UNIT 8

IONIC EQUILIBRIUM

Peter Joseph William Debye

Peter Joseph William Debye was Dutch-American physicist greatly contributed to the theory of electrolyte solutions. He also studied the dipole moments of molecules, Debye won the Nobel Prize in Chemistry (1936) for his contributions to the determination of molecular structure through his investigations on dipole moments and X-rays diffraction.

B8E6G1

Learning Objectives

After studying this unit, the students will be able to

- classify the substances into acids and bases based on Arrhenius, Lowry – Bronsted and Lewis concepts.
- define pH scale and establish relationship between pH and pOH
- describe the equilibrium involved in the ionisation of water.
- explain Ostwald's dilution Law and derive a relationship between the dissociation constant and degree of dissociation of a weak electrolyte.
- recognise the concept of common ion effect and explain buffer action.
- apply Henderson equation for the preparation of buffer solution
- calculate solubility product and understand the relation between solubility and solubility product.
- solve numerical problems involving ionic equilibria.

INTRODUCTION

We have already learnt the chemical equilibrium in XI standard. In this unit, we discuss the ionic equilibria, specifically acid – base equilibria. Some of the important processes in our body involve aqueous equilibria. For example, the carbonic acid – bicarbonate buffer in the blood.

$$H_3O^+(aq)+HCO_3^-(aq) \rightleftharpoons H_2CO_3(aq)+H_2O(l)$$

We have come across many chemical compounds in our daily life among them acids and bases are the most common. For example, milk contains lactic acid, vinegar acetic acid, tea tannic acid and antacid tablet aluminium hydroxide / magnesium hydroxide. Acids and bases have many important industrial applications. For example, sulphuric acid is used in fertilizer industry and sodium hydroxide in soap industry etc… Hence, it is important to understand the properties of acids and bases.

In this unit we shall learn the definitions of acids and bases and study, their ionisation in aqueous solution. We learn the pH scale and also apply the principles of chemical equilibrium to determine the concentration of the species furnished in aqueous solution by acids and bases.

8.1 Acids and bases

The term 'acid' is derived from the latin word '*acidus*' meaning sour. We have already learnt in earlier classes that acid tastes sour, turns the blue litmus to red and reacts with metals such as zinc and produces hydrogen gas. Similarly base tastes bitter and turns the red litmus to blue.

These classical concepts are not adequate to explain the complete behaviour of acids and bases. So, the scientists developed the acid – base concept based on their behaviour.

Let us, learn the concept developed by scientists Arrhenius, Bronsted and Lowry and Lewis to describe the properties of acids and bases.

8.1.1 Arrhenius Concept

One of the earliest theories about acids and bases was proposed by swedish chemist Svante Arrhenius. According to him, an acid is a substance that dissociates to give hydrogen ions in water. For example, HCl, H_2SO_4 etc., are acids. Their dissociation in aqueous solution is expressed as

$$HCl(g) \xrightleftharpoons{H_2O} H^+(aq)+Cl^-(aq)$$

The H^+ ion in aqueous solution is highly hydrated and usually represented as H_3O^+, the simplest hydrate of proton $[H(H_2O)]^+$. We use both $H^+$and H_3O^+ to mean the same.

Similarly a base is a substance that dissociates to give hydroxyl ions in water. For example, substances like NaOH, $Ca(OH)_2$ etc., are bases.

$$Ca(OH)_2 \xrightleftharpoons{H_2O} Ca^{2+}(aq)+2OH^-(aq)$$

Limitations of Arrhenius concept

i. Arrhenius theory does not explain the behaviour of acids and bases in non aqueous solvents such as acetone, Tetrahydrofuran etc...

ii. This theory does not account for the basicity of the substances like ammonia (NH_3) which do not possess hydroxyl group.

Evaluate yourself – 1

Classify the following as acid (or) base using Arrhenius concept

i) HNO_3 ii) $Ba(OH)_2$ iii) H_3PO_4 iv) CH_3COOH

8.1.2 Lowry – Bronsted Theory (Proton Theory)

In 1923, Lowry and Bronsted suggested a more general definition of acids and bases. According to their concept, an acid is defined as a substance that has a tendency to donate a proton to another substance and base is a substance that has a tendency to accept a proton from other substance. In other words, an acid is a proton donor and a base is a proton acceptor.

When hydrogen chloride is dissolved in water, it donates a proton to the later. Thus, HCl behaves as an acid and H_2O is base. The proton transfer from the acid to base can be represented as

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

When ammonia is dissolved in water, it accepts a proton from water. In this case, ammonia (NH_3) acts as a base and H_2O is acid. The reaction is represented as

$$H_2O + NH_3 \rightleftharpoons NH_4^+ + OH^-$$

Let us consider the reverse reaction in the following equilibrium

$$\underset{\text{Proton donar (acid)}}{HCl} + \underset{\text{Proton acceptor (Base)}}{H_2O} \rightleftharpoons \underset{\text{Proton donar (acid)}}{H_3O^+} + \underset{\text{Proton acceptor (Base)}}{Cl^-}$$

H_3O^+ donates a proton to Cl^- to form HCl i.e., the products also behave as acid and base.

In general, Lowry – Bronsted (acid – base) reaction is represented as

$$Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1$$

The species that remains after the donation of a proton is a base ($Base_1$) and is called the conjugate base of the Bronsted acid ($Acid_1$). In other words, chemical species that differ only by a proton are called conjugate acid – base pairs.

Conjugate acid - base pair

$$\underset{\text{Proton donar (acid)}}{HCl} + \underset{\text{Proton acceptor (Base)}}{H_2O} \rightleftharpoons \underset{\text{Proton donar (acid)}}{H_3O^+} + \underset{\text{Proton acceptor (Base)}}{Cl^-}$$

Conjugate acid - base pair

HCl and Cl^-, H_2O and H_3O^+ are two conjugate acid – base pairs. i.e., Cl^- is the conjugate base of the acid HCl. (or) HCl is conjugate acid of Cl^-. Similarly H_3O^+ is the conjugate acid of H_2O.

Limitations of Lowry – Bronsted theory

i. Substances like BF_3, $AlCl_3$ etc., that do not donate protons are known to behave as acids.

Evaluate yourself – 2

Write a balanced equation for the dissociation of the following in water and identify the conjugate acid –base pairs.

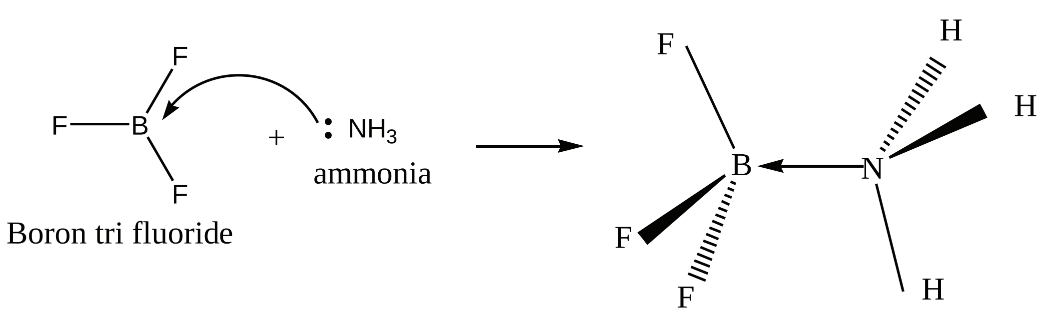
i) NH_4^+ ii) H_2SO_4 iii) CH_3COOH.

8.1.3 Lewis concept

In 1923, Gilbert . N. Lewis proposed a more generalised concept of acids and bases. He considered the electron pair to define a species as an acid (or) a base. According to him, an acid is a species that accepts an electron pair while base is a species that donates an electron pair. We call such species as Lewis acids and bases.

A Lewis acid is a positive ion (or) an electron deficient molecule and a Lewis base is a anion (or) neutral molecule with at least one lone pair of electrons.

Les us consider the reaction between Boron tri fluoride and ammonia



electron deficient - electron pair donar - adduct

(Lewis acid) - (Lewis base)

Here, boron has a vacant 2p orbital to accept the lone pair of electrons donated by ammonia to form a new coordinate covalent bond. We have already learnt that in coordination compounds, the Ligands act as a Lewis base and the central metal atom or ion that accepts a pair of electrons from the ligand behaves as a Lewis acid.

