H_2}][p_{I_2}]} = \frac{[HI(g)]^2[RT]^2}{[H_2(g)]RT \cdot [I_2(g)]RT}$$

$$= \frac{[HI(g)]^2}{[H_2(g)][I_2(g)]} = K_C$$

In this example, $K_p = K_C$, i.e. both equilibrium constants are equal.

21 (*b*) For the given reaction,

$$\Delta n_g = n_P - n_R$$

where, n_P = number of moles of products and n_R = number of moles of reactants

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

$$\therefore \qquad \Delta n_g = -\frac{1}{2}$$

Thus, the value of $x = -\frac{1}{2}$

22 (*d*) We know that, $K_p = K_C(RT)^{\Delta n_g}$

For the given reaction,

$$\Delta n_g = (2+1) - 2 = 1$$

$$\therefore \qquad K_p = 3.75 \times 10^{-6}\ (0.0831 \times 1069)$$

$$\Rightarrow \qquad K_p = 0.00033$$

23 (*b*) $N_2(g) + 3H_2(g) \rightleftharpoons 2NH_3(g)$

At : $p_{N_2} = P, \quad p_{H_2} = 3P, \quad p_{NH_3} = 2P$

$$\Rightarrow p_{(\text{total})} = p_{N_2} + p_{H_2} + p_{NH_3} \simeq p_{N_2} + p_{H_2}$$

$$[\because P_{(\text{total})} >> p_{NH_3}]$$

$$= p + 3p = 4p$$

$$\text{Now, } K_p = \frac{p^2_{NH_3}}{p_{N_2} \times p^3_{H_2}} = \frac{p^2_{NH_3}}{p \times (3p)^3}$$

$$= \frac{p^2_{NH_3}}{27 \times p^4} = \frac{p^2_{NH_3}}{27 \times \left(\frac{P}{4}\right)^4} \qquad [\because P = 4p]$$

$$K_p = \frac{p^2_{NH_3} \times 4^4}{3^2 \times 3 \times P^4}$$

$$\Rightarrow p^2_{NH_3} = \frac{3^2 \times 3 \times P^4 \times K_p}{4^4}$$

$$\Rightarrow p_{NH_3} = \frac{3 \times 3^{1/2} \times P^2 \times K_p^{1/2}}{4^2} = \frac{3^{3/2} \times P^2 \times K_p^{1/2}}{16}$$

24 (*a*) Given,

$$I_2(g) \rightleftharpoons 2I(g)$$

$\because$ I-atoms in iodine vapours = 40% by volume

$\therefore$ Iodine vapours of I_2 molecule = 60% by volume

Now, partial pressure of I-atoms

$$p_1 = \frac{40}{100} \times 10^5 = 0.40 \times 10^5 \text{ Pa}$$

Similarly, partial pressure of iodine molecule (I_2),

$$p_2 = \frac{60}{100} \times 10^5 = 0.60 \times 10^5 \text{ Pa}$$

$$\therefore \qquad K_p = \frac{p_I^2}{p_{I_2}} = \frac{(0.40 \times 10^5 \text{ Pa})^2}{(0.60 \times 10^5 \text{ Pa})} = 2.67 \times 10^4 \text{ Pa}$$

25 (*b*) $2SO_2(g) + O_2(g) \rightleftharpoons 2SO_3(g)$;

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

$\because \quad \Delta n_g = 2 - 3 = -1$

Given, $\quad K_p = 2.0 \times 10^{10}\ \text{bar}^{-1}$

$$R = 0.0831\ \text{L bar K}^{-1}\text{mol}^{-1} \text{ and } T = 450\ \text{K}$$

$$\therefore \quad K_C = \frac{K_p}{(RT)^{\Delta n_g}} = \frac{K_p}{(RT)^{-1}}$$

or $K_C = K_p \times RT$

$$= 2.0 \times 10^{10}\ \text{bar}^{-1} \times 0.0831\ \text{L bar K}^{-1}\text{mol}^{-1} \times 450\ \text{K}$$

$K_C = 7.479 \times 10^{11}\ \text{L mol}^{-1}$

26 (*b*) Molar mass of $NH_4SH = 18 + 33 = 51\ \text{g mol}^{-1}$

Number of moles of NH_4SH introduced in the vessel $= \dfrac{\text{Weight}}{\text{Molar mass}} = \dfrac{5.1}{51} = 0.1\ \text{mol}$

$$NH_4SH(s) \rightleftharpoons NH_3(g) + H_2S(g)$$

	$NH_4SH(s)$	$NH_3(g)$	$H_2S(g)$
Number of moles at $t = 0$	0.1	0	0
At $t = t_{eq}$	$0.1(1 - 0.3)$	30% of $0.1 = 0.03$	30% of $0.1 = 0.03$
Active mass (mol L^{-1})		$\frac{0.03}{3} = 0.01$	$\frac{0.03}{3} = 0.01$

$$K_C = \frac{[NH_3][H_2S]}{[NH_4HS(s)]} = \frac{0.01 \times 0.01}{1} = 10^{-4}\ (\text{mol L}^{-1})^2$$

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

[where, $\Delta n_g = \Sigma n_{\text{product}} - \Sigma n_{\text{reactant}}] = 2 - 0 = 2$

$$\therefore \quad K_p = K_C(RT)^2$$

$$= 10^{-4} \times [0.082 \times (273 + 327)]^2\ \text{atm}^2$$

$$= 0.242\ \text{atm}^2$$

27 (*c*) $H_2(g) + S(s) \rightleftharpoons H_2S(g)$

Suppose x moles of H_2S are formed, then at equilibrium,

$$[H_2] = (0.2 - x), \quad [H_2S] = x$$

$$p_{H_2} = \left(\frac{0.2 - x}{0.2 - x + x}\right) \times p = \frac{0.2 - x}{0.2} \times p$$

$$p_{H_2S} = \left(\frac{x}{0.2 - x + x}\right) \times p = \frac{x}{0.2} \times p$$

$$\because \quad K_p = \frac{p_{H_2S}}{p_{H_2}}$$

$$\therefore \quad 6.8 \times 10^{-2} = \frac{x}{0.2 - x}$$

or $0.068(0.2 - x) = x$ or $x = 0.0127\ \text{mol}$

Now, pressure of 0.0127 mole of H_2S at 363 K in 1 L vessel is given as,

$$p = \frac{nRT}{V}$$

$$\Rightarrow \quad p = \frac{0.0127 \times 0.0821 \times 363}{1}$$

$$= 0.38\ \text{atm}$$

28 (*d*) $CaCO_3(s) \overset{\Delta}{\rightleftharpoons} CaO(s) + CO_2\uparrow; K_{p_1} = 8 \times 10^{-2}$

$$CO_2(g) + C(s) \longrightarrow 2CO(g); K_{p_2} = 2$$

Thus, for the reaction,

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

$$K'_p = K_{p1} \times K_{p2} = 8 \times 10^{-2} \times 2 = 16 \times 10^{-2}$$

$$\therefore \quad K'_p = (p_{CO}(g))^2$$

$$\Rightarrow \quad p_{CO} = \sqrt{K'_p} = \sqrt{16 \times 10^{-2}} = 4 \times 10^{-1} = 0.4\ \text{atm}$$

29 (*c*) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$;

As we know that,

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

Here, $K_p = K_C, \Delta n_g = 2 - 1 = 1 \Rightarrow (RT)^{\Delta n_g} = 1$

$$(0.0821 \times T) = 1$$

Thus, $T = \dfrac{1}{0.0821} = 12.18\text{K}$

30 (*b*) Given,

$$N_2 = 3.0 \times 10^{-3}\text{M}$$

$$O_2 = 4.2 \times 10^{-3}\text{M}$$

$$NO = 2.8 \times 10^{-3}\text{M}$$

For the given reaction,

$$N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$$

equilibrium constant K_C can be written as,

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

$$\therefore \quad K_C = \frac{(2.8 \times 10^{-3}\text{M})^2}{(3.0 \times 10^{-3}\text{M})\,(4.2 \times 10^{-3}\text{M})} = 0.622$$

$$\because \quad K_p = K_C \cdot (RT)^{\Delta n}$$

$\Delta n =$ Number of moles of gaseous products − number of moles of gaseous reactants

$$\Delta n = 2 - 2 = 0$$

$$\therefore \quad K_p = K_C \cdot (RT)^0$$

or, $\quad K_p = K_C$

or, $\quad K_p = 0.622\ \text{atm}$

31 (*b*) We know that, the relationship between K_p and K_C of a chemical equilibrium state (reaction) is

