Chapter 8

CHEMICAL EQUILIBRIUM

MATHEMATICAL EQUATIONS

(i) Law of mass-action:

For the reversible chemical reaction

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

$$K_c = \frac{[C]^c [D]^d}{[A]^a [B]^b} \text{ or } K_c = \frac{C_C^c . C_D^d}{C_A^a C_B^b} \left[\text{When conc. is in mol dm}^{-3}\right]$$

$$K_p = \frac{p_C^c p_D^d}{p_A^a p_B^b} \left[\text{when the concentrations are in partial pressures}\right]$$

$$K_x = \frac{X_C^c X_D^d}{X_A^a X_B^b} \left[\text{when the concentrations are in mole fractions}\right]$$

$$K_n = \frac{n_C^c n_D^d}{n_A^a n_B^b} \left[\text{when the concentractions are in number of moles}\right]$$

(ii) Relationship between three equilibrium constants:

$$K_p = K_c (RT)^{\Delta n}, \quad K_p = K_x (P)^{\Delta n}, \quad K_p = K_n (P/N)^{\Delta n}$$

where

R = General gas constant, T = Absolute temperature of system

P = Pressure of the system

N = Total number of moles of reactants and products

Δn = Difference of number of moles of reactants and products

Some other relations are

$$K_c(RT)^{\Delta n} = K_x (P)^{\Delta n}, \; K_x(P)^{\Delta n} = K_n (P/N)^{\Delta n}, \; K_c(RT)^{\Delta n} = K_n (P/N)^{\Delta n}$$

when $\Delta n = 0$

$$K_p = K_c = K_x = K_n$$

(iii) Quantitative expressions of K_c for some important reactions:

1. $CH_3COOH_{(aq)} + C_2H_5OH \rightleftharpoons CH_3COOC_2H_{5(aq)} + H_2O$

$$K_c = \frac{x^2}{(a-x)(b-x)}$$

2. $H_{2(g)} + I_{2(g)} \rightleftharpoons 2HI_{(g)}$, $K_c = \frac{4x^2}{(a-x)(b-x)}$

3. $PCl_{5(g)} \rightleftharpoons PCl_{3(g)} + Cl_{2(g)}$, $K_c = \frac{x^2}{V(a-x)}$

4. $N_2O_{4(g)} \rightleftharpoons 2NO_{2(g)}$, $K_c = \frac{4x^2}{V(a-x)}$

5. $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$, $K_c = \frac{4x^2 V}{(a-2x)(b-x)}$

6. $N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$, $K_c = \frac{4x^2 V^2}{(a-x)(b-3x)^3}$

(iv) Ionic product of water:

$[H^{\oplus}][OH^{\ominus}] = K_w = 10^{-14}$ at 25°C in neutral water

$[H^+] = 10^{-7}$ moles dm^{-3} at 25°C in neutral water

$[OH^-] = 10^{-7}$ moles dm^{-3} at 25°C in neutral water

when $[H^{\oplus}] > [OH^{\ominus}]$, but $K_w = 10^{-14}$ at 25°C (acidic solution)

$[OH^-] > [H^{\oplus}]$, but $K_w = 10^{-14}$ at 25°C (basic solution)

$pH = -\log_{10}[H^{\oplus}]$

$pOH = -\log_{10}[OH^{\ominus}]$

$pK_w = -\log_{10}[K_w] = +14$ (at 25°C)

(v) % age dissociation of an acid:

$$\text{Percentage ionization} = \frac{\text{Amount of acid ionized}}{\text{Amount of acid initially available}} \times 100$$

$H_2O + HX \rightleftharpoons H^+ + X^{\ominus}$

$K_a = \frac{[H^+][X^-]}{[HX]}$ K_a = Dissociation constant of an acid

$B + H_2O \rightleftharpoons BH^{\oplus} + OH^-$

$K_b = \frac{[BH^+][OH^-]}{[B]}$ K_b = Dissociation constant of a base

$K_a . K_b = K_w = 10^{-14}$ (at 25 °C)

$\therefore K_a = \frac{10^{-14}}{K_b}$ and $K_b = \frac{10^{-14}}{K_a}$

$K_a \propto \frac{1}{K_b}$ $K_b \propto \frac{1}{K_a}$

$pK_a = -\log K_a$ $pK_b = -\log K_b$

$pK_a + pK_b = +14$ at 25 °C.

(iv) Henderson equation for buffer solutions:

$pH = pK_a + \log \frac{[salt]}{[acid]}$ (for acidic buffers)

$$pOH = pK_b + \log \frac{[salt]}{[base]} \text{ (for basic buffers)}$$

(v) Relationship for solubility product of a general ionic substance:

$$A_xB_y \rightleftharpoons xA^{+y} + yB^{-x} \quad , \quad K_{sp} = [A^{+y}]^x [B^{-x}]^y$$

METHODS TO SOLVE THE NUMERICAL PROBLEMS

(1) In order to calculate equilibrium constant (K_C), put the concentrations in moles dm^{-3} of products in the numerator and reactants in the denominator along with the units.

(2) To calculate the equilibrium constant K_p, put the values of partial pressures.

(3) To convert one type of equilibrium constant into other, write the balanced chemical equation. Calculate Δn and by knowing the pressure, temperature and total number of moles of reactants and products, calculate the other equilibrium constants.

(4) To convert $H^{\oplus}$ and $OH^{\ominus}$ into pH and pOH, take the negative log of these concentrations. The sum of pH and pOH is always equal to 14 at 25°C.

(5) In order to convert K_a and K_b into pK_a and pK_b, take the negative log of K_a and K_b.

(6) If we are given pK_a and pK_b values for acids and bases, we take the antilogs of $-pK_a$ and $-pK_b$ to get K_a and K_b.

(7) If we know the pK_a value of an acid, we can get the pK_b value of conjugate base from equation

$$pK_a + pK_b = pK_w.$$

(8) Knowing the concentrations of salt and acid and the pK_a of the acid forming an acidic buffer solution, we can calculate the pH of the buffer from Henderson equation:

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

(9) Knowing the concentrations of salt and base, along with the pK_b value of base forming a buffer solution, we can calculate the pOH of the buffer solution from Henderson equation

$$pOH = pK_b + \log \frac{[salt]}{[base]}$$

(10) If we know the concentrations of a sparingly soluble substance, which has become soluble, then we get its concentration in moles/dm^3. Balanced equation is written. The expression of K_{sp} is constructed. The values of ionic concentration are substituted to get K_{sp}.

(11) If we know the solubility product of a sparingly soluble substance, then solubility of a salt can be calculated. For this purpose a balanced equation is written and the word 'S' for solubility is used.