Lewis acids	Lewis bases
Electron deficient molecules such as $BF_3, AlCl_3, BeF_2$ etc...	Molecules with one (or) more lone pairs of electrons. $NH_3, H_2O, R\text{-}O\text{-}H, R\text{-}O\text{-}R, R - NH_2$
All metal ions Examples: $Fe^{2+}, Fe^{3+}, Cr^{3+}, Cu^{2+}$ etc...	All anions $F^-, Cl^-, CN^-, SCN^-, SO_4^{2-}$ etc...
Molecules that contain a polar double bond Examples : SO_2, CO_2, SO_3 etc...	Molecules that contain carbon – carbon multiple bond Examples: $CH_2{=}CH_2, CH \equiv CH$ etc...
Molecules in which the central atom can expand its octet due to the availability of empty d – orbitals Example: $SiF_4, SF_4, FeCl_3$ etc..	All metal oxides CaO, MgO, Na_2O etc...
Carbonium ion $(CH_3)_3C^+$	Carbanion CH_3^-

Example

Identify the Lewis acid and the Lewis base in the following reactions.

$Cr^{3+} + 6\,H_2O \rightarrow [Cr(H_2O)_6]^{3+}$

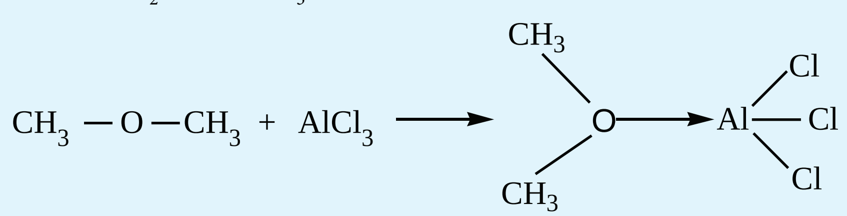
In the hydration of ion, each of six water molecules donates a pair of electron to Cr^{3+} to from the hydrated cation, hexaaquachromium (III) ion, thus, the Lewis acid is Cr^{3+} and the Lewis base H_2O.

Evaluate yourself – 3

Identify the Lewis acid and the Lewis base in the following reactions.

i. $CaO + CO_2 \rightarrow CaCO_3$

ii.



Evaluate yourself – 4

H_3BO_3 accepts hydroxide ion from water as shown below

$H_3BO_3(aq)+H_2O(l) \rightleftharpoons B(OH)_4^- + H^+$

Predict the nature of H_3BO_3 using Lewis concept

8.2 Strength of Acids and Bases

The strength of acids and bases can be determined by the concentration of H_3O^+ (or) OH^- produced per mole of the substance dissolved in H_2O. Generally we classify the acids / bases either as strong or weak. A strong acid is the one that is almost completely dissociated in water while a weak acid is only partially dissociated in water.

Let us quantitatively define the strength of an acid (HA) by considering the following general equilibrium.

$$\underset{\text{acid 1}}{HA} + \underset{\text{base 2}}{H_2O} \rightleftharpoons \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 1}}{A^-}$$

The equilibrium constant for the above ionisation is given by the following expression

$$K=\frac{[H_3O^+][A^-]}{[HA][H_2O]} \quad .....(8.1)$$

We can omit the concentration of H_2O in the above expression since it is present in large excess and essentially unchanged.

$$K_a=\frac{[H_3O^+][A^-]}{[HA]} \quad .....(8.2)$$

Here, K_a is called the ionisation constant or dissociation constant of the acid. It measures the strength of an acid. Acids such as HCl, HNO_3 etc... are almost completely ionised and hence they have high K_a value (K_a for HCl at 25°C is 2×10^6) Acids such as formic acid ($K_a=1.8\times10^{-4}$ at 25°C), acetic acid (1.8×10^{-5} at 25°C) etc.. are partially ionised in solution and in such cases, there is an equilibrium between the unionised acid molecules and their dissociated ions. Generally, acids with K_a value greater than ten are considered as strong acids and less than one are considered as weak acids.

Let us consider the dissociation of HCl in aqueous solution,

$$\underset{\text{acid 1}}{HCl} + \underset{\text{base 2}}{H\text{-}OH} \rightleftharpoons \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 1}}{Cl^-}$$

As discussed earlier, due to the complete dissociation, the equilibrium lies almost 100% to the right. i.e., the Cl^- ion has only a negligible tendency to accept a proton form H_3O^+. It means that the conjugate base of a strong acid is a weak base and vice versa.

The following table illustrates the relative strength of conjugate acid – base pairs.

$HClO_4$	Strong acids	ClO_4^-	Very weak bases
HCl		Cl^-	
H_2SO_4		HSO_4^-	
HNO_3		NO_3^-	
H_3O^+	Weak acids	H_2O	Weak bases
HNO_2		NO_2^-	
HF		F^-	
CH_3COOH		CH_3COO^-	
NH_3	Very weak acids	NH_2^-	Strong bases
OH^-		O^{2-}	
H_2		H^-	

8.3 Ionisation of water

We have learnt that when an acidic or a basic substance is dissolved in water, depending upon its nature, it can either donate (or) accept a proton. In addition to that the pure water itself has a little tendency to dissociate. i.e, one water molecule donates a proton to an another water molecule. This is known as auto ionisation of water and it is represented as below.

$$\underset{\text{acid 1}}{HO\text{-}H} + \underset{\text{base 2}}{H_2\ddot{O}} \rightleftharpoons \underset{\text{acid 2}}{H_3O^+} + \underset{\text{base 1}}{OH^-}$$

Conjugate acid - base pairs

In the above ionisation, one water molecule acts as an acid while the another water molecule acts as a base.

The dissociation constant for the above ionisation is given by the following expression

$$K = \frac{[H_3O^+][OH^-]}{[H_2O]^2} \qquad .....(8.3)$$

The concentration of pure liquid water is one. i.e, $[H_2O]^2 = 1$

$$\because \; K_w = [H_3O^+][OH^-] \qquad .....(8.4)$$

Here, K_w represents the ionic product (ionic product constant) of water

It was experimentally found that the concentration of H_3O^+ in pure water is 1×10^{-7} at $25^\circ C$. Since the dissociation of water produces equal number of H_3O^+ and OH^-, the concentration of OH^- is also equal to 1×10^{-7} at $25^\circ C$.

Therefore, the ionic product of water at 25°C is

$$K_w = [H_3O]^+[OH^-] ......(8.4)$$

$$K_w = (1\times10^{-7})(1\times10^{-7})$$

$$= 1\times10^{-14}.$$

Like all equilibrium constants, K_w is also a constant at a particular temperature. The dissociation of water is an endothermic reaction. With the increase in temperature, the concentration of H_3O^+ and OH^- also increases, and hence the ionic product also increases.

In neutral aqueous solution like NaCl solution, the concentration of H_3O^+ is always equal to the concentration of OH^- whereas in case of an aqueous solution of a substance which may behave as an acid (or) a base, the concentration of H_3O^+ will not be equal to $[OH^-]$.

K_w **values at different temperatures are given in the following below**

Temperature (°C)	K_w
0	1.14×10^{-15}
10	2.95×10^{-15}
25	1.00×10^{-14}
40	2.71×10^{-14}
50	5.30×10^{-14}

We can understand this by considering the aqueous HCl as an example. In addition to the auto ionisation of water, the following equilibrium due to the dissociation of HCl can also exist.

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

In this case, in addition to the auto ionisation of water, HCl molecules also produces H_3O^+ ion by donating a proton to water and hence $[H_3O^+]>[OH^-]$. It means that the aqueous HCl solution is acidic. Similarly, in basic solution such as aqueous NH_3, NaOH etc..... $[OH^-]>[H_3O^+]$.

Example 8.1

Calculate the concentration of OH^- in a fruit juice which contains 2×10^{-3} M, H_3O^+ ion. Identify the nature of the solution.

Given that $H_3O^+ = 2\times10^{-3}M$

$$K_w = [H_3O^+][OH^-]$$

$$\therefore [OH^-] = \frac{K_w}{[H_3O^+]} = \frac{1\times10^{-14}}{2\times10^{-3}} = 5\times10^{-12}M$$

$$2\times10^{-3} >> 5\times10^{-12}$$

i.e., $[H_3O^+]>>[OH^-]$, hence the juice is acidic in nature

Evaluate yourself - 5

At a particular temperature, the K_w of a neutral solution was equal to 4×10^{-14}. Calculate the concentration of $[H_3O^+]$ and $[OH^-]$.

8.4 The pH scale

We usually deal with acid / base solution in the concentration range 10^{-1} to $10^{-7}M$. To express the strength of such low concentrations, Sorensen introduced a logarithmic scale known as the pH scale. The term pH is derived from the French word *'Purissance de hydrogene'* meaning, the power of hydrogen. pH of a solution is defined as the negative logarithm of base 10 of the molar concentration of the hydronium ions present in the solution.

$$pH = -\log_{10}[H_3O^+] \qquad .....(8.5)$$

The concentration of H_3O^+ in a solution of known pH can be calculated using the following expression.

$$[H_3O^+]=10^{-pH} \text{ (or) } [H_3O^+]= \text{antilog of } (-pH) \qquad .....(8.6)$$

Similarly, pOH can also be defined as follows

$$pOH = -\log_{10}[OH^-] \qquad .....(8.7)$$

As discussed earlier, in neutral solutions, the concentration of $[H_3O^+]$ as well as $[OH^+]$ is equal to $1\times10^{-7}M$ at $25^\circ C$. The pH of a neutral solution can be calculated by substituting this H_3O^+concentration in the expression (8.5)

$$pH = -\log_{10}[H_3O^+]$$

$$= -\log_{10}10^{-7}$$

$$=(-7)(-1)\log_{10}10= +7\,(1)= 7 \qquad [\because \log_{10}10=1]$$

Similary, we can calculate the pOH of a neutral solution using the expression (8.7), it is also equal to 7.