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

$$\Rightarrow \quad \frac{K_p}{K_C} = (RT)^{\Delta n_g}$$

where, $\Delta n_g = \Sigma n_{\text{Products}} - \Sigma n_{\text{Reactants}}$

(i) $N_2(g) + O_2(g) \rightleftharpoons 2NO(g)$

$$\Rightarrow (RT)^{2-(1+1)} = (RT)^0 = 1$$

(ii) $N_2O_4(g) \rightleftharpoons 2NO_2(g)$

$\Rightarrow (RT)^{2-1} = RT = 24.62\,dm^3$ atm mol^{-1}

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

$$\Rightarrow (RT)^{2-(3+1)} = (RT)^{-2}$$

$$= \frac{1}{(24.62\,dm^3 \text{ atm } mol^{-1})^2}$$

$$= 1.649 \times 10^{-3}\ dm^{-6}\ atm^{-2}\ mol^2$$

32 (*c*) For a reaction,

$$\underset{\text{Reactant}}{A} \rightleftharpoons \underset{\text{Product}}{B}$$

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

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

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

33 (*c*) Consider the gaseous reaction of H_2 with I_2.

$$H_2(g) + I_2(g) \rightleftharpoons 2HI(g);\ K_C = 57.0 \text{ at } 700\text{ K}$$

$$\Rightarrow \quad Q_C = \frac{[HI]^2}{[H_2]\,[I_2]} = \frac{(0.40)^2}{(0.10) \times (0.20)} = 8.0$$

34 (*b*) For the reaction,

$$2A \rightleftharpoons B + C;\ K_C = 2 \times 10^{-3}$$

the reaction quotient Q_C is given by,

$$Q_C = [B][C]/[A]^2$$

$$\because \quad [A] = [B] = [C] = 3 \times 10^{-4}\text{ M}$$

$$\therefore \quad Q_C = \frac{(3\times10^{-4})(3\times10^{-4})}{(3\times10^{-4})^2} = 1$$

As $Q_C > K_C$, so the reaction will proceed in the reverse direction.

35 (*b*)

	$PCl_5 \rightleftharpoons$	PCl_3 +	Cl_2
Initial conc.	3	0	0
At equil.	$(3-x)$	x	x

$$\therefore \quad K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} \text{ or } 1.8 = \frac{x^2}{(3-x)}$$

$\Rightarrow x^2 + 1.8x - 5.4 = 0$

$$x = \frac{[-1.8 \pm \sqrt{(1.8)^2 - 4(-5.4)}]}{2}$$

$$x = \frac{[-1.8 \pm 4.98]}{2}$$

$$x = \frac{[-1.8 + 4.98]}{2} = 1.59$$

Thus, $[PCl_5] = 3.0 - x = 3 - 1.59 = 1.41$ M

$[PCl_3] = [Cl_2] = x = 1.59$ M

36 (*a*) $\Delta G = \Delta G° + RT \ln Q$

At equilibrium, when $\Delta G = 0$ and $Q = K_C$, the equation becomes,

$$\Delta G = \Delta G° + RT \ln K = 0$$

$$\Delta G° = -RT \ln K$$

$$\ln K = -\Delta G°/RT$$

Taking antilog on both sides, we get,

$$K = e^{-\Delta G°/RT}$$

38 (*d*) Given, $\Delta G° = 13.8$ kJ/mol

$= 13.8 \times 10^3$ J/mol

$\because \quad \Delta G° = -RT \ln K_C$

Hence, $\ln K_C = -13.8 \times 10^3$ J/mol

/(8.314 J mol^{-1} $K^{-1} \times 298$ K)

$\Rightarrow \quad \ln K_C = -5.57$

$\Rightarrow \quad K_C = 3.81 \times 10^{-3}$

39 (*d*) Sucrose + $H_2O \longrightarrow$ Glucose + Fructose

We know that, $R = 8.314$ J $mol^{-1}K^{-1}$

Given, $T = 300$ K; $K_C = 2 \times 10^{13}$

$\because \quad \Delta G° = -RT \ln K_C$ or $-2.303\, RT \log K_C$

$\therefore \Delta G° = -2.303 \times 8.314$ J mol^{-1} K^{-1}

$\times 300$ K $\times \log(2 \times 10^{13})$

$\Rightarrow \quad \Delta G° = -7.64 \times 10^4$ J mol^{-1}

40 (*b*) Given, $\Delta G° = 2494.2$ J

$$[A] = \frac{1}{2};\quad [B] = 2;\quad [C] = \frac{1}{2}$$

$R = 8.314$ J/K mol

For the reaction, $2A \rightleftharpoons B + C$

$$Q = \frac{[B][C]}{[A]^2} = \frac{2 \times \frac{1}{2}}{(1/2)^2} = 4$$

$\therefore$ We know that,

$$\Delta G = \Delta G° + RT \ln Q$$

$$= 2494.2 + 8.314 \times 300 \ln 4$$

$$= 5951.89 \text{ J (+ ve value)}$$

Also, we have $\Delta G = RT \ln Q/K$,

If ΔG is positive, $Q > K_C$.

Therefore, reaction shifts in reverse direction.

41 (*c*) According to Le-Chatelier's principle, if a system at equilibrium is subjected to change of concentration, pressure or temperature, the equilibrium shifts in the direction that tends to undo the effect.

So, the equilibrium constant of a chemical reaction can be calculated.

43 (*a*) Production of ammonia according to the reaction,

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

$$\Delta H = -92.38 \text{ kJ } mol^{-1}$$

is an exothermic process. According to Le-Chatelier's principle, raising the temperature, shifts the equilibrium to left and decreases the equilibrium concentration of ammonia. In other words, low temperature is favourable for high yield of ammonia or reaction proceed in forward direction.

44 (*d*) According to Le-Chatelier's principle, equilibrium shifts in the opposite direction to undo the change.

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

(a) **Increasing the concentration of $NH_3(g)$** On increasing the concentration of $NH_3(g)$, the equilibrium shifts in the backward direction where concentration of $NH_3(g)$ decreases.

(b) **Decreasing the pressure** Equilibrium shifts in the backward direction where number of moles are increasing.

(c) **Decreasing the concentration of $N_2(g)$ and $H_2(g)$** Equilibrium shifts in the backward direction, when concentration of $N_2(g)$ and $H_2(g)$ decreases.

(d) **Increasing pressure and decreasing temperature** On increasing pressure, equilibrium shifts in the forward direction where number of moles decreases, while on decreasing temperature, it will move in forward direction where temperature increases.

45 (*a*) A catalyst simply helps to attain the equilibrium quickly and it does not affect the concentration of ammonia.

48 (*b*) An acid on losing a proton produces a species which has the tendency to accept H^+.

It is called conjugate base of that acid.

$$\underset{\text{Acid}}{H_2O} \rightleftharpoons \underset{\text{Conjugate base}}{OH^-} + H^+, \quad \underset{\text{Acid}}{HF} \rightleftharpoons \underset{\text{Conjugate base}}{F^-} + H^+$$

Water (H_2O) is amphoteric in nature and, thus act both as an acid and base.

e.g. $$\underset{\text{Acid}}{HF} + \underset{\text{Base}}{H_2O} \rightleftharpoons \underset{\text{Conjugate base}}{F^-} + \underset{\text{Conjugate acid}}{H_3O^+}$$

49 (*c*) HCl can only act as Bronsted acid because it can only donate proton.

$$\underset{\text{Acid}}{HCl} + \underset{\text{Base}}{H_2O} \rightleftharpoons H_3O^+ + Cl^-$$

The remaining options contains substances which act both as Bronsted acid and Bronsted base.

(a) $HCO_3^- + HCO_3^- \rightleftharpoons H_2CO_3 + CO_3^{2-}$

(b) $NH_3 + NH_3 \rightleftharpoons NH_4^+ + NH_2^-$

(c) $HSO_4^- + HSO_4^- \rightleftharpoons H_2SO_4 + SO_4^{2-}$

51 (*b*) Higher the tendency to give H^+ ion (i.e. to undergo ionisation), stronger will be the acid or *vice-versa.*

HF has poor tendency to give H^+ ion, hence it is the weakest acid among the given.

The order of acidity of given acids is

$H_2SO_4 > HNO_3 > HCl > HF$.

52 (*c*) NH_3 donates electron pair, while Cu^{2+} accepts electron pairs.

Therefore, $4NH_3 + [Cu(H_2O)_4]^{2+} \rightleftharpoons [Cu(NH_3)_4]^{2+} + 4H_2O$

describes an acid-base reaction using the Lewis acid-base definition and not using Bronsted-Lowry defination.

54 (*c*) $NaNO_2$ solution is slightly basic, NaCl solution is neutral, H_2S is weakly acidic, whereas H_2SO_4 is strong acid.

Thus, the correct order of increasing $[H_3O]^+$ in the aqueous solution is

$0.01N\ NaNO_2 < 0.01\ N NaCl < 0.01\ N\ H_2S < 0.01\ N\ H_2SO_4$.

55 (*a*) The conjugate acids of the given bases are H—OH, NH_3, $H — C \equiv C — H$ and $CH_3 — CH_3$.

Their acidic character follows the trend,

$H — OH > CH \equiv CH > NH_3 > CH_3 — CH_3$.