DEFINITIONS

(May be used in short questions with examples)

(1) Acid strength:

It is the capability of an acid to release a proton in the solution or to accept a lone pair from a base. It is a quantitative way of comparing the acids with each other. It is expressed in values of K_a and pK_a. Greater the pK_a, weaker the acid. pK_a of CH_3COOH is 4.76.

(2) Acidic buffer:

A buffer solution which is consisted of a solution of a weak acid and salt of it with a strong base. The pH of such buffers are mostly below seven. The equimolar mixture of a solution of CH_3COOH and CH_3COONa gives buffer solution with pH 4.76 and has maximum buffer capacity.

(3) Arrhenius acid:

That compound which dissociates into $H^{\oplus}$ and negative ion in the solution state is called arrhenius acid.

$$HCl \rightleftharpoons H^{\oplus} + Cl^{\ominus} \qquad CH_3COOH \rightleftharpoons CH_3COO^{\ominus} + H^{\oplus}$$

(4) Arrhenius base:

The compound which dissociates into $OH^{\ominus}$ ion and positive ion in the solution state is called Arrhenius base.

$$NaOH \rightleftharpoons Na^{\oplus} + OH^{\ominus}, \quad Ca(OH)_2 \rightleftharpoons Ca^{2+} + 2OH^{\ominus}$$

(5) Basic buffer:

A buffer solution which is consisted of a solution of a weak base and salt with a strong acid. The pH of such buffers are mostly greater than seven. The equimolar mixture of solution of NH_4OH and NH_4Cl is basic buffer with pOH = 4.76. It has maximum buffer capacity.

(6) Buffer capacity:

It is the number of moles of an acid and a base required by one dm^3 of the buffer solution for changing its pH by one unit.

(7) Buffer solution: **(B. Pur 2014)**

A solution which resists the change of pH when a small quantity of an acid or a base is added to that is called buffer solution. $CH_3COOH + CH_3COONa$ in water gives an acidic buffer solution. $NH_4OH + NH_4Cl$ in water gives a basic buffer solution.

(8) Chemical equilibrium state:

It is an apparent state of rest in which two opposing chemical reactions proceeds in opposite directions at the same rate. N_2 and H_2 combine to give NH_3. It is reversible reaction and attains equilibrium at is certain stage.

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

(9) Common ion effect: **(Faisalabad 2010, Rwp. 2010, Guj. 2010, Rwp. 2014)**

It is the suppression of dissociation of a weak electrolyte by adding a common ion from outside in a solution. Pure crystals of NaCl can be obtained by passing $Cl^{\ominus}$ ion in saturated solution of NaCl.

$$NaCl \rightleftharpoons Na^{\oplus} + Cl^{\ominus}$$
$$HCl \rightleftharpoons H^{\oplus} + Cl^{\ominus}$$

$$Na^{\oplus} + Cl^{\ominus} \rightleftharpoons NaCl$$

HCl is acid, $Cl^{\ominus}$ is its conjugate base. H_2O is a base but $H_3O^{\oplus}$ is its conjugate acid.

(10) Conjugate acid-base pair:

It is the pair of species, which is produced when an acid and a base reaction happens according to Lowry-Bronsted concept.

$$HCl + H_2O \rightleftharpoons H_3O^{\oplus} + Cl^{\ominus}$$

(11) Degree of ionization:

It is the number of moles of dissociated moles as compared to the number of moles of solute in the solution. It may be fractional or may be expressed in % age ionization. The degree of ionization of CH_3COOH is very low but of HCl is very high.

(12) Dissociation constant of an acid:

It is the product of the concentration of dissociated ions of the acid divided by concentration of undissociated acid at a given temperature. It is expressed as K_a. Greater the K_a values stronger the acid.

For $HCl + H_2O \rightleftharpoons H_3O^{\oplus} + Cl^{\ominus}$

$$K_a = \frac{[H_3O^+][Cl^-]}{[HCl]}$$

$$NaOH + H_2O \rightleftharpoons Na^{\oplus} + OH^{\ominus}$$

$$K_b = \frac{[Na^+][OH^-]}{[NaOH]}$$

(13) Dissociation constant of a base:

It is the product of concentrations of dissociated ion of the base divided by the concentration of undissociated base at a given temperature. It is expressed as K_b. Greater the K_b values stronger the base.

(14) Electrolyte:

A substance which allows the electrical current to pass through it in the solution state or molten state along with its decomposition. Solution of NaCl or molten NaCl can allow the electricity to pass through along its decomposition.

(15) Equilibrium concentration: (Sarg. 2014)

Those concentrations of reactants and products which are present at equilibrium stage of the chemical reaction are called equilibrium concentrations. These conc. remain constant at given conditions of reaction.

(16) Equilibrium constant: (Sarg. 2014)

It is the ratio of the product of concentration of products to the product of concentration of reactants at equilibrium stage of the chemical reaction. It is constant quantity for a reaction at particular conditions. It is expressed in terms of K_c, K_p etc.

(17) Equilibrium mixture:

It is the mixture of reactants and products at equilibrium stage of the chemical reaction.

(18) Henderson equation: (Lahore 2014)

It is the mathematical relationship between the pH of the buffer, pK_a and pK_b of an acid or a base along with the log ratio of salt with acid or base, respectively.

$$pH = pK_a + \log\frac{[S]}{[A]}, \quad pOH = pK_b + \log\frac{[S]}{[B]}$$

Here [S], [A] and [B] are molar conc. of salt, acid and base.

(19) Heterogeneous equilibria:

A chemical equilibrium in which substances are present in more than one physical states is called heterogeneous equilibria. In $CaCO_3 \rightleftharpoons CaO_{(s)} + CO_{2(g)}$, two substances are solids and one is gas.

(20) Homogeneous equilibria:

A chemical equilibrium in which all the substances are present in same physical state.

$$N_{2(g)} + 3H_{2(g)} \rightleftharpoons 2NH_{3(g)}$$

(21) Hydrogen ion concentration:

It is the number of gram ions of hydrogen present in one dm^3 of solution. It is 10^{-7} mol dm^{-3} in neutral water. When $[H^+] = 10^{-6}$ mol dm^{-3} the solution is acidic.

(22) $H_3O^{\oplus}$ ion:

That ion which is consisted of H_2O molecule with an extra attached proton and is written as $H_3O^{\oplus}$. This ion is produced when acids are dissolved in water.

$$HBr + H_2O \rightleftharpoons H_3O^{\oplus} + Br^{\ominus}$$

(23) Ionic concentration:

It is the number of ions per unit volume of the solution.

(24) Ionic equilibria:

It is the state of equilibrium which is set up between the ionized and unionized molecules of a substance.