The negative sign in the expression (8.5) indicates that when the concentration of $[H_3O^+]$ increases the pH value decreases. For example, if the $[H_3O^+]$ increases from to $10^{-7}$to$10^{-5}M$, the pH value of the solution decreases from 7 to 5. We know that in acidic solution, $[H_3O^+]>[OH^-]$, i.e., $[H_3O^+]>10^{-7}$. Similarly in basic solution $[H_3O^+]<10^{-7}$. So, we can conclude that acidic solution should have pH value less than 7 and basic solution should have pH value greater than 7.

8.4.1 Relation between pH and pOH

A relation between pH and pOH can be established using their following definitions

$$pH=-\log_{10}[H_3O^+] \qquad .....(8.5)$$

$$pOH = -\log_{10}[OH^-] \qquad .....(8.7)$$

Adding equation (8.5) and (8.7)

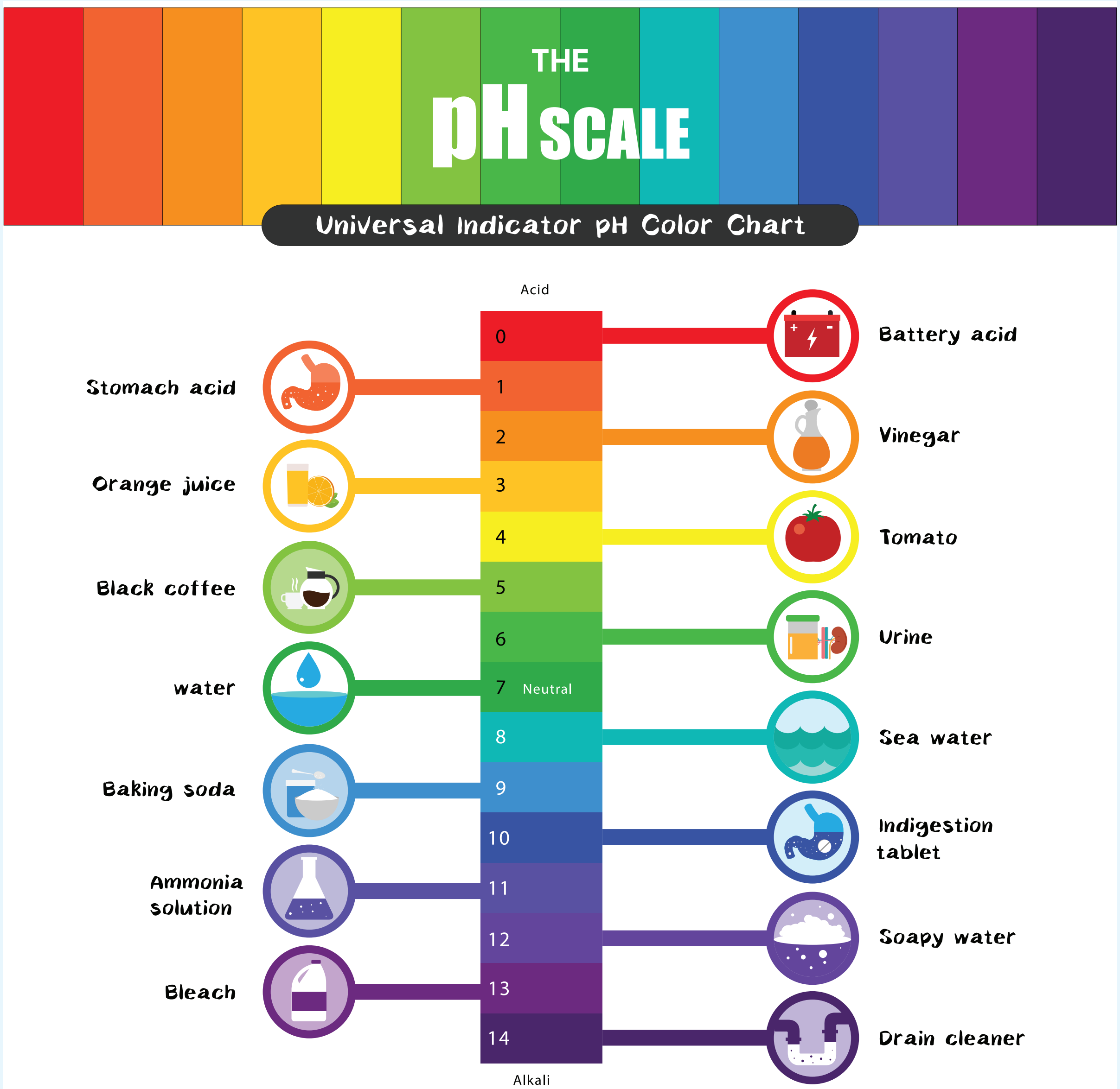


Figure 8.1 The pH scale

$$pH + pOH = -\log_{10}[H_3O^+] - \log_{10}[OH^-]$$

$$= -\left(\log_{10}[H_3O^+] + \log_{10}[OH^-]\right)$$

$$pH + pOH = -\log_{10}[H_3O^+][OH^-] \qquad [\because \log a + \log b = \log ab]$$

We know that $[H_3O^+][OH^-] = K_W$

$$\Rightarrow pH + pOH = -\log_{10} K_W$$

$$\Rightarrow pH + pOH = pK_W \qquad \left[\because pK_W = -\log_{10} K_w\right] \qquad .....(8.8)$$

at $25^\circ C$, the ionic product of water, $K_W = 1\times 10^{-14}$

$$pK_W = -\log_{10} 10^{-14} = 14 \log_{10} 10$$

$$= 14$$

$\therefore$ (8.7) $\Rightarrow$ $\therefore$ At $25^\circ C$, $pH + pOH = 14$

Example 8.2

Calculate the pH of 0.001M HCl solution

$$\underset{0.001\ M}{HCl} \underset{}{\overset{H_2O}{\rightleftharpoons}} \underset{0.001\ M}{H_3O^+} + \underset{0.001M}{Cl^-}$$

H_3O^+ from the auto ionisation of $H_2O\ (10^{-7}M)$ is negligible when compared to the H_3O^+ from $10^{-3}M$ HCl.

Hence $[H_3O^+] = 0.001\ mol\ dm^{-3}$

$$pH = -\log_{10}[H_3O^+]$$

$$= -\log_{10}(0.001)$$

$$= -\log_{10}(10^{-3}) = 3$$

Note: If the concentration of the acid or base is less than 10^{-6} M, the concentration of H_3O^+ produced due to the auto ionisation of water cannot be negleted and in such cases

$[H_3O^+] = 10^{-7}$ (from water) + $[H_3O^+]$ (from the acid)

similarly, $[OH^-] = 10^{-7}$M (from water) + $[OH^-]$ (from the base)

Example 8.3

Calculate pH of 10^{-7} M HCl

If we do not consider $[H_3O^+]$ from the ionisation of H_2O,

then $[H_3O^+] = [HCl] = 10^{-7}M$

i.e., pH = 7, which is a pH of a neutral solution. We know that HCl solution is acidic whatever may be the concentration of HCl i.e, the pH value should be less than 7. In this case the concentration of the acid is very low (10^{-7}M) Hence, the H_3O^+ (10^{-7}M) formed due to the auto ionisation of water cannot be neglected.

so, in this case we should consider $[H_3O^+]$ from ionisation of H_2O

$[H_3O^+] = 10^{-7}$ (from HCl) $+ 10^{-7}$ (from water)

$= 10^{-7}(1+1) \quad = 2\times10^{-7}$

$$pH = -\log_{10}[H_3O^+]$$

$$= -\log_{10}(2\times10^{-7}) = -\left[\log 2 + \log 10^{-7}\right]$$

$$= -\log 2 - (-7).\log_{10} 10$$

$$= 7 - \log 2$$

$$= 7 - 0.3010 = 6.6990$$

$$= 6.70$$

Evaluate yourself - 6

a) Calculate pH of 10^{-8}M H_2SO_4

B) Calculate the concentration of hydrogen ion in moles per litre of a solution whose pH is 5.4

c) Calculate the pH of an aqueous solution obtained by mixing 50ml of 0.2 M HCl with 50ml 0.1 M NaOH

8.5 Ionisation of weak acids

We have already learnt that weak acids are partially dissociated in water and there is an equilibrium between the undissociated acid and its dissociated ions.