Since, a strong acid has a weak conjugate base.

Hence, the strength of bases will be,

$$CH_3 — CH_2^- > NH_2^- > H — C \equiv C^- > OH^-$$

56 (*b*) Among the given salts $FeCl_3$ is acidic in nature i.e., have acidic solution as it is the salt of weak base and strong acid.

$Al(CN)_3$ and $Pb(CH_3COO)_2$ are the salts of weak acid and weak base.

CH_3COOK is the salt of strong base and weak acid.

Hence, the solution of CH_3COOK will be most basic because of the following reaction.

$$CH_3COOK + H_2O \rightleftharpoons \underset{\text{(Weak acid)}}{CH_3COOH} + \underset{\text{Strong base}}{KOH}$$

57 (*d*) $\because$ $pH = -\log[H^+]$

$$\therefore \quad pH = -\log[3.8 \times 10^{-3}] = -\{\log(3.8) + \log(10^{-3})\}$$
$$= -\{(0.58) + (-3.0)\} = -\{-2.42\} = 2.42$$

Therefore, the pH of the soft drink is 2.42 and it can be inferred that, it is acidic.

58 (*d*)

$$\begin{array}{llll} & CH_3COOH & \rightleftharpoons CH_3COO^- & + H^+ \\ \text{Initial} & C & 0 & 0 \\ \text{At equil.} & C(1-\alpha) & C\alpha & C\alpha \end{array}$$

$$\therefore \quad K = \frac{C\alpha \cdot C\alpha}{C(1-\alpha)} = \frac{C\alpha^2}{1-\alpha} = C\alpha^2$$

$$\text{or,} \quad C = \frac{K}{\alpha^2} = \frac{1.8 \times 10^{-5}}{(0.02)^2} = 0.045\ M$$

59 (*c*) Given, $K = 1.69 \times 10^{-5}$

$$\because \quad C\alpha << 0.01$$

$$\therefore \quad K = \frac{C\alpha(C\alpha + 0.01)}{C(1-\alpha)} = 0.01\alpha$$

$$\text{or} \quad \alpha = \frac{1.69 \times 10^{-5}}{0.01} = 0.169 \times 10^{-2}$$

60 (*b*) Given, conc. of formic acid solution = 0.2 M

$$\alpha = 0.032$$

As we know that,

$$K = C\alpha^2$$

$$K = 0.2 \times (0.032)^2 = 2.1 \times 10^{-4}$$

61 (*d*)

$$\begin{array}{llll} & HAc(aq) & \rightleftharpoons H^+(aq) + & Ac^-(aq) \\ \text{Initial conc.(M)} & 0.05 & 0 & 0.05 \\ \text{Equil. conc. } (M) & 0.05 - x & x & 0.05 + x \end{array}$$

$$K_a = \frac{[H^+][Ac^-]}{[HAc]} = \frac{\{(x)(0.05 + x)\}}{(0.05 - x)}$$

As K_a is small for a very weak acid, $x << 0.05$

Hence, $(0.05 + x) \approx (0.05 - x) \approx 0.05$

Thus, $1.8 \times 10^{-5} = \dfrac{x(0.05)}{(0.05)}$

$\therefore \quad x = [H^+] = 1.8 \times 10^{-5}$ M

$\therefore \quad pH = -\log(1.8 \times 10^{-5}) = 4.74$

62 (*a*)

$$\begin{array}{llll} & CH_3COOH & \rightleftharpoons CH_3COO^- & + H^+ \text{ (weak acid)} \\ \text{Initially} & C & 0 & 0 \\ \text{At equil.} & C(1-\alpha) & C\alpha & C\alpha \end{array}$$

$\therefore \quad [H^+] = C\alpha \text{ or } C \cdot \sqrt{\dfrac{K_a}{C}} = \sqrt{K_aC} \qquad \left[\because \alpha = \sqrt{\dfrac{K_a}{c}}\right]$

$\Rightarrow \quad \sqrt{1.8 \times 10^{-5} \times 0.1} = 1.34 \times 10^{-3}$ M

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

$$= -\log(1.34 \times 10^{-3}) = 2.9$$

63 (*c*)

$$\begin{array}{llll} & NH_4OH & \rightleftharpoons NH_4^+ & + OH^- \\ \text{Initial conc.} & C & 0 & 0 \\ \text{At equil.} & C(1-\alpha) & C\alpha & C\alpha \end{array}$$

$\therefore \quad [OH^-] = C\alpha = 0.01 \times 0.05 = 0.0005$ M

64 (*c*) Weight of NaOH dissolved = 2 g

$\therefore$ Equivalent of NaOH dissolved $= \dfrac{2}{40}$

$\Rightarrow \quad N_{NaOH} = \dfrac{2}{40} = 0.05$

$\Rightarrow \quad [OH]^- = 0.05 = 5 \times 10^{-2}$

$\Rightarrow \quad pOH = -\log[OH^-]$

$$= -\log(5 \times 10^{-2}) = 1.3010$$

$\because \quad pH + pOH = 14$

$\therefore \quad pH = 14 - pOH$

$$= 14 - 1.3010 = 12.70$$

65 (*c*) NaOH is a strong base, thus

$$[OH^-] = 0.01M = 10^{-2} \text{ M}$$

$$pOH = -\log[OH^-] = -\log(10^{-2}) = 2$$

We know that, pH + pOH = 14

$\therefore \quad pH = 14 - 2 = 12$

66 (*b*) For pH = 1, $[H^+] = 10^{-1}$ M

For pH = 2, $[H^+] = 10^{-2}$ M

$$M_1V_1 + M_2V_2 = M_R(V_1 + V_2)$$

$$10^{-1} \times 50 + 10^{-2} \times 50 = M_R \times 100$$

Thus, $M_R = 5.5 \times 10^{-2}$ M

(Resultant molarity of H^+ ions)

$\therefore \quad pH = -\log 5.5 \times 10^{-2} = 1.26$

67 (*c*) $[H^+]$ in 0.1 M HCl = 0.1 M

For same pH, $[H^+]$ in H_2SO_4 = 0.1 M

One mole H_2SO_4 gives 2 moles of H^+ ions

$$H_2SO_4 \longrightarrow 2H^+ + SO_4^{2-}$$

$\therefore$ 0.1 M $[H^+]$ will be given by

$$= \frac{0.1}{2} = 0.05 \text{ M } H_2SO_4$$

68 (*b*) pH = 1 $\therefore$ $[H^+] = 10^{-1} = 0.1$ M

pH = 2 $\therefore$ $[H^+] = 10^{-2} = 0.01$ M

For dilution of HCl,

$$M_1V_1 = M_2V_2$$

$$0.1 \times 1 = 0.01 \times V_2$$

$$V_2 = 10 \text{ L}$$

Volume of water to be added = 10 − 1 = 9 L

69 (*b*) $N_{Mix}V_{Mix} = \underset{\text{(Base)}}{N_1V_1} - \underset{\text{(Acid)}}{N_2V_2}$ … (i)

Given, $M_1 = 0.2$M, $N_1 = 0.2$ N

$M_2 = 0.1$ M, $N_2 = 0.1$ N

$V_1 = 50$ mL, $V_2 = 50$ mL, $V_{mix} = 100$ mL

On substituting the given values in equation. (i),

we get $N_{mix} \times 100 = 50 \times 0.2 - 50 \times 0.1$

$$N_{mix} = \frac{5}{100} = 5 \times 10^{-2}$$

$\therefore \quad [OH^-] = 5 \times 10^{-2}$

Now, $pOH = -\log[OH^-] = -\log[5 \times 10^{-2}]$

$$= 2 - \log 5 = 1.3$$

Also, pH + pOH = 14

$\therefore \quad pH = 14 - 1.3 = 12.7$

70 (*c*) Given, $pH_1 = 9; V_1 = 10$ mL, $pH_2 = 8; V_2 = 25$ mL

V = volume of acid required for the equivalence point

$\because \quad pH = 14 - pK_b - \log \dfrac{[B^+]}{[BOH]}$

$\therefore \quad (pH_1) = 9 = 14 - pK_b - \log \dfrac{10}{V - 10}$ …(i)

$$(\mathrm{pH}_2) = 8 = 14 - \mathrm{p}K_b - \log \frac{25}{V - 25} \qquad \ldots\text{(ii)}$$

On subtracting Eq. (ii) from Eq. (i)

$$1 = \log \frac{25}{V - 25} - \log \frac{10}{V - 10} = \log \frac{25\,(V - 10)}{10(V - 25)}$$

$$\Rightarrow \quad V = 30\,\mathrm{mL}$$

71 (*d*) 75 mL $\frac{M}{5}$ HCl + 25 mL $\frac{M}{5}$ NaOH

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

$$= \frac{1}{5} \times 75 = 15$$

Milliequivalent of NaOH = 25 mL of $\frac{M}{5}$ NaOH

$$= \frac{1}{5} \times 25 = 5$$

$\therefore$ Milliequivalent of HCl left unused = 15 − 5 = 10

Volume of solution = 100 mL

$\therefore$ Molarity of $[\mathrm{H}^+]$ in the resulting mixture = $\frac{10}{100} = \frac{1}{10}$

