Unit One

Acid-Base Equilibrium

Learning Objectives

By the end of this section, you will be able to:

- Define acids and bases according to the Arrhenius concept, Brønsted-Lowry concept, and Lewis concept.
- Explain what conjugate acids and conjugate bases are.
- Identify the acid-base conjugate pairs from a given reaction.
- Calculate the percent dissociation of weak acids and bases.
- Write the expression for the acid-dissociation constant, Ka.
- Calculate Ka for an acid from the concentration of a given solution and its pH.
- Write the expression for the base-dissociation constant, Kb.
- Calculate Kb for a base from the concentration of a basic solution and its pOH, and calculate the [OH–] and pOH of a basic solution from a given value of Kb and the initial concentration of the solution.
- Assess the relative strengths of acids and bases according to their ionization constants.
- Explain how buffering actions affect our daily lives, using some examples.
- determine the equivalents of acids and base, respectively, that are required to neutralize specific amounts of base and acid;
- predict, in qualitative terms, whether a solution of a specific salt will be acidic, basic or neutral

1. Introduction

There are different definitions for acids and bases.

- The Arrhenius concept of acids and bases
- The Brønsted-Lowry concept acids- bases
- Lewis Acid-Base

What are the drawbacks of the Arrhenius' concepts of acids and bases?

1.1 The Arrhenius concept of acids and bases

The Swedish chemist Svante Arrhenius framed the first successful concept of acids and bases. He defined acids and bases in terms of the effect these substances have on water.

1.1.1 Arrhenius acid

- According to Arrhenius, acids are substances that increase the concentration of H + (proton ion) in aqueous solution.
- In Arrhenius's theory, a strong acid is a substance that completely ionizes in aqueous solution to give H_3O^+ + (aq) and an anion. Other examples of strong acids are H SO2 4 , HI , HBr, HCl , and HNO3 .
- An example is perchloric acid, $HClO_4(aq) + H_2O \rightarrow ClO_4^-(aq) + H_3O+$ (aq)

- Defining an acid as a substance that simply "dissociates" into its component parts

$$HA \rightarrow H^+ + AB–$$
$$HA \rightarrow H^+ + AB–$$

- An Arrhenius acid is is a substance that dissociates in water to produce H^+ ions.

- E.g 1 $HCl(aq)+H_2O(l)\rightleftharpoons H_3O+(aq)+Cl-(aq)HCl(aq)+H_2O(l)\rightleftharpoons H_3O+(aq)+Cl-(aq)$ or generally
- $HA(aq)+H_2O(l)\rightleftharpoons H_3O+(aq)+A-(aq)HA(aq)+H_2O(l)\rightleftharpoons H_3O+(aq)+A-(aq)$

1.1.2 Arrhenius base.

- According to Arrhenius, bases are substances that increase the concentration of OH − (a hydroxide ion) in aqueous solution or An Arrhenius base is is a substance that dissociates in water to produce OH^- ions.
- A strong base completely ionizes in aqueous solution to give OH − and a cation.
- Sodium hydroxide is an example of a strong base. $NaOH\ (s)\ + H_2O\ \rightarrow\ Na^+\ (aq)\ + HO^-(aq)$
- The principal strong bases are the hydroxides of Group IA elements and Group IIA elements (except Be). Despite its early successes and continued usefulness, the Arrhenius theory does have limitations.
- A base in water can accept a proton from water to produce OH^-.

Generally

- $B(aq)+H_2O(l)\rightleftharpoons OH-(aq)+HB+(aq)B(aq)+H_2O(l)\rightleftharpoons OH-(aq)+HB+(aq)$

  Weak base example: $NH_3(aq) + H_2O \rightleftharpoons NH_4^+(aq) + OH^-(aq)$

Limitation of Arrhenius concept of acids and bases

Despite its early success and usefulness, the definition of an acid, first proposed by Arrhenius has some limitations.