Consider the ionisation of a weak monobasic acid HA in water.

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

Applying law of chemical equilibrium, the equilibrium constant K_c is given by the expression

$$K_C = \frac{[H_3O^+][A^-]}{[HA][H_2O]} \quad .....(8.9)$$

The square brackets, as usual, represent the concentrations of the respective species in moles per litre.

In dilute solutions, water is present in large excess and hence, its concentration may be taken as constant say K. Further H_3O^+ indicates that hydrogen ion is hydrated, for simplicity it may be replaced by H^+. The above equation may then be written as,

$$K_C = \frac{[H^+][A^-]}{[HA] \times K} \quad .....(8.10)$$

The product of the two constants K_C and K gives another constant. Let it be K_a

$$K_a = \frac{[H^+][A^-]}{[HA]} \quad .....(8.11)$$

The constant K_a is called dissociation constant of the acid. Like other equilibrium constants, K_a also varies only with temperature.

Similarly, for a weak base, the dissociation constant can be written as below.

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \quad ....(8.12)$$

8.5.1 Ostwald's dilution law

Ostwald's dilution law relates the dissociation constant of the weak acid (K_a) with its degree of dissociation (α) and the concentration (c). Degree of dissociation (α) is the fraction of the total number of moles of a substance that dissociates at equilibrium.

$$\alpha = \frac{\text{Number of moles dissociated}}{\text{total number of moles}}$$

We shall derive an expression for ostwald's law by considering a weak acid, i.e. acetic acid (CH_3COOH). The dissociation of acetic acid can be represented as

$$CH_3COOH \rightleftharpoons H^+ + CH_3COO^-$$

The dissociation constant of acetic acid is,

$$k_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} \quad .....(8.13)$$

	CH_3COOH	H^+	CH_3COO^-
Initial number of moles	1	-	-
Degree of dissociation of CH_3COOH	α	-	-
Number of moles at equilibrium	$1-\alpha$	α	α
Equilibrium concentration	$(1-\alpha)C$	αC	αC

Substituting the equilibrium concentration in equation (8.13)

$$k_a = \frac{(\alpha C)(\alpha C)}{(1-\alpha)C}$$

$$k_a = \frac{\alpha^2 C}{1-\alpha} \quad .....(8.14)$$

We know that weak acid dissociates only to a very small extent. Compared to one, α is so small and hence in the denominator $(1-\alpha) \simeq 1$. The above expression (8.14) now becomes,

$$K_a = \alpha^2 C$$

$$\Rightarrow \alpha^2 = \frac{K_a}{C}$$

$$\alpha = \sqrt{\frac{K_a}{C}} \quad .....(8.15)$$

Let us consider an acid with K_a value 4×10^{-4} and calculate the degree of dissociation of that acid at two different concentration $1 \times 10^{-2}M$ and $1 \times 10^{-4}M$ using the above expression (8.15)

For $1 \times 10^{-2}M$,

$$\alpha = \sqrt{\frac{4 \times 10^{-4}}{10^{-2}}}$$

$$= \sqrt{4 \times 10^{-2}}$$

$$= 2 \times 10^{-1}$$

$$= 0.2$$

For 1×10^{-4}M acid,

$$\alpha = \sqrt{\frac{4 \times 10^{-4}}{10^{-4}}}$$

$$= 2$$

i.e, When the dilution increases by 100 times, (Concentration decreases from 1×10^{-2}M to 1×10^{-4}M), the dissociation increases by 10 times.

Thus, we can conclude that, when dilution increases, the degree of dissociation of weak electrolyte also increases. This statement is known as Ostwald's dilution Law.

The concentration of $H^+(H_3O^+)$ can be calculated using the K_a value as below.

$[H^+] = \alpha C$ (Refer table) .....(8.16)

Equilibrium molar concentration of $[H^+]$ is equal to αC

$$\therefore [H^+] = \left(\sqrt{\frac{K_a}{C}}\right) C \qquad [\because \text{ equation (8.15)}]$$

$$= \sqrt{\frac{K_a C^2}{C}}$$

$$[H^+] = \sqrt{K_a C} \qquad .....(8.17)$$

Similarly, for a weak base

$$K_b = \alpha^2 C \quad \text{and } \alpha = \sqrt{\frac{K_b}{C}}$$

$$[OH^-] = \alpha C$$

(or)

$$[OH^-] = \sqrt{K_b C} \qquad .....(8.18)$$

Example 8.4

A solution of 0.10M of a weak electrolyte is found to be dissociated to the extent of 1.20% at $25^{\circ}C$. Find the dissociation constant of the acid.

Given that $\alpha = 1.20\% = \frac{1.20}{100} = 1.2\times 10^{-2}$

$$K_a = \alpha^2 c$$

$$= (1.2 \times 10^{-2})^2 (0.1) = 1.44\times 10^{-4}\times 10^{-1}$$

$$= 1.44 \times 10^{-5}$$

Example 8.5

Calculate the pH of 0.1M CH_3COOH solution. Dissociation constant of acetic acid is 1.8×10^{-5}.

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

For weak acids,

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

$$=\sqrt{1.8\times10^{-5}\times0.1}$$

$$=1.34\times10^{-3}M \qquad pH=-\log\left(1.34\times10^{-3}\right)$$

$$=3-\log1.34$$

$$=3-0.1271$$

$$=2.8729\simeq2.87$$

Evaluate yourself - 7

K_b for NH_4OH is 1.8×10^{-5}. Calculate the percentage of ionisation of 0.06M ammonium hydroxide solution.

8.6 Common Ion Effect

When a salt of a weak acid is added to the acid itself, the dissociation of the weak acid is suppressed further. For example, the addition of sodium acetate to acetic acid solution leads to the suppression in the dissociation of acetic acid which is already weakly dissociated. In this case, CH_3COOH and CH_3COONa have the common ion, CH_3COO^-

Let us analyse why this happens. Acetic acid is a weak acid. It is not completely dissociated in aqueous solution and hence the following equilibrium exists.

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

However, the added salt, sodium acetate, completely dissociates to produce Na^+ and CH_3COO^- ion.

$$CH_3COONa(aq)\longrightarrow Na^+(aq)+CH_3COO^-(aq)$$

Hence, the overall concentration of CH_3COO^- is increased, and the acid dissociation equilibrium is disturbed. We know from Le chatelier's principle that when a stress is applied to a system at equilibrium, the system adjusts itself to nullify the effect produced by that stress. So, inorder to maintain the equilibrium, the excess CH_3COO^- ions combines with H^+ ions to produce much more unionized CH_3COOH i.e, the equilibrium will shift towards the left. In other words, the dissociation of CH_3COOH is suppressed. Thus, the dissociation of a weak acid (CH_3COOH) is suppressed in the presence of a salt (CH_3COONa) containing an ion common to the weak electrolyte. It is called the common ion effect.

8.7 Buffer Solution

Do you know that our blood maintains a constant pH, irrespective of a number of cellular acid – base reactions. Is it possible to maintain a constant hydronium ion concentration in such reactions? Yes, it is possible due to buffer action.

Buffer is a solution which consists of a mixture of a weak acid and its conjugate base (or) a weak base and its conjugate acid. This buffer solution resists drastic changes in its pH upon addition of a small quantities of acids (or) bases, and this ability is called buffer action. The buffer containing carbonic acid (H_2CO_3) and its conjugate base HCO_3^- is present in our blood. There are two types of buffer solutions.

1. Acidic buffer solution : a solution containing a weak acid and its salt.

   Example : solution containing acetic acid and sodium acetate

2. Basic buffer solution : a solution containing a weak base and its salt.

   Example : Solution containing NH_4OH and NH_4Cl

8.7.1 Buffer action

To resist changes in its pH on the addition of an acid (or) a base, the buffer solution should contain both acidic as well as basic components so as to neutralize the effect of added acid (or) base and at the same time, these components should not consume each other.

Let us explain the buffer action in a solution containing CH_3COOH and CH_3COONa. The dissociation of the buffer components occurs as below.

$$CH_3COOH\,(aq) \rightleftharpoons CH_3\text{-}COO^-_{(aq)} + H_3O^+(aq)$$

$$CH_3\,COONa\,(s) \xrightarrow{H_2O_{(l)}} CH_3\text{-}COO^-_{(aq)} + Na^+(aq)$$

If an acid is added to this mixture, it will be consumed by the conjugate base CH_3COO^- to form the undissociated weak acid i.e, the increase in the concentration of H^+ does not reduce the pH significantly.

$$CH_3COO^-(aq) + H^+(aq) \longrightarrow CH_3COOH\,(aq)$$

If a base is added, it will be neutralized by H_3O^+, and the acetic acid is dissociated to maintain the equlibrium. Hence the pH is not significantly altered.

$$OH^-(aq) + \cancel{H_3O^+}(aq) \longrightarrow H_2O\,(l)$$

$$CH_3COOH\,(aq) \xrightleftharpoons{H_2O\,(l)} CH_3COO^-(aq) + \cancel{H_3O^+}(aq)$$

$$OH^-(aq) + CH_3COOH\,(aq) \longrightarrow CH_3COO^-(aq) + H_2O\,(l)$$

These neutralization reactions are identical to those reactions that we have already discussed in common ion effect.