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

72 (*c*) $\mathrm{F}^- + \mathrm{H_2O} \rightleftharpoons \mathrm{HF} + \mathrm{OH}^-$

$$K_b = \frac{[\mathrm{HF}][\mathrm{OH}^-]}{[\mathrm{F}^-]} \qquad \ldots\text{(i)}$$

$$K_w = [\mathrm{H_3O^+}][\mathrm{OH}^-] = 10^{-14} \qquad \ldots\text{(ii)}$$

Given, $\mathrm{p}K_b = 10.83$

Dissociation of HF in water is represented by the equation,

$$\mathrm{HF} + \mathrm{H_2O} \rightleftharpoons \mathrm{H_3O^+} + \mathrm{F}^-$$

$$K = \frac{[\mathrm{H_3O^+}][\mathrm{F}^-]}{[\mathrm{HF}]} \qquad \ldots\text{(iii)}$$

$$K_b \cdot K = [\mathrm{H_3O^+}][\mathrm{OH}^-] = K_w$$

or $$\frac{K_w}{K_b} = K$$

Taking log on both sides, we get

$$\begin{aligned}\log K &= \log K_w - \log K_b \\ &= -\mathrm{p}K_w + \log K_b \\ &= -14 + 10.83 = -3.17\end{aligned}$$

or $$K = 6.76 \times 10^{-4}$$

73 (*b*) $\mathrm{C_{18}H_{21}NO_3} + \mathrm{H_2O} \rightleftharpoons \text{Codeine H}^+ + \mathrm{OH}^-$

$$\mathrm{pH} = 9.95$$

or $\quad \mathrm{pOH} = 14 - 9.95 = 4.05$

$\because \quad \mathrm{pOH} = -\log[\mathrm{OH}^-]$

$\therefore \log[\mathrm{OH}^-] = -4.05 = \bar{5}.95$

$$[\mathrm{OH}^-] = \text{antilog } \bar{5}.95 = 8.913 \times 10^{-5}$$

Now, $$K_b = \frac{[\text{Codeine H}^+]\,[\mathrm{OH}^-]}{[\text{Codeine}]} = \frac{[\mathrm{OH}^-]^2}{[\text{Codeine}]}$$

(because [codeine H^+] = $[\mathrm{OH}^-]$)

$$\Rightarrow \quad K_b = \frac{(8.913 \times 10^{-5})^2}{0.005} = 1.588 \times 10^{-6}$$

$$\Rightarrow \quad \mathrm{p}K_b = -\log[K_b] = -\log[1.588 \times 10^{-6}]$$

$$\therefore \quad \mathrm{p}K_b = 6 + [-0.2009] = 5.7791 \approx 5.80$$

78 (*c*) Given, $\mathrm{p}K_a$ (acetic acid) = 4.76

$\Rightarrow$ $\mathrm{p}K_b$ (ammonium hydroxide) = 4.75

Since, it is a salt of weak acid and weak base.

Thus, $\mathrm{pH} = 7 + \frac{1}{2}[\mathrm{p}K_a - \mathrm{p}K_b] = 7 + \frac{1}{2}[4.76 - 4.75]$

$$= 7 + \frac{1}{2}[0.01] = 7 + 0.005 = 7.005$$

79 (*a*) pH of buffer solution of weak acid and weak base is calculated, using the following formula.

$$\mathrm{pH} = \frac{1}{2}[\mathrm{p}K_w + \mathrm{p}K_a - \mathrm{p}K_b]$$

Given : $\mathrm{p}K_a = 4$

$\mathrm{p}K_b = 5$

$\mathrm{p}K_w = 14$

$$\therefore \quad \mathrm{pH} = \frac{1}{2}[14 + 4 - 5]$$

$$\mathrm{pH} = 6.5$$

80 (*c*) Ammonium acetate is a salt of weak acid and weak base. When solutions are of weak acid and weak base, pH of solution is calculated from the following relationship.

$$\mathrm{pH} = 7 + \left(\frac{1}{2}\,\mathrm{p}K_a - \frac{1}{2}\,\mathrm{p}K_b\right)$$

$\because \quad \mathrm{p}K_a \approx \mathrm{p}K_b$ (given)

$\therefore$ pH of solution = 7

82 (*d*) pH of buffer does not change on adding 10 mL of distilled water as there are no ions present in it.

83 (*b*) When $\mathrm{CH_3COOH} + \mathrm{NaOH}$ are mixed in the ratio of 2 : 1, they will form acidic buffer. This is because, 1 mole of weak acid will be left unreacted and 1 mole of $\mathrm{CH_3COONa}$ will be formed.

The reaction is given below,

$$\underset{\text{2 mole}}{\mathrm{CH_3COOH}} + \underset{\text{1 mole}}{\mathrm{NaOH}} \rightleftharpoons \underset{\text{1 mole}}{\mathrm{CH_3COONa}} + \mathrm{H_2O}$$

84 (*c*) Handerson - Hasselbalch equation for acidic buffer solution is given as,

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\text{Conjugate base}]}{[\text{Acid}]}$$

Therefore, if the molar concentration of acid is equal to the molar concentration of conjugate base, we have

$$\text{pH} = \text{p}K_a + \log 1$$

or $$\text{pH} = \text{p}K_a \qquad [\because \log 1 = 0]$$

Hence, pH of a buffer solution becomes equal to pK_a of acid only if,

$$[\text{Acid}] = [\text{Conjugate base}]$$

85 (*c*) Henderson - Hasselbalch equation for acetic acid and sodium acetate buffer is given as,

$$\text{pH} = \text{p}K_a + \log \frac{[CH_3COONa]}{[CH_3COOH]}$$

As, $[CH_3COOH] = [CH_3COONa]$

$$\therefore \quad \text{pH} = \text{p}K_a + \log 1$$

$$\text{pH} = 4.76 + 0$$

$$\text{pH} = 4.76$$

86 (*c*) We can easily calculate the pH by converting the concentration into millimoles.

Millimoles of $CH_3COOH = 0.1 \times 10 = 1.0$ millimole

Millimoles of $CH_3COONa = 0.1 \times 2.0 = 2.0$ millimole

$\therefore$ Using Henderson-Hassebalch equation,

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

$$= 4.74 + \log \frac{2}{1} = 4.74 + 0.30 = 5.04$$

87 (*b*) NH_4Cl reacts with NaOH to form NH_4OH and unreacted NH_4Cl forms a basic buffer.

Millimoles of $NH_4Cl = 75 \times 0.1 = 7.5$

Millimoles of $NaOH = 50 \times 0.1 = 5.0$

$$NH_4Cl + NaOH \rightleftharpoons NH_4OH + NaCl$$

Initial conc.	7.5	5.0	0	0
Change	−5.0	−5.0	+5.0	+5.0
Final conc.	2.5	0	5.0	5.0

Given, $\text{p}K_a(NH_4^+) = 9.26$

$$\therefore \quad \text{p}K_b(NH_3) = 14 - 9.26 = 4.74$$

$$\Rightarrow \quad \text{pOH} = \text{p}K_b + \log \frac{[NH_4^+]}{[NH_4OH]}$$

$$= 4.74 + \log \frac{2.5}{5.0}$$

$$\Rightarrow \quad \text{pOH} = 4.44$$

Thus, $$\text{pH} = 14 - 4.44$$

$$\text{pH} = 9.56$$

88 (*a*) $\because \quad \text{pH} = \text{p}K_a + \log \dfrac{[\text{salt}]}{[\text{acid}]}$

As $[\text{salt}] = [\text{acid}]$

$$\therefore \quad \text{pH} = \text{p}K_a = 9.30$$

89 (*c*) Given, conc. of NH_3 (base) $= 0.30$ M

Conc. of NH_4^+ (salt) $= 0.20$ M

$$K_b = 1.8 \times 10^{-5}$$

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

$$\Rightarrow \quad 4.74 + \log \frac{0.20}{0.30}$$

$$= 4.74 + (0.301 - 0.477)$$

$$= 4.74 - 0.176 = 4.56$$

$$\Rightarrow \quad \text{pH} = 14 - 4.56 = 9.44$$

90 (*b*) Given,

conc. of $NH_4OH = 0.1$ M

conc. of $NH_4Cl = 0.01$ M

$$\text{p}K_b = 5$$

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

$$= 5 + \log \frac{0.01}{0.1} = 5 + \log 10^{-1}$$

$$= 5 - 1 = 4$$

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

91 (*b*) Let us consider all the options,

(a) 100 mL of 0.1 M CH_3COOH + 100 mL of 0.1M NaOH

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

Initial conc.	100 mL × 0.1 M = 10 mmol	100 mL× 0.1 M = 10 mmol	0 mmol
Final conc.	0	0	10 mmol

It is not basic buffer because hydrolysis of salt takes place and final solution contains salt of weak acid with strong base only.