$CH_3COOH \rightleftharpoons CH_3COO^{\ominus} + H^{\oplus}$ has ionic equilibria.

(25) Ionic product of water:

It is the product of the concentration of $H^{\oplus}$ and $OH^{\ominus}$ at a given temperature.

$K_w = [H^{\oplus}]\,[OH^{\ominus}]$ and is 10^{-14} in neutral water at 25°C. It changes with temperature.

(26) Ionization:

It is the process in which compound is split up into charged ions in aqueous solution.

$$H_2SO_4 \rightleftharpoons 2H^{\oplus} + SO_4^{2-}$$

(27) Law of mass action:

(Multan 2007, Rwp. 2010, Multan 2012, Sarg. 2014, Lahore 2014, F. Abad 2014)

The rate at which a substance reacts is directly proportional to its active mass, and the rate of the chemical reaction is proportional to the product of the active masses of reacting substances. Rate of forward step = k [A] [B] for the reaction

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

(28) Le-Chaletier's principle: **(Lahore 2009, Rwp. 2010, M. Pure 2012, D.G. Khan 2014)**

If a system in the equilibrium is disturbed, it behaves in such a way as to minimize the effect of that disturbance. The disturbance of the system is done by changing conc., temperature, pressure and adding a catalyst.

(29) Lewis acid:

That substance whose molecules accept a pair of electrons to form a covalent bond is called Lewis acid.

$$H_2\ddot{\underset{..}{O}} + H^{\oplus} \rightleftharpoons H_3O^{\oplus}$$, Here $H^{\oplus}$ is Lewis acid and H_2O is Lewis base.

(30) Lewis base:

A substance whose molecules donate an electron pair to another species to form a covalent bond is called Lewis base.

In, $\ddot{N}H_3 + H^{\oplus} \rightleftharpoons \overset{\oplus}{N}H_4$, $\ddot{N}H_3$ is Lewis base.

(31) Lowry-Bronsted acid:

That compound which donates a proton to a base or have a tendency to donate a proton.

$$H_2O + HBr \rightleftharpoons H_3O^{\oplus} + Br^{\ominus}$$

HBr is Bronsted acid.

(32) Non-electrolyte:

A substance that does not ionize in the solution, or in the molten state and hence does not conduct the electrical current is called non-electrolyte. Glucose is a non-electrolyte.

(33) pH: (Sargodha 2008, Sargodha 2010, D. G. Khan 2012, M. Pure 2012, Rwp. 2014, Lahore 2014, Sahiwal 2014.)

It is negative log of $H^{\oplus}$ concentration and is written as pH.

When $[H^+] = 10^{-7}$ pH = +7 for neutral solution.

(34) pH value: (Lahore 2014)

It gives us information about the relative tendency of a solution to have the proton in it. When pH = 6 then solution has excess protons as compared to neutral water.

(35) pK_a: (Lahore 2014, Guj. 2014)

It is the negative log of dissociation constant of an acid. Greater the value of the pKa of the acid weaker the acid.

$$pK_a = -\log K_a$$

The pK_a of HCOOH is 3.78 and of CH_3COOH is 4.76.

(36) pK_b: (Lahore 2014, Guj. 2014)

It is the negative log of dissociation constant of a base. Greater the pK_b value of the base, weaker the base.

$$pK_b = -\log K_b$$

The pK_b of NH_4OH is 4.75.

(37) pOH: (Sargodha 2008, Sargodha 2010, D.G. Khan 2012, M. Pure 2012)

It is a negative log of $OH^{\ominus}$ concentration. It is denoted by pOH.

$$pOH = -\log [OH^{\ominus}]$$

pOH of neutral water at 25°C is 7.

(38) Reversible reaction:

(Mirpur-2006, Rwp 2011, Multan 2012, M. Pure 2012, B. Pure 2012, D.G. Khan 2014, Sarg. 2014)

That reaction in which the reactants and products are converted into each other under the same set of conditions.

$$N_2 + 3H_2 \rightleftharpoons 2NH_{3(g)}$$

(39) Solubility product:

(Bahawalpur 2009, Rwp. 2010, D.G. Khan 2011, Rwp. 2011, Guj. 2013, Guj. 2014, B. Pur 2014)

It is the product of the ionic concentrations of a weak electrolyte in a saturated solution.

$$AgCl \rightleftharpoons Ag^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)} \qquad K_{sp} = [Ag^{\oplus}_{(aq)}]\,[Cl^{\ominus}_{(aq)}]$$

(40) Strong electrolyte:

A compound which is completely ionized in aqueous solution and becomes a very good conductor of electricity. HCl, HBr, HI etc. are almost completely ionized in water and are strong electrolytes.

(41) Time of equilibrium:

It is the time which is the required to establish a state of equilibrium for a reversible chemical reaction. It depends upon the nature of reaction and external conditions under which it is occurring.

(42) Weak electrolyte:

A compound which is partially ionized in an aqueous solution is called weak electrolyte and consequently less electrical current is passed through that. CH_3COOH, HCOOH, etc. are weak electrolytes. They dissociate to a small extend in water. HCl is a strong electrolyte.

MULTIPLE CHOICE QUESTIONS (EXERCISE OF THE TEXTBOOK)

MULTIPLE CHOICE QUESTIONS	ANSWER WITH REASONS
(1) For which system does the equilibrium constant K_c has units of $(\text{concentration})^{-1}$? (a) $N_2 + 3H_2 \rightleftharpoons 2NH_3$ (b) $H_2 + I_2 \rightleftharpoons 2HI$ (c) $2NO_2 \rightleftharpoons N_2O_4$ (d) $2HF \rightleftharpoons H_2 + F_2$	1. (c) **(Multan Board 2004, Lahore 2013, Lahore 2014, Lahore 2014)** First of all construct the K_c expressions of all the reactions and then find out the units of equilibrium constant K_c. In the following reaction $2NO_2 \rightleftharpoons N_2O_4$, one mole of product is being formed from two moles of reactants. $K_c = \frac{[N_2O_4]}{[NO_2]^2} = \frac{[\text{conc.}]^1}{[\text{conc.}]^2} = (\text{conc.})^{-1}$
(2) Which statement about the following equilibrium is correct? $2SO_{2(g)} + O_{2(g)} \rightleftharpoons 2SO_{3(g)}$ $\Delta H = -188.3\ \text{kJ mol}^{-1}$ (a) The value of K_p falls with a rise in temperature (b) The value of K_p falls with increasing pressure (c) Adding V_2O_5 catalyst increase the equilibrium yield of sulphur trioxide (d) The value of K_p is equal to K_c	2. (a) The given reaction is exothermic. If the temperature is increased for this reaction, the reaction will go to that side where it can absorb more heat. Hence it will go to the backward direction.
(3) The pH of 10^{-3} mol.dm^{-3} of an aqueous solution of H_2SO_4 is: (a) 3.0 (b) 2.7 (c) 2.0 (d) 1.5	3. (b) **(Lahore 2005, Fd. 2009, D.G. Khan 2011, Lahore 2014, Lahore 2014, D.G. Khan 2014, Sahiwal 2014, Guj. 2014, B. Pur 2014, F. Abad 2014)** H_2SO_4 is a dibasic acid, one molecule of H_2SO_4 gives two protons. So 10^{-3} mol dm^{-3} of H_2SO_4 gives 2×10^{-3} mol dm^{-3} of H^+. $[H^+] = 2 \times 10^{-3}$ $pH = -\log 2 \times 10^{-3} = 2.7$