- The Arrhenius definition of acids explains their behaviour only in aqueous solution.
- In addition, it does not explain why some substances show acidic behaviour in the gaseous state and in non-aqueous solutions. For example, when ammonia and hydrogen chloride gases are brought together, they react to form ammonium chloride as follows:

NH_3 (g) + HCl (g) Æ NH_4Cl (s)

In this reaction, the hydrogen chloride provides hydrogen ion (or proton), H+, which reacts with NH_3 to form NH_4 +. But, this happens in the gaseous state not in aqueous solution. Due to the limitations of Arrhenius' definition, chemists tried to define acids in a more general way..

1.2 Brønsted-Lowry Concept of Acids and Bases

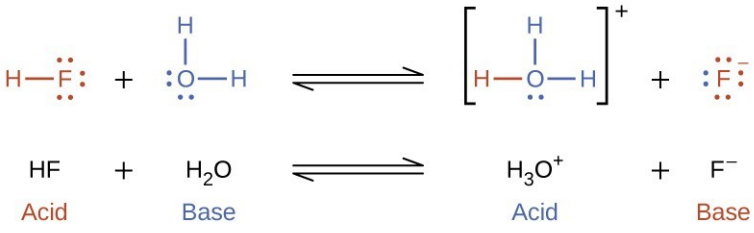
In 1923, J. N. Brønsted in Denmark and T. M. Lowry in Great Britain independently proposed a new acid base theory. They pointed out that acid–base reactions can be seen as proton-transfer reactions and those acids and bases can be defined in terms of this proton (H) transfer.

1.2.1 Brønsted-Lowry acid

- A Brønsted-Lowry acid is a substance that donates a proton (i.e. is a proton donor).

A general scheme can be written as

- $HA(aq) + H_2O(l) \rightleftharpoons H_3O+(aq) + A-(aq)$
- For example, when hydrogen fluoride dissolves in water and ionizes, protons are transferred from hydrogen fluoride molecules to water molecules, yielding hydronium ions and fluoride ions:



$$K = \frac{[H_3O^+][F^-]}{[HF]}$$

- E.g $HCl(aq) + H_2O(l) \rightleftharpoons H_3O+(aq) + Cl-(aq)$ Here, HCl, an acid, donates its proton to water.

1.2.2 Brønsted-Lowry base

- A Brønsted-Lowry base is a substance that accepts a proton (i.e. is a proton acceptor).
- A general scheme can be written as

  $B(aq) + H_2O(l) \rightleftharpoons OH-(aq) + HB+(aq)$ or $A-(aq)+H_2O(l) \rightleftharpoons OH-(aq) +HA(aq)A-(aq)$

- $NH_3(aq)+ H_2O(l) \rightleftharpoons OH-(aq) + NH+_4(aq)$ Here, NH_3, an base, accepts a proton from water.

1.2.2.1 Conjugate Acid-Base Pairs

Conjugate base

- The word *conjugate* means “joined together” (e.g. coupled) especially “in pairs”.
- In acid/base chemistry, a conjugate is a pairing of reactant and product. For example, a deprotonated acid, A^-), is the **conjugate base** of the starting acid, HA.
- $HA \rightleftharpoons H+ + A-$, acid $\rightleftharpoons$ proton + conjugate base
- An acid can also be generalized as HB^+.

  $HB^+ \rightleftharpoons H^+ + B$

  acid $\rightleftharpoons$ proton + conjugate base

- To determine the conjugate base of any acid, simply deprotonate the acid (remove an H^+). The resulting species is the conjugate base.

Conjugate acid

- A **conjugate acid** is the opposite of a conjugate base. A conjugate acid can be generally written as HB^+ or HA.