(b) 100 mL of 0.1M HCl + 200 mL of 0.1 M NH_4OH

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

Initial conc.	100 mL × 0.1 M = 10 mmol	200 mL × 0.1 M = 20 mmol	0 mmol
Final conc.	0	10 mmol	10 mmol

It is basic buffer because final solution contains weak base and its salt with strong acid.

(c) 100 mL of 0.1 M HCl+100 mL of 0.1 MNaOH

$$HCl + NaOH \longrightarrow NaCl + H_2O$$

Initial conc.	100 mL × 0.1 M = 10 mmol	100 mL × 0.1 M = 10 mmol	0 mmol
Final conc.	0	0	10 mmol

It is a neutral solution.

(d) 50 mL of 0.1 M NaOH + 25mL of 0.1 MCH_3COOH

$$CH_3COOH + NaOH \longrightarrow CH_3COONa + H_2O$$

Initial conc.	25 mL × 0.1 M = 2.5 mmol	50 mL × 0.1 M = 5 mmol	0 mmol
Final conc.	0	2.5 mol	2.5 mmol

It is a basic solution.

92 (*c*) A solid salt of the general formula, $M_x^{p+}X_y^{q-}$ with molar solubility S in equilibrium with its saturated solution may be represented by the equation,

$$M_xX_y(s) \longrightarrow xM^{p+}(aq) + yX^{q-}(aq)$$

$$(\text{,where } x \times p^{+} = y \times q^{-})$$

and its solubility product constant is given by

$$K_{\text{sp}} = [M^{p+}]^x[X^{q-}]^y = (xS)^x(yS)^y$$

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

$$S^{(x+y)} = \frac{K_{\text{sp}}}{x^x \cdot y^y} \text{ or } S = (K_{\text{sp}}/x^x \cdot y^y)^{1/x+y}$$

93 (*d*) $\text{BaSO}_4(s) \underset{\text{in water}}{\overset{\text{Saturated solution}}{\rightleftharpoons}} \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq)$

If molar solubility is S, then $1.1 \times 10^{-10} = (S)(S) = S^2$

or, $S = 1.05 \times 10^{-5}$

Thus, molar solubility of barium sulphate (BaSO_4) will be equal to 1.05×10^{-5} mol L^{-1}.

94 (*d*) $\therefore \text{Ag}_2\text{CrO}_4 \rightleftharpoons \underset{2S}{2\text{Ag}^+} + \underset{S}{\text{CrO}_4^{2-}}$

$\therefore$ Solubility product,

$$K_{\text{sp}} = (2S)^2 \times S = 4S^3,\ K_{\text{sp}} = (1.1 \times 10^{-12})$$

$$\Rightarrow \quad S = \sqrt[3]{\frac{K_{\text{sp}}}{4}} = 0.65 \times 10^{-4}$$

Now, $\quad \text{AgCl} \rightleftharpoons \underset{(S)}{\text{Ag}^+} + \underset{(S)}{\text{Cl}^-}$

$$\therefore \quad K_{\text{sp}} = S \times S \qquad (K_{\text{sp}} = 1.8 \times 10^{-10})$$

$$\Rightarrow \quad S = \sqrt[2]{K_{\text{sp}}} = 1.34 \times 10^{-5}$$

$$\text{AgBr} \rightleftharpoons \underset{S}{\text{Ag}^+} + \underset{S}{\text{Br}^-}$$

$$\therefore \quad K_{\text{sp}} = S \times S \qquad (K_{\text{sp}} = 5.0 \times 10^{-13})$$

$$\Rightarrow \quad S = \sqrt{K_{\text{sp}}} = 0.71 \times 10^{-6}$$

$$\text{AgI} \rightleftharpoons \underset{S}{\text{Ag}^+} + \underset{S}{\text{I}^-}$$

$$\therefore \quad K_{\text{sp}} = S \times S \qquad (K_{\text{sp}} = 8.3 \times 10^{-17})$$

$$\Rightarrow \quad S = \sqrt{K_{\text{sp}}} = 0.9 \times 10^{-8}$$

$\because$ Solubility of Ag_2CrO_4 is highest. Therefore, it is added to the solution.

95 (*b*) Consider a salt, zirconium phosphate of molecular formula $(\text{Zr}^{4+})_3(\text{PO}_4^{3-})_4$. It dissociates into 3 zirconium cations of charge +4 and 4 phosphate anions of charge –3.

$$[\text{Zr}^{4+}] = 3S \quad \text{and} \quad [\text{PO}_4^{3-}] = 4S$$

and $\quad K_{\text{sp}} = (3S)^3(4S)^4 = 6912\,(S)^7$

or $\quad S = \{K_{\text{sp}}/(3^3 \times 4^4)\}^{1/7} = (K_{\text{sp}}/6912)^{1/7}$

96 (*c*) $A_2X_3 \longrightarrow 2A^{3+} + 3X^{2-}$

$$K_{\text{sp}} = [A^{3+}]^2[X^{2-}]^3 = 1.1 \times 10^{-23}$$

If S = solubility of A_2X_3, then

$$[A^{3+}] = 2S; \quad [X^{2-}] = 3S$$

therefore, $\quad K_{\text{sp}} = (2S)^2(3S)^3$

$$= (108)S^5 = 1.1 \times 10^{-23}$$

Thus, $\quad S^5 = 1 \times 10^{-25}$

$$S = 1.0 \times 10^{-5} \text{ mol L}^{-1}$$

97 (*c*) Let the solubility of CaF_2 in 0.1 M NaF is 'S' mol L^{-1}

$$\text{CaF}_2(s) \rightleftharpoons \underset{S}{\text{Ca}^{2+}(aq)} + \underset{2S}{2\,\text{F}^-(aq)}$$

$$\text{NaF(aq)} \rightleftharpoons \underset{0.\,1\text{ M}}{\text{Na}^+} + \underset{0.\,1\text{ M}}{\text{F}^-(aq)}$$

$$[\text{F}^-] = 2S + 0.1$$

$$K_{\text{sp}} \text{ of } \text{CaF}_2 = [\text{Ca}^{2+}]\ [\text{F}^-]^2$$

$$= [S][2\text{S} + 0.1]^2$$

$$= 5.3 \times 10^{-11} = [S][2S + 0.1]^2$$

$$\Rightarrow \quad 5.3 \times 10^{-11} = [S][0.1]^2 \qquad [\because\ 2S << 0.1]$$

$$[S] = \frac{5.3 \times 10^{-11}}{(0.1)^2} = 5.3 \times 10^{-9} \text{ mol L}^{-1}$$

98 (c) For a general reaction,

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

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

For BaSO_4 (binary solute giving two ions)

$$\text{BaSO}_4(s) \rightleftharpoons \underset{S}{\text{Ba}^{2+}(aq)} + \underset{S}{\text{SO}_4^{2-}(aq)}$$

$$\therefore \quad K_{\text{sp}} = [\text{Ba}^{2+}]\ [\text{SO}_4^{2-}]$$

$$= (S)(S) = S^2 \qquad \ldots\text{(i)}$$

[,where S = Solubility]

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

Molar mass of BaSO_4 = 233 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

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

$$= 1.08 \times 10^{-10} \text{ mol}^2 \text{ L}^{-2}$$

99 *(d)* For a sparingly soluble salt, if S is the molar solubility,

$$A_xB_y(s) + \text{H}_2\text{O} \rightleftharpoons xA^{y+} + yB^{x-}$$

At saturation,

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

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

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

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

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

Given, $2S = 2.2 \times 10^{-4}$ or $S = 1.1 \times 10^{-4}$ M

$\therefore$ $K_{sp} = [2.2 \times 10^{-4}]^2\,[1.1 \times 10^{-4}] = 5.3 \times 10^{-12}$

100 (*c*) AX_2 is ionised as follows:

$$\underset{S \text{ mol L}^{-1}}{AX_2} \rightleftharpoons \underset{S}{A^{2+}} + \underset{2S}{2X^-}$$

Solubility product of AX_2

$$K_{sp} = [A^{2+}][X^-]^2 = [S] \times [2S]^2 = 4S^3$$

$\because$ K_{sp} of $AX_2 = 3.2 \times 10^{-11}$

$\therefore$ $3.2 \times 10^{-11} = 4S^3$

or, $S^3 = 0.8 \times 10^{-11} = 8 \times 10^{-12}$

or, $S = \sqrt[3]{8 \times 10^{-12}} = 2 \times 10^{-4}$ mol / L

Solubility $= 2 \times 10^{-4}$ mol / L

101 (*a*) $\underset{S}{Ag_2CrO_4} \longrightarrow \underset{2S}{2Ag^+} + \underset{S}{CrO_4^{2-}}$

$$K_{sp} = (2S)^2 S = 4S^3 \text{ or } S = \left(\frac{K_{sp}}{4}\right)^{1/3}$$

$$= \left(\frac{4 \times 10^{-12}}{4}\right)^{1/3} = 1.0 \times 10^{-4} \text{ mol L}^{-1}$$