Les us analyse the effect of the addition of 0.01 mol of solid sodium hydroxide to one litre of a buffer solution containing 0.8 M CH_3COOH and 0.8 M CH_3COONa. Assume that the volume change due to the addition of NaOH is negligible. (Given: K_a for CH_3COOH is 1.8×10^{-5})

$$\underset{0.8-\alpha}{CH_3\text{-}COOH(aq)} \xrightleftharpoons{H_2O} \underset{\alpha}{CH_3COO^-(aq)} + \underset{\alpha}{H^+(aq)}$$

$$\underset{0.8}{CH_3COONa(aq)} \xrightarrow{H_2O} \underset{0.8}{CH_3COO^-(aq)} + \underset{0.8}{Na^+(aq)}$$

The dissociation constant for CH_3COOH is given by

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]};$$

$$[H^+] = K_a\frac{[CH_3COOH]}{[CH_3COO^-]}$$

The above expression shows that the concentration of H^+ is directly proportional to $\frac{[CH_3COOH]}{[CH_3COO^-]}$.

Let the degree of dissociation of CH_3COOH be α then,

$[CH_3COOH]=0.8\text{-}\alpha$ and $[CH_3COO^-]=\alpha+0.8$

$$\therefore [H^+] = K_a\frac{(0.8-\alpha)}{(0.8+\alpha)}$$

$\alpha<<0.8$, $\therefore 0.8\text{-}\alpha \simeq 0.8$ and $0.8+\alpha \simeq 0.8$

$$[H^+] = \frac{K_a(0.8)}{(0.8)} \Rightarrow [H^+] = K_a$$

Given that

K_a for CH_3COOH is 1.8×10^{-5}

$$\therefore [H^+] = 1.8\times10^{-5}; pH = -\log(1.8\times10^{-5})$$
$$= 5 - \log 1.8$$
$$= 5 - 0.26$$
$$pH = 4.74$$

Calculation of pH after adding 0.01 mol NaOH to 1 litre of buffer.

Given that the volume change due to the addition of NaOH is negligible $\therefore$ $[OH^-] = 0.01M$. The consumption of OH^- are expressed by the following equations.

$$\underset{0.8-\alpha}{CH_3COOH\ (aq)} \rightleftharpoons \underset{\alpha}{CH_3COO^-(aq)} + \underset{\alpha}{H^+(aq)}$$

$$\underset{0.8}{CH_3COONa(aq)} \rightarrow \underset{0.8}{CH_3COO^-(aq)} + \underset{0.8}{Na^+(aq)}$$

$$CH_3COOH + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O\ (l)$$

$$\therefore [CH_3COOH] = 0.8 - \alpha - 0.01 = 0.79 - \alpha$$

$$[CH_3COO^-] = \alpha + 0.8 + 0.01 = 0.81 + \alpha \qquad \alpha << 0.8;$$

$$0.79 - \alpha \simeq 0.79 \text{ and } 0.81 + \alpha \simeq 0.81$$

$$\therefore\ [H^+] = (1.8 \times 10^{-5}) \times \frac{0.79}{0.81}$$

$$[H^+] = 1.76 \times 10^{-5}$$

$$\therefore pH = -\log(1.76 \times 10^{-5})$$

$$= 5 - \log 1.76$$

$$= 5 - 0.25$$

$$pH = 4.75$$

The addition of a strong base (0.01 M NaOH) increased the pH only slightly ie., from 4.74 to 4.75 . So, the buffer action is verified.

Evaluate yourself - 8

a) Explain the buffer action in a basic buffer containing equimolar ammonium hydroxide and ammonium chloride.

b) Calculate the pH of a buffer solution consisting of 0.4M CH_3COOH and 0.4M CH_3COONa . What is the change in the pH after adding 0.01 mol of HCl to 500ml of the above buffer solution. Assume that the addition of HCl causes negligible change in the volume. Given: ($K_a = 1.8 \times 10^{-5}$.)

8.7.2 Buffer capacity and buffer index

The buffering ability of a solution can be measured in terms of buffer capacity. Vanslyke introduced a quantity called buffer index, β, as a quantitative measure of the buffer capacity. It is defined as the number of gram equivalents of acid or base added to 1 litre of the buffer solution to change its pH by unity.

$$\beta = \frac{dB}{d(pH)} \qquad ....(8.19)$$

Here,

dB = number of gram equivalents of acid / base added to one litre of buffer solution.

d(pH) = The change in the pH after the addition of acid / base.

8.7.3 Henderson – Hasselbalch equation

We have already learnt that the concentration of hydronium ion in an acidic buffer solution depends on the ratio of the concentration of the weak acid to the concentration of its conjugate base present in the solution i.e.,

$$\left[H_3O^+\right] = K_a \frac{[acid]_{eq}}{[base]_{eq}} \qquad ....(8.20)$$

The weak acid is dissociated only to a small extent. Moreover, due to common ion effect, the dissociation is further suppressed and hence the equilibrium concentration of the acid is nearly equal to the initial concentration of the unionised acid. Similarly, the concentration of the conjugate base is nearly equal to the initial concentration of the added salt.

$$\left[H_3O^+\right]=K_a\frac{[acid]}{[salt]} \quad ....(8.21)$$

Here [acid] and [salt] represent the initial concentration of the acid and salt, respectively used to prepare the buffer solution

Taking logarithm on both sides of the equation

$$\log\,[H_3O^+]=\log K_a+\log\frac{[acid]}{[salt]} \quad ....(8.22)$$

reverse the sign on both sides

$$-\log\,[H_3O^+]=-\log K_a-\log\frac{[acid]}{[salt]} \quad ....(8.23)$$

We know that

$pH = -\log\,[H_3O^+]$ and $pK_a = -\log K_a$

$$\Rightarrow pH = pK_a - \log\frac{[acid]}{[salt]} \quad ....(8.24)$$

$$\Rightarrow pH = pK_a + \log\frac{[salt]}{[acid]} \quad ....(8.25)$$

Similarly for a basic buffer, $pOH = pK_b+\log\frac{[salt]}{[base]}$ ....(8.26)

Example 8.6

1. Find the pH of a buffer solution containing 0.20 mole per litre sodium acetate and 0.18 mole per litre acetic acid. K_a for acetic acid is 1.8×10^{-5} .

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

Given that $K_a = 1.8 \times 10^{-5}$

$$\therefore\ pK_a = -\log(1.8\times10^{-5}) = 5-\log 1.8$$
$$= 5 - 0.26$$
$$= 4.74$$

$$\therefore pH = 4.74 + \log\frac{0.20}{0.18}$$
$$= 4.74 + \log {}^{10}\!/_{9} = 4.74 + \log 10 - \log 9$$
$$= 4.74 + 1 - 0.95 = 5.74 - 0.95$$
$$= 4.79$$

Example 8.7

What is the pH of an aqueous solution obtained by mixing 6 gram of acetic acid and 8.2 gram of sodium acetate making the volume equal to 500 ml. (Given: K_a for acetic acid is 1.8×10^{-5})

According to Henderson – Hasselbalch equation,

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

$P^{K_a} = -\log K_a = -\log(1.8\times10^{-5}) = 4.74$ (Refer previous example)

$$[Salt] = \frac{\text{Number of moles of sodium acetate}}{\text{Volume of the solution (litre)}}$$

$$\text{Number of moles of sodium acetate} = \frac{\text{mass of sodium acetate}}{\text{molar mass of sodium acetate}}$$

$$= \frac{8.2}{82} = 0.1$$

$$\therefore [Salt] = \frac{0.1\text{ mole}}{{}^{1}\!/_{2}\text{ Litre}} = 0.2M$$

$$[acid] = \frac{\left(\frac{\text{mass of } CH_3COOH}{\text{molar mass of } CH_3COOH}\right)}{\text{Volume of solution in litre}}$$

$$= \frac{\left(\frac{6}{60}\right)}{{}^{1}\!/_{2}}$$

$$= 0.2M$$

$$\therefore pH = 4.74 + \log\frac{(0.2)}{(0.2)}$$

$$pH = 4.74 + \log 1$$

$$pH = 4.74 + 0 = 4.74$$

Evaluate yourself - 9

a) How can you prepare a buffer solution of pH 9. You are provided with 0.1M NH_4OH solution and ammonium chloride crystals. (Given: pK_b for NH_4OH is 4.7 at $25^{\circ}C$.

b) What volume of 0.6M sodium formate solution is required to prepare a buffer solution of pH 4.0 by mixing it with 100ml of 0.8M formic acid. (Given: pK_a for formic acid is 3.75.)