(71) When HCl is added to H_2S aqueous solution, its ionization
(a) increases
(b) remains constant
(c) decreases
(d) first increases, then decreases

71. (c) (Multan 2008, Lahore 2010, Rwp. 2011, Bahawalpur 2011)
Due to common ion i.e. $H^{\oplus}$, the ionization of H_2S decreases.

Solubility Product

(72) The K_{sp} value for $PbSO_4$ is 1.8×10^{-8}. The maximum concentration of Pb^{2+} ion is:
(a) 1.8×10^{-8} (b) 1×10^{-8}
(c) 1.34×10^{-4} (d) 1.69×10^{-8}.

72. (c) (Faisalabad 2008)
The K_{sp} value of $PbSO_4$, is 1.8×10^{-8}. In order to calculate the maximum concentration of Pb^{+2} ions, we will take the square root of this value.

$$PbSO_4 \rightleftharpoons Pb^{+2} + SO_4^{-2}$$
$$K_{sp} = [Pb^{+2}][SO_4^{-2}]$$
$$\because [Pb^{+2}] = [SO_4^{-2}]$$
$$1.8 \times 10^{-8} = [Pb^{+2}][Pb^{+2}]$$
$$[Pb^{+2}]^2 = 1.8 \times 10^{-8}$$
$$[Pb^{+2}] = \sqrt{18 \times 10^{-8}}$$
$$= 1.34 \times 10^{-4}$$

(73) A solution is said to be saturated with respect to the electrolyte, if its:
(a) Ionic product < K_{sp}
(b) Ionic product > K_{sp}
(c) Ionic product = K_{sp}
(d) $(\text{Ionic product})^2 = K_{sp}$

73. (c)
When the ionic product of the sparingly soluble substance is equal to the K_{sp} of the substance. Then the solution is said to be saturated.

(74) Precipitation occurs when the product of ionic concentration:
(a) exceeds their solubility product
(b) is less than their solubility product
(c) is equal to their solubility product
(d) and solubility product become equal

74. (a)
When the product of ionic concentrations exceeds the solubility product, then the precipitation occurs.

ANSWERS TO THE SHORT QUESTIONS

General Features of Chemical Equilibrium

Q.1 What is meant by stage of chemical equilibrium?
(Guj. 2008, Lahore 2012, D.G. Khan 2012, Lahore 2014)

-1 کسی ری ایکشن کے کیمیائی توازن کی سٹیج سے کیا مراد ہے؟

Ans: In reversible chemical reactions, two opposing (ایک دوسرے کے الٹ) reactions occur. A stage reaches for the reaction when the rates (رفتاریں) of two opposing reactions are equal. This stage is called stage of chemical equilibrium (کیمیائی توازن).

Q.2 Justify that chemical equilibrium is dynamic in nature.
(Rwp. 2008, Fd. 2009)

-2 درست ثابت کریں کہ کیمیائی توازن حرکت میں رہنے والی عادت کا ہوتا ہے؟

Ans: In reversible chemical reactions, the molecules of reactants collide (تصادم کرتے ہیں) and convert into products. At the same time the molecules of the products are converting into reactants. When two opposing forces (مقابلہ کرنے والی طاقتیں) maintain the equal rates then equilibrium is there and that is dynamic equilibrium (حرکی توازن) in nature.

Law of Mass Action

Q.3 The rates of chemical reactions depend upon the concentrations of reactants. Why?

-3 کسی کیمیائی تعامل کی رفتار آپس میں تعامل کرنے والے کیمیائی چیزوں کے ارتکاز پر انحصار کرتی ہے۔ کیوں؟

Ans: This is according to the law of mass action. The rates of chemical reactions are directly proportional (سیدھا متناسب) to the product (حاصل ضرب) of the active masses of reactants. Greater the number of molecules, greater the collisions and greater the rate.

Q.4 Why is the equilibrium established, only when the reaction vessel is closed for a gaseous reaction?

-4 گیس فیز میں ہونے والے تعامل میں صرف اس وقت توازن قائم ہو گا۔ جب وہ بند برتن میں ہو گا ایسا کیوں ہے؟

Ans: If some of the products or the reactants in the open vessel leave the vessel (برتن کو چھوڑ جاتے ہیں) during the progress (ترقی) of the reaction then the stage of equal rates is disturbed (دخل اندازی کرنا) and equilibrium cannot be established (توازن قائم نہیں ہوتا). In such situation the reaction is pushed to the forward direction or backward direction.

Q.5 Why the equilibrium constant value has its units for some of the reversible reactions, but has no units for some other reactions?
(Model Paper-2006-07, R. Pindi 2012, Faisalabad 2013)

-5 پلٹا کھانے والے کچھ تعاملات میں توازن کا مستقلہ اکائیاں رکھتا ہے اور کچھ میں نہیں رکھتا۔ کیوں؟

Ans: If the number of moles of reactants and products are equal in a reversible balanced (الٹ ہونے والی متوازن کیمیائی مساوات) equation, then the units are cancelled and the value of K_c has no units.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = \frac{[HI]^2}{[H_2][I_2]}$$

If the number of moles of reactants and products are unequal (برابر نہ ہو) then K_c has net units.

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \qquad K_c = [conc]^{+1}$$

$$N_2 + 3H_2 \rightleftharpoons 2NH_3 \qquad K_c = [conc]^{-2}$$

Q.6 When four types of chemical equilibrium constants for a reaction become equal? How K_p and K_c are related? (Guj. 2012, Faisalabad 2013, Lahore 2014)

-6 کن حالات میں توازن کے چاروں مستقلے برابر ہو جاتے ہیں۔ بتائیں کہ K_p اور K_c کا آپس میں کیسا رشتہ ہے؟

Ans: When we have such a reversible reaction, in which the total number of moles of reactants and products are equal, then $K_p = K_c = K_x = K_n$. In other words, $\Delta n = 0$ where Δn is the difference of number of moles of reactants and products.
In the following equation K_p and K_c are related by

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

Controlling Factors For Equilibrium Position

Q.7 What happens to the directions of a reversible reaction, when the ratio of the concentrations is less than actual K_c? (Guj. 2013, Guj. 2014)

-7 کسی پلٹا کھانے والے تعامل میں جب ارتکاز کی نسبت K_c سے کم ہو تو تعامل کی سمت کیا ہوتی ہے؟

Ans: When the ratio of the concentrations (ارتکاز) for a reversible reaction is less than K_c, then it means that the reaction is not at equilibrium stage. It has to go to the forward direction to attain the actual value of K_c (اصل قیمت).