102 (*b*) Suppose solubility of $PbCl_2$ in water is 5 mol L^{-1}

$$PbCl_2(s) \rightleftharpoons \underset{S}{Pb^{2+}(aq)} + \underset{2S}{2Cl^-(aq)}$$

$$K_{sp} = [Pb^{2+}][Cl^-]^2$$

$$K_{sp} = [S][2S]^2 = 4S^3$$

$$3.2 \times 10^{-8} = 4S^3$$

$$S^3 = \frac{3.2 \times 10^{-8}}{4}$$

$$S^3 = 0.8 \times 10^{-8} = 8.0 \times 10^{-9}$$

Solubility, $PbCl_2 = S = 2 \times 10^{-3}$ mol L^{-1}

Solubility of $PbCl_2$ in $gL^{-1} = 278 \times 2 \times 10^{-3}$

$= 0.556\ gL^{-1}$

0.556 g of $PbCl_2$ dissolve in 1 L of water

$\therefore$ 0.1 g of $PbCl_2$ will dissolve in $\frac{1 \times 0.1}{0.556}$ L of water

$= 0.1798$ L

$= 179.8$ mL $\approx$ 180 mL

103 (*b*) K_{sp} of $Cr(OH)_3$ at 298 K is 6.0×10^{-31}.

$[OH^-]$ in saturated solution of $Cr(OH)_3$ = ?

$$Cr(OH)_3 \rightleftharpoons \underset{S}{Cr^{3+}} + \underset{S}{3OH^-}$$

In a saturated solution, $K_{sp} = [Cr^{3+}][OH^-]^3$

$$= S(3S)^3 = 27S^4 = 6.0 \times 10^{-31}$$

$\therefore$ $$S^4 = \frac{6.0 \times 10^{-31}}{27}$$

$\Rightarrow$ $$S = \left(\frac{6.0 \times 10^{-31}}{27}\right)^{\frac{1}{4}}$$

$$[OH]^- = 3S = 3\left(\frac{6.0 \times 10^{-31}}{27}\right)^{\frac{1}{4}}$$

$$= \left(\frac{6.0 \times 3^4}{3^3} \times 10^{-31}\right)^{\frac{1}{4}} = (18 \times 10^{-31})^{\frac{1}{4}}$$

104 (*d*) $\underset{S}{PbCl_2} \longrightarrow \underset{S}{Pb^{2+}} + \underset{2S}{2Cl^-}$

$$K_{sp} = S(2S)^2 = 4S^3$$

$$= 4 \times (10^{-2})^3 = 4 \times 10^{-6}$$

In 0.1 M NaCl, $[Cl^-] = 0.1 + 2 \times 10^{-2} \approx 0.1$ M

As 0.01 M $PbCl_2 \equiv 0.02$ M Cl^-

$$[Pb^{2+}][Cl^-]^2 = K_{sp}$$

or $[Pb^{2+}](0.10)^2 = 4 \times 10^{-6}$

or $[Pb^{2+}] = 4 \times 10^{-4}$ M

105 (*c*) $Ag_2CrO_4 \longrightarrow 2Ag^+ + CrO_4^{2-}$

$$[CrO_4^{2-}] = \frac{1}{2}[Ag^+] = \frac{1.5 \times 10^{-4}}{2} = 0.75 \times 10^{-4} \text{ mol/L}$$

$\because$ $K_{sp} = [Ag^+]^2\,[CrO_4^{2-}]$

$\therefore$ $K_{sp} = (1.5 \times 10^{-4})^2 (0.75 \times 10^{-4})$

$= 1.6875 \times 10^{-12}$

106 (*b*) $\because$ $S = \frac{10W}{M}$ mol/L

For $Ca_3(PO_4)_2 \rightleftharpoons \underset{3S}{3Ca^{2+}} + \underset{2S}{2PO_4^{3-}}$

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

$\therefore K_{sp}$ of $Ca_3(PO_4)_2 = 108\,S^5$

$$\Rightarrow 108\left(\frac{10W}{M}\right)^5$$

$$\Rightarrow 10^7\left(\frac{W}{M}\right)^5 \text{ (approximately)}$$

107 (*b*) $0.01 \text{ M } CaCl_2 \equiv 0.02 \text{ M } Cl^-$,s

$0.01 \text{ M NaCl} \equiv 0.01 \text{ M } Cl^-$,

$0.05 \text{ M } AgNO_3 \equiv 0.05 \text{ M } Ag^+$

$[Ag^+][Cl^-] = K_{sp}$ (constant)

Hence, $S_1 = \sqrt{K_{sp}}$ = maximum; $S_2 = \dfrac{K_{sp}}{0.02} = 50\,K_{sp}$

$$S_3 = \frac{K_{sp}}{0.01} = 100\,K_{sp}; \quad S_4 = \frac{K_{sp}}{0.05} = 20K_{sp}$$

Thus, the correct order of solubilities is

$$S_1 > S_3 > S_2 > S_4$$

108 (*a*) $S_{\text{I}} = \left[\dfrac{K_{sp}}{4}\right]^{1/3}$ for A_2X;

$S_{\text{II}} = \sqrt{K_{sp}}$ for *AX;* $S_{\text{III}} = \left[\dfrac{K_{sp}}{27}\right]^{1/4}$ for AX_3

$\therefore \quad S_{\text{II}} > S_{\text{I}} > S_{\text{III}}$

109 (*b*) $AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$

$$K_{sp} \text{ of AgCl} = [Ag^+][Cl^-] = 1.8 \times 10^{-10} \quad \ldots \text{(i)}$$

Now, $[Ag(NH_3)_2]^+(aq) \rightleftharpoons Ag^+(aq) + 2NH_3(aq)$

$$\therefore K_C = \frac{[Ag^+][NH_3]^2}{[Ag\ (NH_3)_2]^+} = 6.2 \times 10^{-8} \quad \ldots\text{(ii)}$$

From eq. (i) and (ii), we get

$$\frac{K_C}{K_{sp}} = \frac{[NH_3]^2}{[Ag(NH_3)_2]^+\,[Cl^-]} \quad \ldots\text{(iii)}$$

$$\begin{array}{lcc} AgCl + 2NH_3 \rightleftharpoons & [Ag(NH_3)_2]^+ & +\ Cl^- \\ \quad\quad 1 & 0 & 0 \\ \quad\quad 1-a & a & a \end{array}$$

Thus, on substituting the values in eq. (iii), we get

$$\frac{6.2 \times 10^{-8}}{1.8 \times 10^{-10}} = \frac{1}{a^2} \quad \text{or, } a = 0.0539 \text{ M}$$

110 (*b*) $\Delta G°$ is related to K_{sp} by the equation,

$$\Delta G° = -\,2.303\,RT \log K_{sp} \quad \ldots\text{(i)}$$

Given, $\Delta G° = +\,63.3 \text{ kJ} = 63.3 \times 10^3 \text{ J}$

Thus, substitute $\Delta G° = 63.3 \times 10^3$ J

$$R = 8.314 \text{ JK}^{-1}\text{mol}^{-1}$$

and $T = 298 \text{ K } (25 + 273 \text{ K})$

into equation (i) to get,

$$63.3 \times 10^3 = -\,2.303 \times 8.314 \times 298 \log K_{sp}$$

$\therefore \quad \log K_{sp} = -\,11.09$

$\Rightarrow \quad K_{sp} = 8.0 \times 10^{-12}$

111 (*b*) Given,

pH of $Ba(OH)_2 = 12$

$$\text{pOH} = 14 - \text{pH} = 14 - 12 = 2$$

We know that, $\text{pOH} = -\log[OH^-]$

$$2 = -\log[OH^-]$$

$\Rightarrow \quad [OH^-] = 10^{-2}$

$Ba(OH)_2$ dissolve in water as

$$\underset{S \text{ mol L}^{-1}}{Ba(OH)_2} \rightleftharpoons \underset{S}{Ba^{2+}} + \underset{2S}{2OH^-}$$

$$[OH^-] = 2S = 10^{-2}$$

$$K_{sp} = [Ba^{2+}][OH^-]^2 = (10^{-2}) \times \frac{(10^{-2})^2}{2}$$

$$= 0.5 \times 10^{-6} = 5 \times 10^{-7}$$

112 (*a*) $AgCN \rightleftharpoons Ag^+ + CN^-$

$$K_{sp} = [Ag^+][CN^-] = 6 \times 10^{-17}$$

$$Ni(OH)_2 \rightleftharpoons Ni^{2+} + 2OH^-$$

$$K_{sp} = [Ni^{2+}][OH^-]^2 = 2 \times 10^{-15}$$

Let $[Ag^+] = S_1$, then $[CN^-] = S_1$

Let $[Ni^{2+}] = S_2$, then $[OH^-] = 2S_2$

$$S_1^2 = 6 \times 10^{-17}, \quad S_1 = 7.7 \times 10^{-9}$$

$$(S_2)(2S_2)^2 = 2 \times 10^{-15}, \quad S_2 = 7.9 \times 10^{-6}$$

$\therefore$ $Ni(OH)_2$ is more soluble than AgCN.