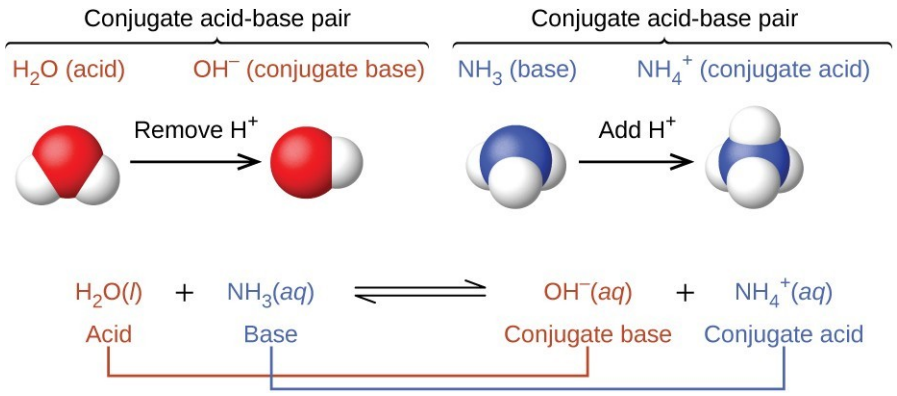
2 B + H+ ⇌ HB^+

base + proton ⇌ conjugate acid

3 A− + H+ ⇌ HA

base + proton ⇌ conjugate

A water molecule (functioning as an acid) transfers a proton to an ammonia molecule (functioning as a base), yielding the conjugate base of water, OH^-, and the conjugate acid of ammonia, NH_4^+ :



- Species that differ by a single proton (H +) constitute a conjugate acid–base pair. Within this pair, the species with the added H + is the acid, and the species without the H + is the base.
    - The conjugate base has one fewer H and one more minus charge than the acid.
    - The conjugate acid has one more H and one fewer minus charge than the base.

Limitation of the Brønsted-Lowry concept acids- bases

$HCl(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + Cl^-(aq)$

In the above reactions, HCl in the first, H_2O are Brønsted-Lowry acids because they are proton donors. Here it is very important to realize that all Arrhenius acids are Brønsted-Lowry acids. However, the reverse is not true because Brønsted-Lowry acids include substances that are not acids according to Arrhenius.

Although the Brønsted-Lowry definition of an acid is more general than the definition proposed by Arrhenius, it still depends on the transfer of protons. However, the presence of acids that are not proton-donors, initiated chemists to search for another definition of acids

1.2.2.1.1 Strengths of Conjugate Acid-Base Pairs

The net direction of an acid-base reaction depends on relative acid and base strengths:

- A reaction proceeds to the greater extent in the direction in which a stronger acid and stronger base form a weaker acid and weaker base.
- The stronger the acid, the weaker is its conjugate base. Similarly, the stronger the base, the weaker is its conjugate acid.

For example, HCl is a strong acid, and its conjugate base Cl^- is a weak base. Acetic acid, CH_3COOH, is a weak acid, and its conjugate base, CH_3COO^-, is a strong base.