Q.8 Why is the factor of volume cancelled out in the final expression of K_c, when the number of moles of reactants and products are equal?

-8 جب ری ایکشن کرنے والے اور بننے والے کیمیائی اشیاء کے مولز کیمیائی مساوات میں برابر ہوں تو K_c فارمولا بنانے کے بعد volume کا فیکٹر ختم ہو جاتا ہے۔ کیوں؟

Ans: If the number of moles of reactants and products are equal, then the factors of volume cancel each other and the factor of volume vanishes (ختم ہونا). For such reactions, the factor of volume does not control the K_c value and also the equilibrium stage (توازن کی حالت) of the reaction.

$$H_2 + I_2 \rightleftharpoons 2HI \qquad K_c = \frac{4x^2}{(a-x)(b-x)}$$

Q.9 Why the factor of volume in K_c expression goes to the denominator, when the number of moles of products are greater than the reactants for a reversible reaction? (Bahawalpur 2008, Multan 2009, Faisalabad 2011, Multan 2011)

-9 جب ری ایکشن کرنے والوں کے مولز کم اور بننے والوں کے زیادہ ہوں تو جسامت کا فیکٹر نسب نما میں کیوں آتا ہے؟

Ans: Those reversible gaseous reactions whose number of moles of products are greater than the reactants have greater value of volume for products. So, the factor of volume goes to the denominator (نسب نما).

One mole of PCl_5 dissociates to give two moles of products

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2$$

$$K_c = \frac{\frac{x}{V}\cdot\frac{x}{V}}{\left(\frac{a-x}{V}\right)} = \frac{x^2}{V(a-x)}$$

Q.10 Those gaseous reactions which happen with the increase of volume go to the backward direction, when the volume is decreased. Why? (Bahawalpur 2008)

-10 وہ گیس فیز میں ہونے والے ری ایکشنز جن کے ہونے کے دوران جسامت بڑھتی ہے وہ جسامت کم کرنے سے کس طرف جاتے ہیں؟

Ans: When such reactions proceed (آگے بڑھنا) and attain the equilibrium position (توازن کی حالت), then the volume of the gaseous mixture of reactants and products increases. Decrease of volume at equilibrium stage (توازن پر پہنچے ہوئے تعامل کی جسامت کم کرنے سے), makes the reaction to go to that side where the volume is less, and that is the side of the reactants.

Q.11 How does the equilibrium constant of a chemical reaction tells us the direction of a chemical reaction?

(Model Paper, Guj. 2011, R. Pindi 2012, Guj. 2013, D.G. Khan 2013)

-11 کسی تعامل کی K_c کی قیمت کس طرح سے ہمیں اس کی سمت کا پتہ دیتی ہے؟

Ans: When the concentrations of a reversible reaction are measured at any stage of its progress (آگے بڑھنے کے دوران کسی سٹیج پر) and equilibrium constant is calculated, then it is called calculated Q. If actual K_c is also known, then there are following three possibilities (امکانات)

(i) $Q < K_c$. The reaction goes to the forward direction.
(ii) $Q > K_c$. The reaction goes to the backward direction.
(iii) $Q = K_c$. The reaction will not go to any side.

Q.12 The change of volume disturbs the equilibrium position for some of the gaseous phase reactions but not the equilibrium constant. Why?

(Faisalabad 2007, D.G. Khan 2011)

-12 جسامت کی تبدیلی کسی پلٹا کھانے والے تعامل کی توازن کی سٹیج کو بدل دیتی ہے۔ لیکن توازن کا مستقلہ نہیں بدلتا کیوں؟

Ans: Those gaseous phase reversible reactions (گیس فیز میں پلٹا کھانے والے تعاملات), which happen with changing number of moles are affected (متاثر ہونا) by the change of volume at equilibrium stage. Their equilibrium position is disturbed (دخل اندازی ہوتی ہے), but equilibrium constant is not changed.

Q.13 Solid ice at 0°C can be melted by applying pressure without supply of heat from outside. Why? **(Multan Board 2004, Rawalpindi 2007)**

-13 0°C پر ٹھوس برف صرف دباؤ ڈالنے سے پگھل جاتی ہے اور باہر سے حرارت نہیں دینی پڑتی۔ کیا وجہ ہے؟

Ans: When pressure is applied to the broken pieces of ice (برف کے کوٹے ہوئے ٹکڑے) at 0°C, then according to Le-Chatelier's principle, the ice moves to that direction where its volume should decrease *i.e.*, towards liquid water. Actually ice occupies (جگہ گھیرتی ہے) more volume than liquid water.

Q.14 Why are the exothermic reactions favoured to the forward direction by cooling, but reverse is true for endothermic reactions?

(Rwp-2007, Sargodha 2008, Lahore 2010)

-14 حرارت کو باہر نکال کر ہونے والے تعاملات ٹھنڈ پیدا کرنے سے کیوں آگے کی سمت جاتے ہیں جب کہ حرارت کو جذب کرنے والے اس کا اُلٹ کرتے ہیں؟

Ans: The amount of heat which is being evolved by the exothermic reaction is taken up by that body which has a cooling effect (ٹھنڈ پیدا کرنا). So, the reactions move to that direction where there is less energy (ری ایکشن کم انرجی والی چیزوں کی طرف جاتا ہے). The endothermic reactions (حرارت جذب کرنے والے) require extra energy to take place. If the system is cooled, it will go to that direction, where there is a less energy and that is the backward direction of reaction.

Q.15 The change of temperature disturbs the equilibrium position and the equilibrium constant of reaction. Justify.

(Sarg. 2010, Lahore 2011, Lahore 2012, Rwp. 2014)

-15 درجہ حرارت کی تبدیلی سے توازن کی پوزیشن اور توازن کا مستقلہ دونوں تبدیل ہو جاتے ہیں۔ درست ثابت کریں۔

Ans: All the reversible reactions are distributed by changing their equilibrium position and equilibrium constant by disturbing the temperature (درجہ حرارت بدلنے سے تعاملات کا K_c اور توازن والی جگہ دونوں بدل جاتے ہیں). Actually, change of temperature changes the energy contents of reactants and products.