113 (*c*) Let the solubility of $Ni(OH)_2$ be equal to *S*.

Dissolution of *S* mol/L of $Ni(OH)_2$ provides *S* mol/L of Ni^{2+} and 2*S* mol/L of OH^-, but the total concentration of $OH^- = (0.10 + 2S)$ mol/L because the solution already contains 0.10 mol/L of $\overline{\text{O}}$H from NaOH.

$$K_{sp} = 2.0 \times 10^{-15} = [Ni^{2+}][OH^-]^2$$

$$= (S)\,(0.10 + 2S)^2$$

As K_{sp} is small, $2S << 0.10$, thus, $(0.10 + 2S) \approx 0.10$

Hence, $2.0 \times 10^{-15} = S(0.10)^2$

$$S = 2.0 \times 10^{-13} \text{ M}$$

Thus, $[Ni^{2+}] = 2.0 \times 10^{-13}$ M

114 (*b*) $Na_2SO_4(s) + (aq) \rightleftharpoons Na_2SO_4(aq) + \text{Heat}$

By Le-Chatelier principle, on heating, equilibrium shifts in the backward direction. So, some sodium sulphate will be precipitated out.

116 (*a*) Precipitation of AgCl will occur only when ionic product is greater than solubility product. This is possible only in case, when 10^{-4} M Ag^+ and 10^{-4} M Cl^- are mixed, i.e. ionic product = $10^{-4} \times 10^{-4} = 10^{-8}$

117 (*c*) Given that,

$$K_{sp}\ Mg(OH)_2 = [Mg^{2+}][OH^-]^2$$

$$1.2 \times 10^{-11} = [0.1][OH^-]^2$$

$$[OH^-]^2 = 1.2 \times 10^{-10}$$

$$[OH^-] = 1.0954 \times 10^{-5} M$$

$$pOH = -\log (1.0954 \times 10^{-5}) = 4.96$$

$$pH = 14 - 4.96 = 9.04$$

Thus, at 9.04 pH, precipitation will not take place.

118 (*b*) Statement (b) is incorrect.

It's correct form is as follows :

The reaction never ceases at equilibrium because equilibrium is dynamic in nature.

Rest other statements are correct.

120 (*c*) Statement (c) is incorrect.

It's correct form is as follows :

Chemical equilibrium cannot take place in an open vessel if one of the reactants or products is a gas.

Rest other statements are correct.

121 (*d*) Statement (d) is incorrect.

It's correct form is as follows :

The reaction can reach the state of equilibrium even if it starts with only *C* and *D*; i.e. there is no *A* and *B* being present initially.

This is because, equilibrium can be reached from either direction.

Rest other statements are correct.

123 (*b*) Statement (b) is incorrect.

It's correct form is as follows :

Chemical equilibrium in the reaction,

$H_2(g) + I_2(g) \rightleftharpoons 2HI(g)$ can be attained from either direction.

Rest other statements are correct.

124 (*d*) Statement (d) is incorrect.

It's correct form is as follows :

The reaction takes place in the presence of a catalyst which is $V_2O_5(s)$ in contact process or $NO(g)$ in chamber process.

Rest other statements are correct.

125 (*a*) The value of K_p does not depend upon volume

but on changing the volume, degree of dissociation; α changes because on both sides the number of moles are different.

Thus, statement (a) is correct.

127 (*a*) Statement (a) is incorrect.

It's correct form is as follows :

NaCl exist in solid state as a cluster of negatively charged chloride ions and positively charged sodium ions.

Rest other statements are correct.

128 (*c*) $RCOOH + NaHCO_3 \rightleftharpoons RCOONa + H_2O + CO_2$

or $RCOOH + HCO_3^- \rightleftharpoons RCOO^- + H_2O + CO_2$

conjugate base, $RCOO^-$ is more stable than the free carboxylic acid.

That's why, equilibrium shifts in forward direction.

Thus, statement (c) is correct.

129 (*c*) Statement (c) is incorrect.

It's correct form is as follows :

Addition of NH_4Cl to NH_4OH decreases the ionisation of NH_4OH due to common ion effect.

Rest other statements are correct.

130 (c) Statement (c) is correct, while the other statements are incorrect.

Corrected form are as follows :

(a) Acidic buffer consists of a weak acid and its salt with strong base in a fixed proportion
e.g. $CH_3COOH + CH_3COONa$

(b) pH of the buffer solution is not affected by dilution because ratio under the logarithmic terms remains unchanged.

(d) Glycine + glycine hydrochloride is an example of basic buffer.

133 (*c*) Statement III is correct, while the other statements are incorrect.

Corrected form are as follows :

I. Expression for the equilibrium constant is applicable when concentrations of the reactants and products have atttained constant value at equilibrium state.

II. The value of equilibrium constant is independent of initial concentrations of the reactants and products.

IV. The equilibrium constant for the reverse reaction is equal to the inverse of the equilibrium constant for the forward reaction.

134 (*d*) Statements I, III and IV are correct, while the statement II is incorrect.

It's correct form is as follows.

To restore equilibrium, the reaction will proceed in the direction where H_2 is consumed, i.e. equilibrium shifts in the forward direction.

137 (*c*) For the given reaction,

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

the value of Δn and $\Delta H = -$ ve. Therefore, according to the Le-Chatelier's principle, the increase in pressure and decrease in temperature, shifts the equilibrium in forward direction.

Thus, option (c) is correct.

138 (*d*) Statements I, II and III are correct the while statement IV is incorrect. It's correct form is as follows :

Le-Chatelier's principle is applicable to common ion effect. Because, in presence of common ion (given) by strong electrolyte (say, $Na^+ \overline{A}$), the product of the concentration terms in RHS increases.

For the weaker electrolyte, HA (say) the equilibrium shifts to the LHS, $HA \rightleftharpoons H^{\oplus} + A^{s}$.

As a result dissociation of HA gets suppressed.

140 (c) Dissolution of gases in liquid is that the concentration of a gas in liquid is proportional to the pressure (concentration) of the gas over the liquid.

Thus, A is correct but R is incorrect.

141 (a) When a gas is dissolved in water, an equilibrium is developed between the gaseous molecules and dissolved molecules of the gas under pressure,

e.g. $CO_2(g) \rightleftharpoons CO_2$ (solution). Such equilibrium is governed by Henry's law.

Both A and R are correct and R is the correct explanation of the A.

142 (c) For the homogeneous equilibrium,

$$N_2O_4(g) \rightleftharpoons 2NO_2(g),$$

K_C has unit mol/L and K_p has unit bar.

Thus, A is correct but R is incorrect.

143 (c) $PCl_5 \longrightarrow PCl_3 + Cl_2$

At constant pressure, when He is added to the equilibrium, volume increases. Thus, in order to maintain the K constant, degree of dissociation of PCl_5 increases. Moreover, He (helium) is unreactive towards chlorine gas.

Thus, A is correct but R is incorrect.

144 (a) Aqueous solution of $FeCl_3$ on standing produces brown precipitate. Due to hydrolysis, it produces precipitate of $Fe(OH)_3$ which is of brown colour.

Both A and R are correct and R is the correct explanation of the A.

145 (a) If the volume is kept constant and an inert gas such as argon is added which does not take part in the reaction, the equilibrium remains undisturbed. It is because the addition of an inert gas at constant volume does not change the partial pressure or the molar concentrations of the substance involved in the reaction. The reaction quotient changes only if the added gas is reactant or product involved in the reaction.

Both A and R are correct and R is the correct explanation of A.

146 (a) Michael Faraday classified the substances into two categories based on their ability to conduct electricity. **Electrolytes** which conduct electricity in aqueous solutions and **non-electrolytes** which donot conduct electricity in their aqueous solutions.

Both A and R are correct and R is the correct explanation of A.

147 (c) Higher order ionisation constants (K_{a_2}, K_{a_3}) are smaller than the lower order ionisation constant (K_{a_1}) of a polyprotic acid. The reason for this is that, it is more difficult to remove a positively charged proton from a negative ion due to electrostatic forces.

This can be seen in the case of removing a proton from the uncharged H_2CO_3 as compared from a negatively charged HCO_3^-.

Thus, A is correct but R is incorrect.

148 (a) The given defination is of common ion effect and it is a phenomenon based on Le-Chatelier's principle.