8.8 Salt Hydrolysis

When an acid reacts with a base, a salt and water are formed and the reaction is called neutralization. Salts completely dissociate in aqueous solutions to give their constituent ions. The ions so produced are hydrated in water. In certain cases, the cation, anion or both react with water and the reaction is called salt hydrolysis. Hence, salt hydrolysis is the reverse of neutralization reaction.

8.8.1 Salts of strong acid and a strong base

Let us consider the reaction between $NaOH$ and nitric acid to give sodium nitrate and water.

$$NaOH(aq)+HNO_3(aq) \rightarrow NaNO_3(aq)+H_2O(l)$$

The salt $NaNO_3$ completely dissociates in water to produce Na^+ and NO_3^- ions.

$$NaNO_3(aq) \rightarrow Na^+(aq)+NO_3^-(aq)$$

Water dissociates to a small extent as

$$H_2O(l) \rightleftharpoons H^+(aq)+OH^-(aq)$$

Since $[H^+]=[OH^-]$, water is neutral

NO_3^- ion is the conjugate base of the strong acid HNO_3 and hence it has no tendency to react with H^+.

Similarly, Na^+ is the conjugate acid of the strong base NaOH and it has no tendency to react with OH^-.

It means that there is no hydrolysis. In such cases $[H^+]=[OH^-]$ pH is maintained and, therefore, the solution is neutral.

8.8.2 Hydrolysis of Salt of strong base and weak acid (Anionic Hydrolysis).

Let us consider the reactions between sodium hydroxide and acetic acid to give sodium acetate and water.

$$NaOH\ (aq) + CH_3COOH(aq) \rightleftharpoons CH_3COONa(aq)+H_2O(l)$$

In aqueous solution, CH_3COONa is completely dissociated as below

$$CH_3COONa\ (aq) \longrightarrow CH_3COO^-(aq)+Na^+(aq)$$

CH_3COO^- is a conjugate base of the weak acid CH_3COOH and it has a tendency to react with H^+ from water to produce unionised acid .

There is no such tendency for Na^+ to react with OH^-.

$CH_3COO^-(aq) + H_2O(l) \rightleftharpoons CH_3COOH\ (aq) + OH^-(aq)$ and therefore $[OH^-]>[H^+]$, in such cases, the solution is basic due to hydrolysis and the pH is greater than 7.

Let us find a relation between the equilibrium constant for the hydrolysis reaction (hydrolysis constant) and the dissociation constant of the acid.

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-][H_2O]}$$

$$K_h = \frac{[CH_3COOH][OH^-]}{[CH_3COO^-]} \quad .....(1)$$

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

$$K_a = \frac{[CH_3COO^-][H^+]}{[CH_3COOH]} \quad .....(2)$$

(1) × (2)

$\Rightarrow K_h.K_a = [H^+][OH^-]$

we know that $[H^+][OH^-] = K_w$

$K_h.K_a = K_w$

K_h value in terms of degree of hydrolysis (h) and the concentration of salt (C) for the equilibrium can be obtained as in the case of ostwald's dilution law. $K_h = h^2C$. and

i.e $[OH^-] = \sqrt{K_h.C}$

pH of salt solution in terms of K_a and the concentration of the electrolyte.

$pH + pOH = 14$

$pH = 14 - p\,OH = 14 - \{-\log [OH^-]\}$

$= 14 + \log [OH^-]$

$\therefore pH = 14 + \log (K_hC)^{1/2}$

$$pH = 14 + \log \left(\frac{K_wC}{K_a}\right)^{1/2}$$

$pH = 14 + \left(\frac{1}{2} \log K_w + \frac{1}{2} \log C - \frac{1}{2} \log K_a\right)$ $\quad [\because K_w = 10^{-14}.$

$pH = 14 - 7 + \frac{1}{2} \log C + \frac{1}{2} pK_a$ $\quad \frac{1}{2} \log K_w = \frac{1}{2} \times \log 10^{-14} = \frac{-14}{2}(1) = -7.$

$pH = 7 + \frac{1}{2} pK_a + \frac{1}{2} \log C.$ $\quad - \log K_a = pK_a]$

8.8.3 Hydrolysis of salt of strong acid and weak base (Cationic Hydrolysis)

Let us consider the reactions between a strong acid, HCl, and a weak base, NH_4OH, to produce a salt, NH_4Cl, and water

$$HCl\ (aq) + NH_4OH\ (aq) \rightleftharpoons NH_4Cl(aq) + H_2O(l)$$

$$NH_4Cl(aq) \longrightarrow NH_4^+ + Cl^-(aq)$$

NH_4^+ is a strong conjugate acid of the weak base NH_4OH and it has a tendency to react with OH^- from water to produce unionised NH_4OH shown below.

$$NH_4^+(aq) + H_2O(l) \rightleftharpoons NH_4OH\ (aq) + H^+(aq)$$

There is no such tendency shown by Cl^- and therefore $[H^+] > [OH^-]$; the solution is acidic and the pH is less than 7.

As discussed in the salt hydrolysis of strong base and weak acid. In this case also, we can establish a relationship between the K_h and K_b as

$$K_h . K_b = K_w$$

Let us calculate the K_h value in terms of degree of hydrolysis (h) and the concentration of salt

$$K_h = h^2C \qquad \text{and } [H^+] = \sqrt{K_h . C}$$

$$[H^+] = \sqrt{\frac{K_w}{K_b} . C}$$

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

$$= -\log \left(\frac{K_w . C}{K_b} \right)^{1/2}$$

$$= -\tfrac{1}{2} \log K_w - \tfrac{1}{2} \log C + \tfrac{1}{2} \log K_b$$

$$pH = 7 - \tfrac{1}{2} pK_b - \tfrac{1}{2} \log C.$$

8.8.4 Hydrolysis of Salt of weak acid and weak base (Anionic & Cationic Hydrolysis).

Let us consider the hydrolysis of ammonium acetate.

$$CH_3COONH_4(aq) \rightarrow CH_3COO^-(aq) + NH_4^+(aq)$$

In this case, both the cation (NH_4^+) and anion (CH_3COO^-) have the tendency to react with water

$$CH_3COO^- + H_2O \rightleftharpoons CH_3COOH + OH^-$$

$$NH_4^+ + H_2O \rightleftharpoons NH_4OH + H^+$$

The nature of the solution depends on the strength of acid (or) base i.e, if $K_a > K_b$; then the solution is acidic and pH < 7, if $K_a < K_b$; then the solution is basic and pH > 7, if $K_a = K_b$; then the solution is neutral.

The relation between the dissociation constant (K_a, K_b) and the hydrolysis constant is given by the following expression.

$$K_a . K_b . K_h = K_w$$

pH of the solution

pH of the solution can be calculated using the following expression,

$$pH = 7 + \tfrac{1}{2} pK_a - \tfrac{1}{2} pK_b.$$

Example 8.8

Calculate i) degree of hydrolysis, ii) the hydrolysis constant and iii) pH of 0.1M CH_3COONa solution (pK_a for CH_3COOH is 4.74).

Solution (a) CH_3COONa is a salt of weak acid (CH_3COOH) and a strong base (NaOH). Hence, the solutions is alkaline due to hydrolysis.

$$CH_3COO^-(aq) + H_2O(aq) \rightleftharpoons CH_3COOH\,(aq) + OH^-(aq)$$

$$\text{i) } h = \sqrt{\frac{K_w}{K_a \times C}}$$

$$= \sqrt{\frac{1 \times 10^{-14}}{1.8 \times 10^{-5} \times 0.1}}$$

$$h = 7.5 \times 10^{-5}$$

Give that $pK_a = 4.74$

$pK_a = -\log K_a$

i.e., $K_a =$ antilog of $(-pK_a)$

$=$ antilog of (-4.74)

$=$ antilog of $(-5 + 0.26)$

$= 10^{-5} \times 1.8$

[antilog of 0.26 = 1.82 $\simeq$ 1.8]

$$\text{ii) } K_h = \frac{K_w}{K_a} = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$= 5.56 \times 10^{-10}$$

$$\text{iii) } pH = 7 + \frac{pK_a}{2} + \frac{\log C}{2}$$

$$= 7 + \frac{4.74}{2} + \frac{\log 0.1}{2} = 7 + 2.37 - 0.5$$

$$= 8.87$$

Evaluate yourself - 10

Calculate the i) hydrolysis constant, ii) degree of hydrolysis and iii) pH of 0.05M sodium carbonate solution (pK_a for HCO_3^- is 10.26).