Q.16 What will be effect of change in pressure on NH_3 and SO_3 synthesis.

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

(Lahore 2005, Lahore 2007, F. Abad 2008, Faisalabad 2011, Lahore 2012, Guj. 2013. Guj. 2014)

-16 NH_3 کی تالیف کے دوران پریشر کی تبدیلی کیا اثر دکھائے گی؟

Ans: This is a gaseous reaction (گیس کی حالت میں ہونے والا) having less number of moles of products. So this reaction happens with the decrease of volume (جسامت کی کمی سے رونما ہوتا ہے). The increase of pressure will shift the equilibrium position (توازن کی حالت) of reaction to the forward direction and greater amount of NH_3 will be produced. Equilibrium constant does not change. In $2SO_2 + O_2 \rightleftharpoons 2SO_3$, the same principle of pressure is applicable.

Q.17 What is the effect of rise in temperature on the solubility of KI in water?

-17 KI کو پانی میں حل کرنا ہو تو درجہ حرارت کے بڑھانے سے اس کی حل پذیری پر کیا اثر ہو گا؟

Ans: The heat of solution of KI in water is positive (ΔH_{solu} مثبت ہے). It means it is an endothermic process. When the temperature is increased, it will absorb more heat and more dissolution (زیادہ حل پذیری دکھائے گا) will take place.

Q.18 Why the solubility of glucose in water is increased by increasing the temperature? **(Gujranwala 2009, Faisalabad 2011, D.G. Khan 2012, Lahore 2012, Sahiwal 2014)**

-18 درجہ حرارت بڑھانے سے پانی میں گلوکوز کی حل پذیری کیوں بڑھتی ہے؟

Ans: The solubility of glucose in water is a endothermic process. Increase of temperature pushes the system (سسٹم کو آگے کی طرف دھکہ ملتا ہے) to that side where heat is absorbed, and that is the side where solubility increases (حل پذیری بڑھتی ہے).

Q.19 The NH_3 synthesis by Haber's process is an exothermic reaction. It should be favoured at low temperature, but the optimum temperature is 400°C. Why? **(Guj. 2013, F. Abad 2014)**

-19 ہابر کے طریقے سے NH_3 بنائی جاتی ہے اور یہ حرارت خارج کرنے والا ری ایکشن ہے۔ یہ کم درجہ حرارت پر آگے جانا چاہیے لیکن اس کا مناسب ترین درجہ حرارت 400°C رہے۔ کیوں؟

Ans: If low temperature is maintained (بندوبست کرنا) for NH_3 synthesis, then the number of collision per unit time decrease and the rate of reaction become slow. In order to increase the rate of reaction, temperature has to be increased.

Q.20 How does a catalyst affect a reversible reaction? **(Bahawalpur 2007)**
(Azad Jammu & Kashmir 2005, D.G. Khan-2006, B.P.-2006, Multan 2008, B.P. 2008, F. Abad 2008, Faisalabad 2010, F. Abad 2012, D.G. Khan 2012, Lahore 2012)

-20 پلٹا کھانے والے ری ایکشنز پر عمل انگیز کا کیا اثر ہوتا ہے؟

Ans: A catalyst affects (عمل انگیز متاثر کرتا ہے) the rates of both steps equally, so the equilibrium position remains the same. It means that equilibrium constant should also be the same. Actually, a catalyst decreases the energy of activation (ایک عمل انگیز E_a کو کم کرتا ہے) of the chemical reaction by giving a new path (تعامل کو ایک نیا راستہ دیتا ہے) to the reaction. In this way, a greater % age of reactant molecules is able to cross the energy barrier and the rate of reaction increases.

Ionic Equilibria

Q.21 Why the ionic product of water (K_w) increases with the increase of temperature? **(Rawalpindi 2009, D.G. Khan 2013, Lahore 2014, Multan 2014)**

-21 درجہ حرارت بڑھانے سے پانی کی K_w کیوں بڑھتی ہے؟

Ans: The value of K_w is 0.11×10^{-14} at 0°C and is 10^{-14} at 25°C. The value increases approximately (تقریباً) 10 times, when the temperature changes from 0°C to 25°C. The reason is that the increase of temperature increases the kinetic energy (حرکی توانائی) of the water and possibility of bond breakage increases.

Q.22 What is the concentration of hydroxide ion in a solution whose pH is 10. **(Lahore Board 2004, Guj. 2013, Multan 2013)**

-22 جس سولیوشن کی pH = 10 ہے اس میں $OH^{\ominus}$ کی ارتکاز کتنی ہے؟

Ans:

$$pH = -\log[H^{\oplus}]$$
$$-\log[H^{\oplus}] = +pH$$
$$\log[H^{\oplus}] = -pH = -10$$
$$[H^{\oplus}] = 10^{-10}$$

Since $[H^{\oplus}][OH] = 10^{-10}$ So $[OH^{\ominus}] = 10^{-4}$

Q.23 Why the sum of pH and pOH of any aqueous solution is always equal to 14 i.e., pK_w at 25°C? **(Model Paper, Guj. 2008, Guj. 2013, Sarg. 2014, , Sarg. 2014B. Pur 2014)**

-23 پانی میں تیار شدہ کسی بھی سولیوشن کی pH اور pOH کا مجموعہ 25°C پر 14 ہوتا ہے۔ کیوں؟

Ans: The $[H^{\oplus}] = [OH^{\ominus}] = 10^{-7}$ moles dm^{-3} for pure H_2O at 25°C. When certain quantity of an acid or a base is added to that, then the $[H^{\oplus}]$ and $[OH^{\ominus}]$ don't remain equal, but their product is always 10^{-14} at 25°C.

So $pH + pOH = 14 = pK_w$

When temperature of the aqueous solution is above 25°C then

$$pH + pOH < 14$$
$$pH + pOH = pK_w$$

Q.24 What is the nature of solution having pH = 7.5? **(Guj. 2012)**

-24 جس سولیوشن کی pH = 7.5 ہو اس کی کیا نیچر ہے یعنی ایسڈک یا بیسک؟

Ans: The solution with pH = 7 is neutral (تعدیل شدہ) and having values more than 7 have greater concentration of $OH^{\ominus}$ and less concentration of $H^{\oplus}$. So, the solution is basic.

Q.25 Why HCl acts as a weak acid in ethanoic acid as compared to, when dissolved in water? **(Model Paper-2006-07, B. Pure 2013)**

-25 جب HCl کو پانی کی بجائے CH_3COOH میں حل کیا جائے تو یہ ایک کمزور تیزاب ہونے کا کیوں مظاہرہ کرتا ہے؟

Ans: When HCl is dissolved in water, it dissociates (ٹوٹتا ہے) to a great extent, releases (چھوڑتا ہے) sufficient $H^{\oplus}$ ions and acts as a strong acid. HCl dissolved in ethanoic acid dissociates to a less extent (کم حد تک). Ethanoic is itself acid and decreases the dissociation of HCl by common ion effect.