Both A and R are correct and R is the correct explanation of A.

149 (d) In biological systems, buffer solution of carbonic acid and sodium bicarbonate is found in our blood. It maintains the pH of blood to a constant value of about 7.4.

Thus, A is incorrect but R is correct.

153 (a) In the reaction,

$$\underset{\text{(Pink)}}{[Co(H_2O)_6]^{3+}(aq)} + 4Cl^-(aq) \rightleftharpoons \underset{\text{(Blue)}}{[CoCl_4]^{2-}(aq)} + 6H_2O(l)$$

On cooling, the equilibrium shifts in backward direction or on heating, the equilibrium shifts in forward direction.

Hence, reaction is endothermic, i.e. $\Delta H > 0$.

154 (d) $\Delta G°$ and K are related as, $\Delta G° = -RT \ln K_C$

when $G° > 0$ means $\Delta G°$ is positive. This can be only, if $\ln K_C$ is negative, i.e. $K_C < 1$.

155 (b) As the acidity or K_a value increases, pH decreases, thus the order of pH value of the acids is

$$\underset{(3.8 \times 10^{-8})}{\text{hypochlorous acid}} > \underset{(1.74 \times 10^{-5})}{\text{acetic acid}} > \underset{(1.8 \times 10^{-4})}{\text{formic acid}}$$

156 (c) Statement (c) is not correct.

It's correct form is as follows.

At the stage of equilibria, physical processes like melting of ice and freezing of water etc., process does not stop but the opposite processes, i.e. forward and reverse process occur with the same rate. The other given statements are the characteristics of physical equilibrium.

Rest other statements are correct.

157 (b) Statement (b) is incorrect.

It's correct form is as follows.

In the reaction,

$$Fe^{3+} + SCN^- \rightleftharpoons \underset{\text{(Red)}}{FeSCN^{2+}}$$

When oxalic acid is added, it combines with Fe^{3+} ions, and equilibrium shifts towards backward direction. Therefore, intensity of red colour decreases.

Rest other statements are correct.

158 (b) For the reaction,

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

At 500 K in a closed container,

$$[PCl_5] = 0.8 \times 10^{-3} \text{ mol L}^{-1}$$

$$[PCl_3] = 1.2 \times 10^{-3} \text{ mol L}^{-1}$$

$$[Cl_2] = 1.2 \times 10^{-3} \text{ mol L}^{-1}$$

$$\Rightarrow \quad K_C = \frac{[PCl_3][Cl_2]}{[PCl_5]} = \frac{(1.2 \times 10^{-3}) \times (1.2 \times 10^{-3})}{(0.8 \times 10^{-3})}$$

$$= 1.8 \times 10^{-3} \text{ mol L}^{-1}$$

159 (*d*) The relationship between K_p and K_C is

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

where, Δn = (number of moles of gaseous products) − (number of moles of gaseous reactants)

For the reaction,

$$NH_4Cl(s) \rightleftharpoons NH_3(g) + HCl(g);$$
$$\Delta n = 2 - 0 = 2$$

160 (*a*) For the reaction,

$$H_2S \rightleftharpoons H^+ + HS^-$$

$$K_{a_1} = \frac{[H^+][HS^-]}{[H_2S]}$$

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

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

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

$$K_{a_3} = \frac{[H^+]^2 [S^{2-}]}{[H_2S]} = K_{a_1} \times K_{a_2}$$

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

161 (*a*) In the reaction,

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

If the total pressure at which the equilibrium is established is increased without changing the temperature, K will remain same. This is because, K changes only with change in temperature.

162 (*d*) In all the given reactions, equilibrium constant (K) remains unaffected on addition of inert gas. This is in accordance with the Le-Chatelier's principle.

163 (*b*) The given compounds are :

$$\underset{\text{(Maximum b. p.)}}{\text{Water}}, \text{ acetone}, \underset{\text{(Minimum b. p.)}}{\text{ether}}$$

Greater the boiling point, lower is the vapour pressure of the solvent.

Hence, the correct order of vapour pressure will be

water < acetone < ether.

164 (*a*) For the reaction,

$$\frac{1}{2}H_2(g) + \frac{1}{2}I_2(g) \rightleftharpoons HI(g)$$

$$K_C = \frac{[HI]}{[H_2]^{1/2}[I_2]^{1/2}} = 5$$

Thus, for the reaction,

$$2HI(g) \rightleftharpoons H_2(g) + I_2(g)$$

$$K_{C_1} = \frac{[H_2][I_2]}{[HI]^2} = \left(\frac{1}{K_C}\right)^2 = \left(\frac{1}{5}\right)^2 = \frac{1}{25} = 0.04$$

165 (*c*) Given that,

K_a for $CH_3COOH = 1.8 \times 10^{-5}$

K_b for $NH_4OH = 1.8 \times 10^{-5}$

Ammonium acetate is salt of weak and weak base.

For such salts,

$$pH = 7 + \frac{pK_a - pK_b}{2}$$

$$= 7 + \frac{[-\log 1.8 \times 10^{-5}] - [-\log 1.8 \times 10^{-5}]}{2}$$

$$= 7 + \frac{4.74 - 4.74}{2} = 7.0$$

166 (*a*) As we know that,

$$\Delta G^{s} = -RT \ln K$$

At the stage of half-completion of the reaction,

$$A \rightleftharpoons B, [A] = [B]$$

Therefore, $K = 1$

Thus, $\Delta G^{s} = 0$

167 (*c*) GN Lewis in 1923 defined an acid as a species which accepts an electron pair and base which donates an electron pair. As, BF_3 is an electron deficient compound, hence it is a Lewis acid.

168 (*c*) When the concentration of NH_4OH (weak base) is higher than the strong acid (HCl), a mixture of weak base and its conjugate acid is obtained, which acts as basic buffer.

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

Initially	0.1 M	0.05 M	0
After reaction	0.05 M	0	0.05 M

169 (*d*) Among the given solvents, AgCl is most soluble in aqueous ammonia solution. AgCl react with aqueous ammonia to form a complex, $[Ag(NH_3)_2]^+Cl^-$.

170 (*c*) The pH of neutral water at 25°C is 7.0.

At 25°C, $[H^+] = [OH^-] = 10^{-7}$

and $K_w = [H^+][OH^-] = 10^{-14}$

On heating, K_w increases, i.e. $[H^+][OH^-] > 10^{-14}$

As $[H^+] = [OH^-]$ or, $[H^+]^2 > 10^{-14}$

$\Rightarrow [H^+] > 10^{-7}$ M

$\therefore$ pH < 7.

With rise in temperature, pH of pure water decreases and it become less than 7 at 60°C.

171 (a) Given that, $K_a = 1.74 \times 10^{-5}$

Concentration of $CH_3COOH = 0.01 \text{ mol dm}^{-3}$

$$[H^+] = \sqrt{K_a \cdot C} = \sqrt{1.74 \times 10^{-5} \times 0.01} = 4.17 \times 10^{-4}$$

$$pH = -\log[H^+]$$

$$= -\log(4.17 \times 10^{-4}) = 3.4$$

172 (a) Ammonium carbonate dissociates as follows :

$$(NH_4)_2CO_3 \longrightarrow 2NH_4^+ + CO_3^{2-}$$

$$2H_2O \longrightarrow 2OH^- + 2H^+$$

$$\underset{\text{Weak base}}{NH_4OH} + \underset{\text{Weak acid}}{H_2CO_3}$$

If K_b of $NH_4OH > K_a$ of H_2CO_3, the solution is basic or if K_a of $H_2CO_3 > K_b$ of NH_4OH, the solution is acidic.

Thus, both A and R are correct and R is the correct explanation of A.

173 (b) H_2S is a weak acid and also a weak electrolyte and its ionisation is suppressed, when small amount of strong electrolyte like HCl is added due to common ion effect.

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

$$HCl \longrightarrow \underset{\substack{\text{Common}\\\text{ion}}}{H^+} + Cl^-$$

Thus, both A and R are correct but R is not the correct explanation of A.

174 (b) An aqueous solution of ammonium acetate can act as a natural buffer as it resist changes in pH on dilution or an addition of small amount of acids or alkalies.

Moreover, ammonium acetate is a salt of weak acid (CH_3COOH) and weak base (NH_4OH).

Thus, both A and R are correct but R is not the correct explanation of A.

175 (a) In the hydrogen halides, the HI is strongest acid but HF is the weak acid. It is because, while comparing acids formed by the elements belonging to the same group of periodic table, H—A bond strength is a more important factor in determining acidity of an acid than the polar nature of the bond.

Thus, both A and R are correct and R is the correct explanation of A.

176 (a) A solution containing a mixture of acetic acid and the sodium acetate acts as a buffer solution as it maintains a constant value of pH (= 4.75) and its pH is not affected on addition of small amounts of acid or alkali.

Thus, both A and R are correct and R is the correct explanation of A.