The following chart (chart 1.1) shows the strength of conjugate acid-base pairs

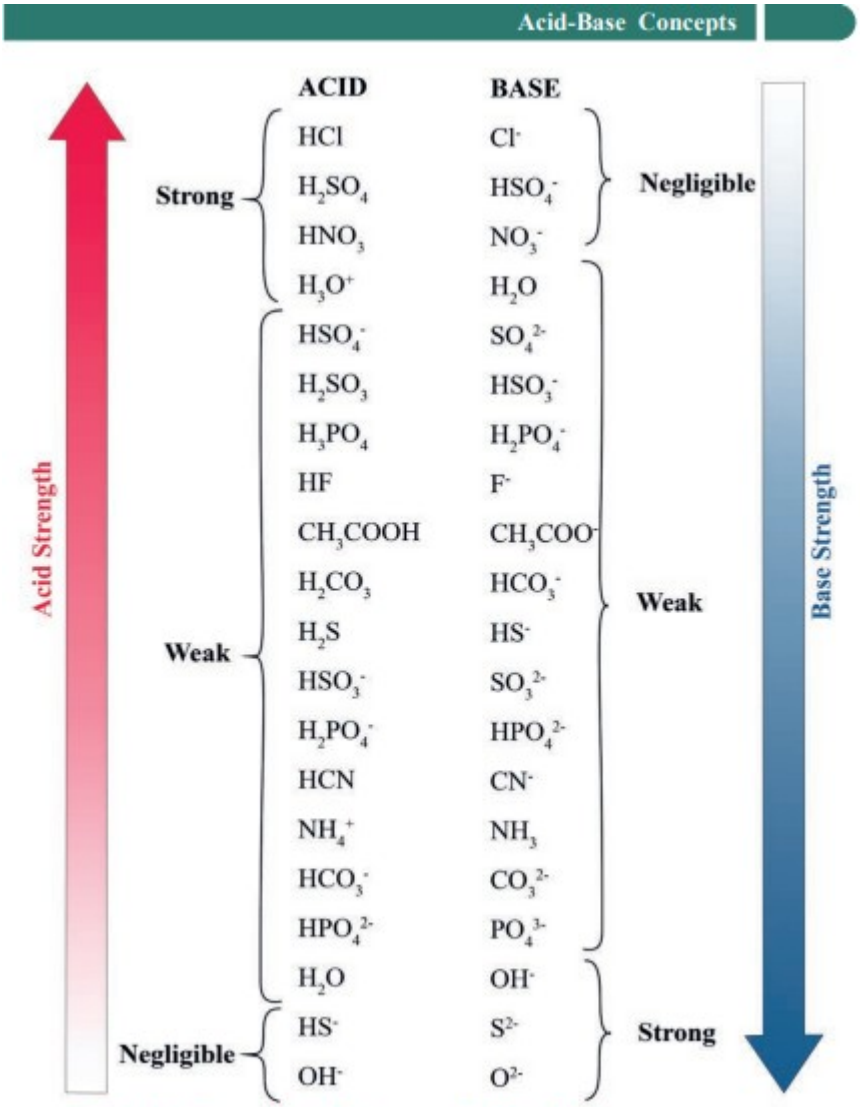
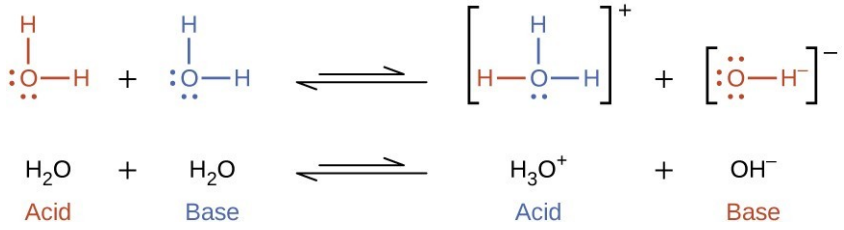


Chart 1.1: Strengths of Conjugate Acid-Base Pairs.

1.2.2.1.2 Auto Ionization of Substances

- Molecular auto ionization (or self-ionization) is a reaction between two identical neutral molecules, especially in a solution, to produce an anion and a cation. If a pure liquid partially dissociates into ions, it is said to be self-ionizing. Water, as we know, is a unique solvent. One of its special properties is its ability to act either as an acid or as a base.
- Water is a very weak electrolyte and therefore a poor conductor of electricity, but it does undergo ionization to a small extent. In pure water or in any aqueous solution, water acts both as an acid and a base.
- A very small fraction of water molecules donate protons to other water molecules to form hydronium ions and hydroxide ions. This type of reaction, in which a substance ionizes when one molecule of the substance reacts with another molecule of the same substance, is referred to as **autoionization**.



- Pure water undergoes autoionization to a very slight extent. Only about two out of every 10^9 molecules in a sample of pure water are ionized at 25 °C. The equilibrium constant for the ionization of water is called the **ion-product constant for water (K_w)**:

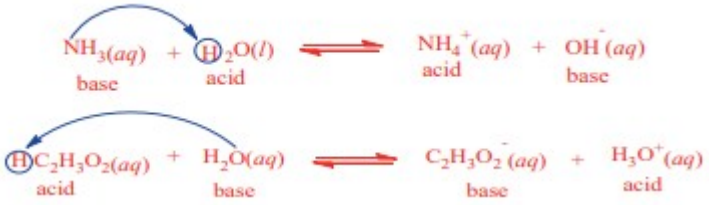
$$H_2O(l) + H_2O(l) \rightleftharpoons H_3O^+(aq) + OH^-(aq) \qquad K_W = [H_3O^+][OH^-]$$

- The slight ionization of pure water is reflected in the small value of the

equilibrium constant; at 25 °C, K_w has a value of $1.0 \times 10{-}14$. The process is endothermic, and so the extent of ionization and the resulting concentrations of hydronium ion and hydroxide ion increase with temperature. For example, at 100 °C, the value for *K*w is about 5.6×10^{-13}, roughly 50 times larger than the value at 25 °C.