8.9 Solubility Product

We have come across many precipitation reactions in inorganic qualitative analysis. For example, dil HCl is used to precipitate Pb^{2+} ions as $PbCl_2$ which is sparingly soluble in water. Kidney stones are developed over a period of time due to the precipitation of Ca^{2+} (as calcium oxalate etc…). To understand the precipitation, let us consider the solubility equilibria that exist between the undissociated sparingly soluble salt and its constituent ions in solution.

For a general salt X_mY_n,

$$X_mY_n(s) \xrightleftharpoons{H_2O} mX^{n+}(aq) + nY^{m-}(aq)$$

The equilibrium constant for the above is

$$K = \frac{[X^{n+}]^m\ [Y^{m-}]^n}{[X_mY_m]}$$

In solubility equilibria, the equilibrium constant is referred as solubility product constant (or) Solubility product.

In such heterogeneous equilibria, the concentration of the solid is a constant and is omitted in the above expression

$$K_{sp} = [X^{n+}]^m \ [Y^{m-}]^n$$

The solubility product of a compound is defined as the product of the molar concentration of the constituent ions, each raised to the power of its stoichiometric co – efficient in a balanced equilibrium equation.

Solubility product finds useful to decide whether an ionic compound gets precipitated when solution that contains the constituent ions are mixed.

When the product of molar concentration of the constituent ions i.e., ionic product, exceeds the solubility product then the compound gets precipitated.

The expression for the solubility product and the ionic product appears to be the same but in the solubility product expression, the molar concentration represents the equilibrium concentration and in ionic product, the initial concentration (or) concentration at a given time 't' is used.

In general we can summarise as,

Ionic product > K_{sp}, precipitation will occur and the solution is super saturated.

Ionic product < K_{sp}, no precipitation and the solution is unsaturated.

Ionic product = K_{sp}, equilibrium exist and the solution is saturated.

Example 8.9

Indicate find out whether lead chloride gets precipitated or not when 1 mL of 0.1M lead nitrate and 0.5 mL of 0.2 M NaCl solution are mixed? K_{sp} of $PbCl_2$ is 1.2×10^{-5}.

$$PbCl_{2(s)} \xrightleftharpoons{H_2O} Pb^{2+}(aq) + 2Cl^-(aq)$$

$$\text{Ionic product} = [Pb^{2+}][Cl^-]^2$$

Total volume = 1.5 mL

$$\underset{0.1M}{Pb(NO_3)_2} \rightleftharpoons \underset{0.1M}{Pb^{2+}} + 2NO_3^-$$

No of moles of Pb^{2+} = Molarity × volume of the solution in litre

$$= 0.1 \times 1 \times 10^{-3} = 10^{-4}$$

$$[Pb^{2+}] = \frac{\text{number of moles of } Pb^{2+}}{\text{Volume of the solution in L}} = \frac{10^{-4}}{1.5 \times 10^{-3} \text{ mL}} = 6.7 \times 10^{-2} M$$

$$\underset{0.2M}{NaCl} \longrightarrow \underset{0.2M}{Na^+} + \underset{0.2M}{Cl^-}$$

No of moles of Cl^- = $0.2 \times 0.5 \times 10^{-3} = 10^{-4}$

$$[Cl^-] = \frac{10^{-4} \text{ moles}}{1.5 \times 10^{-3} \text{ L}} = 6.7 \times 10^{-2} M$$

Ionic product = $(6.7 \times 10^{-2})(6.7 \times 10^{-2})^2 = 3.01 \times 10^{-4}$

Since, the ionic product 3.01×10^{-4} is greater than the solubility product (1.2×10^{-5}), $PbCl_2$ will get precipitated.

8.9.1 Determination of solubility product from molar solubility

Solubility product can be calculated from the molar solubility i.e., the maximum number of moles of solute that can be dissolved in one litre of the solution.

For a solute X_mY_n,

$$X_mY_n(s) \rightleftharpoons mX^{n+}\ (aq) + nY^{m-}(aq)$$

From the above stoichiometrically balanced equation we have come to know that 1 mole of $X_mY_n(s)$ dissociated to furnish 'm' moles of X^{n+} and 'n' moles of Y^{m-} if 's' is molar solubility of X_mY_n, then

$[X^{n+}]=ms$ and $[Y^{m-}]=ns$

$\therefore K_{sp} = [X^{n+}]^m\ [Y^{m-}]^n$

$K_{sp}=(ms)^m(ns)^n$

$K_{sp}=(m)^m(n)^n(s)^{m+n}$

Example 8.10

- Establish a relationship between the solubility product and molar solubility for the following

a) $BaSO_4$ b) $Ag_2(CrO_4)$

$BaSO_4\ (s) \xrightleftharpoons{H_2O} Ba^{2+}(aq)+SO_4^{2-}(aq)$

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

$= (s)\ (s)$

$K_{sp} = S^2$

$Ag_2CrO_4(s) \xrightleftharpoons{H_2O} 2Ag^{+}(aq)+CrO_4^{2-}(aq)$

$K_{sp}=[Ag^{+}]^2[CrO_4^{2-}]$

$= (2s)^2(s)$

$K_{sp}=4s^3$

Summary

- According to Arrhenius, an acid is a substance that dissociates to give hydrogen ions in water.
- According to Lowry and Bronsted concept, an acid is defined as a substance that has a tendency to donate a proton to another substance and base is a substance that has a tendency to accept a proton from other substance.
- According to Gilbert . N. Lewis , an acid is a species that accepts an electron pair while base is a species that donates an electron pair.
- ionic product (ionic product constant) of water $(K_w) = [H_3O^+][OH^-]$
- pH of a solution is defined as the negative logarithm of base 10 of the molar concentration of the hydronium ions present in the solution.

$$pH = -\log_{10}[H_3O^+]$$

- when dilution increases, the degree of dissociation of weak electrolyte also increases. This statement is known as Ostwald's dilution Law.
- When a salt of a weak acid is added to the acid itself, the dissociation of the weak acid is suppressed further this is known as common ion effect
- Buffer is a solution which consists of a mixture of a weak acid and its conjugate base (or) a weak base and its conjugate acid.
- Buffer capacity and buffer index is defined as the number of gram equivalents of acid or base added to 1 litre of the buffer solution to change its pH by unity.

$$\beta = \frac{dB}{d(pH)}$$

- Henderson – Hasselbalch equation

For Acid buffer

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

For Basic buffer

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

- Hydrolysis of Salt of strong base and weak acid

$$K_h.K_a = K_w$$

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

- Hydrolysis of salt of strong acid and weak base

$$K_h.K_b = K_w$$

$$pH = 7 - \frac{1}{2}pK_b - \frac{1}{2}\log C.$$

- Hydrolysis of Salt of weak acid and weak base

$$K_a.K_b.K_h = K_w$$

$$pH = 7 + \frac{1}{2}pK_a - \frac{1}{2}pK_b.$$

- The solubility product of a compound is defined as the product of the molar concentration of the constituent ions, each raised to the power of its stoichiometric co – efficient in a balanced equilibrium equation.

V3R2X6

EVALUATION

Choose the correct answer:

1. Concentration of the Ag^{+} ions in a saturated solution of $Ag_2C_2O_4$ is 2.24×10^{-4} mol L^{-1} solubility product of $Ag_2C_2O_4$ is (NEET – 2017)

   a) 2.42×10^{-8} mol^3L^{-3} b) 2.66×10^{-12} mol^3L^{-3}

   c) 4.5×10^{-11} mol^3L^{-3} d) 5.619×10^{-12} mol^3L^{-3}

2. Following solutions were prepared by mixing different volumes of NaOH of HCl different concentrations. (NEET – 2018)

   i. 60 mL $\frac{M}{10}$ HCl + 40mL $\frac{M}{10}$ NaOH ii. 55 mL $\frac{M}{10}$ HCl + 45 mL $\frac{M}{10}$ NaOH

   iii. 75 mL $\frac{M}{5}$ HCl + 25mL $\frac{M}{5}$ NaOH iv. 100 mL $\frac{M}{10}$ HCl + 100 mL $\frac{M}{10}$ NaOH