Q.26 Define the effect of common ion on solubility? Give examples.
(Gujranwala Board 2005, Lahore 2009, Sargodha 2009, F. Abad 2012)

-26 حل پذیری پر کامن آئن کا تصور کیا اثر کرتا ہے؟ مثال دیں۔

Ans: According to Le-Chatlier's principle, if a common ion is added in a solution then the solubility of the electrolyte decreases and the solute is compelled to settle down (نیچے بیٹھنے پر مجبور ہو جاتا ہے). If $Cl^{\ominus}$ are added in saturated solution of NaCl, then NaCl settles down, because its solubility decreases.

Q.27 By diluting the solution of CH_3COOH, the % age ionization changes, but the dissociation constant of the acid remains the same at a constant temperature. How?

-27 مستقل درجہ حرارت پر CH_3COOH کے سولیوشن کے ارتکاز کو کم کرنے سے ٹوٹنے کی % بدل جاتی ہے لیکن Ka وہی رہتا ہے۔ کیسے؟

Ans: CH_3COOH is a very weak acid. Its dissociating power (ٹوٹنے کی طاقت) is small. When it is 0.1 M, it is 1.3 % dissociated, and 0.01 M is 4.17 % dissociated. It means the diluting the solution ten times, the % age dissociation increases three times. But the K_a value of the CH_3COOH does not change by changing the molarity (مولیریٹی بدلنے سے K_a نہیں بدلتا). The reason is that when the concentration of CH_3COOH in water is greater, then the ratio of dissociated to undissociated molecules remains the same.

Q.28 Why the strong acids have weak conjugate bases and weak acids have strong conjugate bases? (Mirpure Board 2004, Multan 2008)

-28 طاقتور تیزاب جب پانی میں حل ہوتے ہیں تو ان کے conjugate base کمزور ہوتے ہیں جبکہ کمزور تیزابوں کے conjugate base طاقتور ہوتے ہیں۔ کیوں؟

Ans: According to protonic concept, acids are those species which are proton donors or have a tendency (رجحان) to donate a proton.

$$\underset{\text{weak acid}}{CH_3COOH} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{conjugate base}}{CH_3COO^{\ominus}} + \underset{\text{conjugate acid}}{H_3O^{\oplus}}$$

$$\underset{\text{strong acid}}{HCl} + \underset{\text{base}}{H_2O} \rightleftharpoons \underset{\text{conjugate base}}{Cl^{\ominus}} + \underset{\text{conjugate acid}}{H_3O^{\oplus}}$$

CH_3COOH has a little tendency (تھوڑا رجحان) to break the oxygen hydrogen bond and to act as an acid. It means that $CH_3COO^{\ominus}$ ion should have a strong tendency to react with a proton. So $CH_3COO^{\ominus}$ should be a strong base. HCl is a very strong acid and so $Cl^{\ominus}$ ion should have a least tendency to accept proton to act as a base.

Common Ion Effect

Q.29 How NaCl can be purified by common in effect?
(Multan Board 2005, Gujranwala-2006, Rwp. 2008, Bahawalpur 2009, Faisalabad 2010, Sarg. 2011, Guj. 2012, Multan 2012, M. Pure 2012, Multan 2013, Faisalabad 2013, Lahore 2014, Lahore 2014)

-29 NaCl کو کامن آئن کے اثر کے تحت کیسے صاف کیا جا سکتا ہے؟

Ans: The impure sample of NaCl is dissolved in H_2O to prepare the saturated solution.

$$NaCl_{(s)} \rightleftharpoons Na^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$$

If HCl gas is passed in saturated solution of NaCl, the $Cl^{\ominus}$ ions are generated in excess in the solution

$$HCl_{(aq)} \rightleftharpoons H^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$$

Due to excess or $Cl^{\ominus}$, the ionization of NaCl is suppressed (دب جانا) and NaCl settles down (نیچے بیٹھنا) in the form of precipitate.

$$Na^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)} \rightleftharpoons NaCl_{(s)} \quad \left(\text{ionization is suppressed}\right)$$

Moreover the use of HCl in II-group basic radicals is for common ion effect.

Q.29A How common ion effect operates in salt analysis? (Multan 2014)

Ans: In group II, HCl suppresses the ionization of H_2S, in group III NH_4Cl suppresses the ionization of NH_4OH to give ppts of Fe^{+3}, Cr^{+3} and Al^{+3}.

Buffer Solution

Q.30 What is a buffer solution?

(B.P. 2008, Lahore 2008, Sarg. 2011, Bahawalpur 2011, Lahore 2012, B. Pure 2012, Faisalabad 2013, D.G. Khan 2013, Sarg. 2014)

بفر سولیوشن کیا ہوتا ہے؟ -30

Ans: A solution which resists (رکاوٹ کا باعث ہونا) the change of pH, when a small amount of an acid or a base is added in that. Buffers are prepared by mixing two components:

(i) Weak acid + salt with a strong base.
(ii) Weak base + salt with a strong acid.

Q.31 What is Henderson equation?

(Sargodha 2005, Rwp-2005, Rwp-2007, F. Abad 2008, Multan 2009, Sarg. 2011, Bahawalpur 2011, Lahore 2012)

ہنڈرسن کی مساوات کیا ہے؟ -31

Ans: It is the equation which is used for a preparation of a buffer solution of required pH. We have to adjust the ratio of the concentration of salt to acid or base. The acid of suitable pK_a value has to be taken

$$pH = pK_a + \log\frac{[salt]}{[acid]} \quad \text{and} \quad POH = pK_b + \log\frac{[Salt]}{[Base]}$$

Q.32 What is buffer capacity?

(Fd. 2004, Mtn 2008, Fd. 2009, B. Pur 2009, Rwp. 2009, Lahore 2010, F. Abad 2012, Lahore 2013)

بفر کی صلاحیت سے کیا مراد ہے؟ -32

Ans: Buffer capacity (بفر کی صلاحیت) is a ability (قابلیت) of a buffer to resist the change of pH, when a few drops of an acid and base is added from outside. The best buffer is obtained (i) when pH of the buffer is equal to pK_a of the acid and the concentrations of the salt and acid are equal (ii) The pOH of the buffer is equal to pK_b of the base and concentration of both components are equal.