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

   a) iv b) i c) ii d) iii

3. The solubility of $BaSO_4$ in water is $2.42\times10^{-3}gL^{-1}$ at 298K. The value of its solubility product (K_{sp}) will be (NEET -2018). (Given molar mass of $BaSO_4$=233g mol^{-1})

   a) $1.08\times10^{-14}mol^2L^{-2}$ b) $1.08\times10^{-12}mol^2L^{-2}$

   c) $1.08\times10^{-10}mol^2L^{-2}$ d) $1.08\times10^{-8}mol^2L^{-2}$

4. pH of a saturated solution of $Ca(OH)_2$ is 9. The Solubility product (K_{sp}) of $Ca(OH)_2$

   a) 0.5×10^{-15} b) 0.25×10^{-10}

   c) 0.125×10^{-15} d) 0.5×10^{-10}

5. Conjugate base for Bronsted acids H_2O and HF are

   a) OH^- and H_2FH^+, respectively b) H_3O^+ and F^-, respectively

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

6. Which will make basic buffer?

   a) 50 mL of 0.1M NaOH+25mL of 0.1M CH_3COOH

   b) 100 mL of 0.1M CH_3COOH+100 mL of 0.1M NH_4OH

   c) 100 mL of 0.1M HCl+200 mL of 0.1M NH_4OH

   d) 100 mL of 0.1M HCl+100 mL of 0.1M NaOH

7. Which of the following fluro compounds is most likely to behave as a Lewis base?

(NEET – 2016)

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

8. Which of these is not likely to act as Lewis base?

a) BF_3 b) PF_3 c) CO d) F^-

9. The aqueous solutions of sodium formate, anilinium chloride and potassium cyanide are respectively

a) acidic, acidic, basic b) basic, acidic, basic

c) basic, neutral, basic d) none of these

10. The percentage of pyridine (C_5H_5N) that forms pyridinium ion (C_5H_5NH) in a 0.10M aqueous pyridine solution $(K_b$ for $C_5H_5N = 1.7\times10^{-9})$ is

a) 0.006% b) 0.013% c) 0.77% d) 1.6%

11. Equal volumes of three acid solutions of pH 1,2 and 3 are mixed in a vessel. What will be the H^+ ion concentration in the mixture?

a) 3.7×10^{-2} b) 10^{-6} c) 0.111 d) none of these

12. The solubility of AgCl (s) with solubility product 1.6×10^{-10} in 0.1M NaCl solution would be

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

13. If the solubility product of lead iodide is 3.2×10^{-8}, its solubility will be

a) 2×10^{-3}M b) 4×10^{-4}M c) 1.6×10^{-5}M d) 1.8×10^{-5}M

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

a) The salts MY and NY_3 are more soluble in 0.5M KY than in pure water

b) The addition of the salt of KY to the suspension of MY and NY_3 will have no effect on their solubility's

c) The molar solubilities of MY and NY_3 in water are identical

d) The molar solubility of MY in water is less than that of NY_3

15. What is the pH of the resulting solution when equal volumes of 0.1M NaOH and 0.01M HCl are mixed?

a) 2.0 b) 3 c) 7.0 d) 12.65

16. The dissociation constant of a weak acid is 1×10^{-3}. In order to prepare a buffer solution with a pH = 4, the $[\text{Acid}]/[\text{Salt}]$ ratio should be

a) 4:3 b) 3:4 c) 10:1 d) 1:10

17. The pH of 10^{-5}M KOH solution will be

a) 9 b) 5 c) 19 d) none of these

18. $H_2PO_4^-$ the conjugate base of

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

19. Which of the following can act as Lowry – Bronsted acid as well as base?

a) HCl b) SO_4^{2-} c) HPO_4^{2-} d) Br^-

20. The pH of an aqueous solution is Zero. The solution is

a) slightly acidic b) strongly acidic c) neutral d) basic

21. The hydrogen ion concentration of a buffer solution consisting of a weak acid and its salts is given by

a) $[H^+]=\frac{K_a[acid]}{[salt]}$ b) $[H^+]= K_a[salt]$ c) $[H^+]=K_a[acid]$ d) $[H^+]=\frac{K_a[salt]}{[acid]}$

22. Which of the following relation is correct for degree of hydrolysis of ammonium acetate?

a) $h = \sqrt{\frac{K_h}{C}}$ b) $h = \sqrt{\frac{K_a}{K_b}}$ c) $h = \sqrt{\frac{K_w}{K_a.K_b}}$ d) $h = \sqrt{\frac{K_a.K_b}{K_w}}$

23. Dissociation constant of NH_4OH is 1.8×10^{-5} the hydrolysis constant of NH_4Cl would be

a) 1.8×10^{-19} b) 5.55×10^{-10} c) 5.55×10^{-5} d) 1.80×10^{-5}

Answer the following questions:

1. What are Lewis acids and bases? Give two example for each.
2. Discuss the Lowry – Bronsted concept of acids and bases.
3. Indentify the conjugate acid base pair for the following reaction in aqueous solution

   i) $HS^-(aq) + HF \rightleftharpoons F^-(aq) + H_2S(aq)$ ii) $HPO_4^{2-} + SO_3^{2-} \rightleftharpoons PO_4^{3-} + HSO_3^-$

   iii) $NH_4^+ + CO_3^{2-} \rightleftharpoons NH_3 + HCO_3^-$
4. Account for the acidic nature of $HClO_4$ in terms of Bronsted – Lowry theory, identify its conjugate base.
5. When aqueous ammonia is added to $CuSO_4$ solution, the solution turns deep blue due to the formation of tetramminecopper (II) complex, $[Cu(H_2O)_4]^{2+}_{(aq)} + 4NH_3(aq) \rightleftharpoons [Cu(NH_3)_4]^{2+}_{(aq)}$, among H_2O and NH_3 Which is stronger Lewis base.
6. The concentration of hydroxide ion in a water sample is found to be 2.5×10^{-6}M. Identify the nature of the solution.

7. A lab assistant prepared a solution by adding a calculated quantity of HCl gas at 25°C to get a solution with $[H_3O^+] = 4\times10^{-5}M$. Is the solution neutral (or) acidic (or) basic.
8. Calculate the pH of 0.04 M HNO_3 Solution.
9. Define solubility product
10. Define ionic product of water. Give its value at room temperature.
11. Explain common ion effect with an example
12. Derive an expression for Ostwald's dilution law
13. Define pH
14. Calculate the pH of $1.5\times10^{-3}M$ solution of $Ba(OH)_2$
15. 50ml of 0.05M HNO_3 is added to 50ml of 0.025M KOH. Calculate the pH of the resultant solution.
16. The K_a value for HCN is 10^{-9}. What is the pH of 0.4M HCN solution?
17. Calculate the extent of hydrolysis and the pH of 0.1 M ammonium acetate Given that $K_a = K_b = 1.8\times10^{-5}$
18. Derive an expression for the hydrolysis constant and degree of hydrolysis of salt of strong acid and weak base
19. Solubility product of Ag_2CrO_4 is 1×10^{-12}. What is the solubility of Ag_2CrO_4 in 0.01M $AgNO_3$ solution?
20. Write the expression for the solubility product of $Ca_3(PO_4)_2$
21. A saturated solution, prepared by dissolving $CaF_2(s)$ in water, has $[Ca^{2+}] = 3.3\times10^{-4}M$ What is the K_{sp} of CaF_2 ?
22. K_{sp} of AgCl is 1.8×10^{-10}. Calculate molar solubility in 1 M $AgNO_3$
23. A particular saturated solution of silver chromate Ag_2CrO_4 has $[Ag^+] = 5\times10^{-5}$ and $[CrO_4]^{2-} = 4.4\times10^{-4}M$. What is the value of K_{sp} for Ag_2CrO_4?
24. Write the expression for the solubility product of Hg_2Cl_2.
25. K_{sp} of Ag_2CrO_4 is 1.1×10^{-12}. what is solubility of Ag_2CrO_4 in 0.1M K_2CrO_4.
26. Will a precipitate be formed when 0.150 L of 0.1M $Pb(NO_3)_2$ and 0.100L of 0.2 M NaCl are mixed? $K_{sp}(PbCl_2) = 1.2\times10^{-5}$.
27. K_{sp} of $Al(OH)_3$ is $1\times10^{-15}M$. At what pH does $1.0\times10^{-3}M$ Al^{3+} precipitate on the addition of buffer of NH_4Cl and NH_4OH solution?

ICT Corner

Buffers and pH

By using this tool you can simulate the preparation of a buffer and measure its pH values

Please go to the URL http://pages.uoregon.edu/tgreenbo/pHbuffer20.html (or) Scan the QR code on the right side

B264_12_CHEMISTRY_EM

Step – 1

Open the Browser and type the URL given (or) Scan the QR Code. You can see a webpage as shown in the figure.

Step – 2

Now you can select a combination of an acid/base (Box 1) and its corresponding salt (Box 2) from the given choices and also select the desired concentrations (Box 3) and volume (Box 4) of these for the buffer.

Step – 3

In order to measure the pH of the made-up buffer click the 'Insert Probe' (Box 5) on the pH meter. Now the pH meter shows the pH. After measuring you need to remove the probe by clicking 'Remove Probe" (Box 5) to make any changes in the composition.

Step – 4

Now you can vary the concentration and volume of the components and see how the pH changes.