Q.33 By adjusting the ratio of salt and acid, we can adjust the pH of required buffer solution. How? (B.P. 2008, Guj. 2011, D.G. Khan 2014)

سالٹ اور ایسڈ کی باہمی مقداریں سیٹ کر کے ہم اپنی مرضی کا بفر بنا سکتے ہیں۔ کیسے؟ -33

Ans: If we want to prepare an acidic buffer solution, the following equation is used

$$pH = pK_a + \log\frac{[salt]}{[acid]}$$

The pK_a of the acid, which is being used for the preparation of this buffer solution is a constant quantity (مستقل مقدار) at a given temperature. By adjusting the ratio of salt and acid concentration, we can prepare a solution having pH of own choice (اپنی مرضی کا).

Q.34 When the concentration of the salt is increased in an acidic buffer, then the pH of the solution increases. Why?

(Sargodha 2008, Sarg. 2011, Multan 2012, D.G. Khan 2014)

-34 جب کسی تیزابی بفر میں سالٹ کی مقدار بڑھائی جائے تو سولیوشن کی pH کم ہو جائے گی۔ کیوں؟

Ans: Henderson's equation is

$$pH = pK_a + \log \frac{[salt]}{[acid]}$$

According to this equation, when the [salt] is greater than [acid], then the log term becomes bigger and the pH becomes higher. In other words, the solution obtained is of lower acid strength and of higher pH.

Q.35 Why do we need buffer solution?

(Bahawalpur Board 2005, Faisalabad 2007, Multan 2007, Lahore 2007, Lahore 2011, Guj. 2012, D.G. Khan 2012, Guj. 2013, Rwp. 2013, Faisalabad 2013, Guj. 2014, D.G. Khan 2014)

-35 ہمیں بفر سولیوشن کی کیا ضرورت ہوتی ہے؟

Ans: Buffer solutions are used in many industrial processes (صنعتی عمل) as electroplating (ایک میٹل کا دوسری میٹل پر برقی رو سے چڑھایا جانا), manufacture of leather (چمڑے کی تیاری), preparation of dyes (کپڑوں کو رنگ دینے والے مرکبات کی تیاری) and manufacture of photographic materials (فوٹوگرافی کا سامان). Buffer solutions are used by analytical chemists (تجزیاتی کیمیادان) and to calliberate pH meter. They are also used in culture media.

Q.36 Why HCl is added before passing H_2S gas in second group basic radical analysis? **(B.P. 2008)**

-36 سالٹ کی تجزیہ کے دوران دوسرے گروپ کے بیسک ریڈیکلز کے لیے H_2S گیس گزارنے سے پہلے HCl کیوں ڈالتے ہیں؟

Ans: HCl is a strong acid gives sufficient $H^{\oplus}$ ions in solution, suppresses (دبانا) the ionization of H_2S and gives less S^{-2} ions is solution. These less ions are sufficient (کافی ہیں) to give the ppt. of second group.

Q.37 How does a buffer act? Give example of acidic buffer.

(Faisalabad 2010, Lahore 2012, Rwp. 2013, Multan 2013, B. Pure 2013, D.G. Khan 2013, Sarg. 2014)

-37 ایک بفر کام کیسے کرتا ہے؟

Ans: Let us consider the buffer solution consisted of CH_3COOH and CH_3COONa. They are dissociated in water. Sodium acetate being a very strong electrolyte as compared to acetic acid furnishes sufficient $CH_3COO^{\ominus}$ (ایسیٹیٹ آئنز کافی مہیا کرتا ہے) ion as compared to CH_3COOH

$$CH_3COOH \rightleftharpoons CH_3COO^{\ominus}_{(aq)} + H^{\oplus}_{(aq)}$$

$$CH_3COONa \rightleftharpoons CH_3COO^{\ominus}_{(aq)} + Na^{\oplus}_{(aq)}$$

When a few drops of an acid, say HCl are added in this solution, the $H^{\oplus}$ ions provided by HCl are taken up by $CH_3COO^{\ominus}$ (mostly obtained from CH_3COONa), so incoming protons are consumed (خرچ کرتے ہیں) and pH is retained (برقرار رہنا).

When a few drops of a base say NaOH is added from outside, then the protons already present (پہلے سے موجود) in the solution are consumed. To compensate (تلافی کرنا) those protons, there happens a further dissociation of CH_3COOH (ایسٹک ایسڈ مزید ٹوٹ جاتا ہے) and pH is retained.

Q.38 Prove that $pK_a + pK_b = 14$. **(Gujranwala 2010)**

-38 ثابت کریں کہ $pK_a + pK_b = 14$

Ans: Since $K_a \times K_b = K_w$

Take the log of equation

$$\log K_a \times K_b = \log K_w$$

$$\log K_a + \log K_b = \log K_w$$

Multiply it with negative sign

$$-\log K_a - \log K_b = -\log K_w$$

$$pK_a + pK_b = pK_w$$

Since, $PK_w = 14$, of 25^oC so the pK_a and pK_b of the conjugate acid base pair has a very simple relationship with each other.

$$pK_a + pK_b = 14 \text{ at } 25°C$$

Q.39 Calculate the pH of 10^{-4} moles dm^{-3} solution of HCl. **(Guj. 2010)**

-39 HCl کے 10^{-4} مولرنی لیٹر سولیوشن کی pH نکالیں۔

Ans: $HCl \rightleftharpoons H^{\oplus} + Cl^{\ominus}$

10^{-4} mole dm^{-3} $\rightleftharpoons$ 0 + 0 $t = 0$

0 $\rightleftharpoons$ 10^{-4} $moldm^{-3}$ $t = Eq$

So, $[H^+] = 10^{-4}$

$-\log [H^+] = pH = 4$

Q.40 A mixture of NH_4OH and NH_4Cl give basic buffer. Justify.

(Rwp. 2010, Rwp. 2011, B. Pure 2013, D.G. Khan 2013, F. Abad 2014)

-40 NH_4OH اور NH_4Cl کی مکسچر ایک بیسک بفر دیتا ہے اس کو درست ثابت کریں۔

Ans: The mixture of NH_4OH and NH_4Cl gives a buffer solution. The equations are;

$$NH_4OH \rightleftharpoons NH_4^{\oplus} + OH^{\ominus}$$

$$NH_4Cl \rightleftharpoons NH_4^{\oplus} + Cl^{\ominus}$$

Since $OH^{\ominus}$ ions are produced in the solution, pH will be more than 7, and solution will be basic.

Q.41 Give applciation of solubility product. **(Guj. 2014)**

Ans: (i) If $[M^+][X^-]$ is less than K_{sp}, then solution is unsaturated.

(ii) If $[M^+][X^-] = K_{sp}$, solution is saturated.

(iii) If $[M^+][X^-] > K_{sp}$, solution is momentarily supersaturated.