1.2.2.1.3 Amphiprotic Species.

- Molecules or ions that cn either donate or accept a proton, depending on the other reactant, are called amphiprotic species. For example, $HCO3^-$ acts as an acid in the presence of OH^- but as a base in the presence of HF.
- The most important amphiprotic species is water itself. When an acid donates a proton to water, the water molecule is a proton acceptor, and hence a base. Conversely, when a base reacts with water, a water molecule donates a proton, and hence acts as an acid. Consider, for example, the reactions of water with the base NH3 and with the acid CH COOH 3 (acetic acid)
- Consider the following reaction of water with the base NH3 and with the acid CH COOH 3 (acetic acid) given below:



In the first case, water reacts as an acid with the base NH_3 . In the second case, water reacts as a base with the acid CH COOH

1.3.1 Lewis Concept of Acids and Bases

Lewis acid-base reaction, we should look for:

- a species that has an available empty orbital to accommodate an electron pair such as the B atom in BF3 , and

- ❖ a species that has lone-pair electrons such as N in NH3. They all have electron pairs available to donate for electron-deficient species.

Note that any molecule or negatively charged species having an excess of electrons can be considered as a Lewis base, and any electron-deficient molecule or positively charged species can be considered as a Lewis acid.

1.3.1.1 Lewis acid

- ➢ A **Lewis acid** is a substance that accepts a pair of electrons (i.e. a lone-pair acceptor).

- HCl(aq)+H_2O(l)⇌H_3O+(aq)+Cl−(aq)HCl(aq)+H_2O(l)⇌H_3O+(aq)+Cl−(aq) Here, HCl dissociates into H^+ and Cl^-. The oxygen on water donates a lone pair of electrons to the free proton and forms a bond to give the hydronium ion, H_3O^+.

1.3.1.2 Lewis base

- ➢ A **Lewis base** is a substance that donates a lone pair of electrons (i.e. lone-pair donor).

  NH_3(aq) + H_2O(l) ⇌ OH–(aq)+) + NH+$_4$(aq) , Here, the lone pair on the nitrogen in ammonia, NH_3, is donated to a proton on water forming a bond to give NH_4^+.

Exercise 1.4

1. Identify Lewis acids and Lewis bases in each of the following reactions.
   a. $H^+ + OH^- \rightleftharpoons H_2O$
   b. $Cl^- + BCl_3 \rightleftharpoons BCl_4^-$
   c. $K^+ + 6H_2O \rightleftharpoons K(H_2O)_6^+$
   d. $OH^- + Al(OH)_3 \rightleftharpoons Al(OH)_4^-$
   e. $CO_2 + H_2O \rightleftharpoons H_2CO_3$
   f. $Ni + 4CO \rightleftharpoons Ni(CO)_4$

Example

1. Representing the Acid-Base Behavior of an Amphoteric Substance

Write separate equations representing the reaction of HSO_3^-

(a) as an acid with OH^-

(b) as a base with HI

Solution

(a) $HSO_3^-(aq) + OH^-(aq) \rightleftharpoons SO_3^{2-}(aq) + H_2O(l)$

(b) $HSO_3^-(aq) + HI(aq) \rightleftharpoons H_2SO_3(aq) + I^-(aq)$

2. Write separate equations representing the reaction of $H_2PO_4^-$

(a) as a base with HBr

(b) as an acid with OH^-

Answer: (a) $H_2PO_4^-(aq) + HBr(aq) \rightleftharpoons H_3PO_4(aq) + Br^-(aq)$; (b)

$H_2PO_4^-(aq) + OH^-(aq) \rightleftharpoons HPO_4^{2-}(aq) + H_2O(l)$

1.4 Ionic Equilibria Of Weak Acids and Weak Bases

Learning Objectives

At the end of this subunit, you will be able to:

- Describe the ionization of water.
- derive the expression of ion product for water, Kw
- explain why water is a weak electrolyte
- Use Kw to calculate [H3 O+] or [OH-] in aqueous solution write an expression for the percent ionization of weak acids or weak bases.
- calculate the percent dissociation of weak acids and bases
- write the expression for the acid-dissociation constant, Ka
- calculate Ka for an acid from the concentration of a given solution and it's pH
- Calculate [H+] and pH of an acidic solution from given values of Ka and the initial concentration of the solution.
- write the expression for the base-dissociation constant, Kb ;
- Calculate Kb for a base from the concentration of a basic solution and its pOH.
- Calculate the [OH-] and pOH of a basic solution from a given value of Kb and the initial concentration of the solution.

1.4.1 The Ion-Product Water

- Through water undergo self-ionization, it is very weak electrolyte. Therefore, the self-ionization of water is

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

The equilibrium constant for the ionization of water is called the **ion-product constant for water (K_w)**: $K_w = [H_3O^+][OH^-]$

The slight extent of self-ionization of pure water can be seen by the small value of the equilibrium constant, K_c.

The auto-ionization of water yields the same number of hydronium and hydroxide ions. Therefore, in pure water, $[H_3O^+] = [OH^-]$. At 25 °C: Because the concentration of ions formed is very small and the concentration of H_2O remains essentially constant, about 56 M at 25° C, we multiply K_c by $[H_2O]^2$ to obtain a new equilibrium constant, the ion-product constant for water,the value of K_c at room temperature is 1.8×10^{-16}

K_c which characterized a chemical equilibrium, at a constant value(at a given temperature, 25°c is reflected in the small value of the equilibrium constant; at 25 °C, K_w has a value of the equilibrium constant expression.

Thus Kw : $K_c[H_2O]^2 = 56 \times 1.8 \times 10^{-16}$ constant = $[H_3O^+][OH^-] = 1.0 \times 10^{-14}$

- $K_W = [H_3O^+][OH^-] = [H_3O^+]^2 = [OH^-]^2 = 1.0 \times 10^{-14}$ So:
- $[H_3O^+] = [OH^-] = \sqrt{1.0 \times 10^{-14}} = 1.0 \times 10^{-7}\ M$

The hydronium ion concentration and the hydroxide ion concentration are the same, and we find that both equal $1.0 \times 10{-}7\ M$.

We call the equilibrium value of the ion product $[H_3O^+][OH^-]$, the ion-product constant for water, Kw . At 25 ° C, the value of Kw is 1.0×10^{-14}.

If you add an acid or a base to water, the concentrations of $[H_3O^+][OH^-]$, will no longer be equal. The equilibrium-constant equation Kw = [H3 O+]

[OH-] will still hold. In any aqueous solution at 25°C, no matter what it contains, the product of [H^+] and [OH^-]must always equal 1.0×10^{-14}.

The equilibrium nature of auto-ionization allows us to define “acidic” and “basic” solutions in terms of relative magnitudes of [H_3O^+] and [OH^-]:

i. a neutral solution, where [H3 O+]=[OH-] .

ii. an acidic solution, where [H3 O+]>[OH-] .

iii. iii. a basic solution, where [OH-]>[H3 O+].

Exercise

1. The ion product of water at 80 °C is $2.4 \times 10{-}13$. What are the concentrations of hydronium and hydroxide ions in pure water at 80 °C?

   Answer: [H3O+] = [OH−] = $4.9 \times 10{-}7\ M$

THE STRENGTH OF ACIDS AND BASES

The pH scale

What do you mean by pH?

- pH is defined as the negative logarithm of H+ ion concentration. Hence the meaning of the name pH is justified as the power of hydrogen. Thus pH is a measure of the concentration of hydrogen ions, the acidity or alkalinity of a solution.
- pH is a unit of measure which describes the degree of acidity or alkalinity of a solution. It is measured on a scale of 0 to 14.
- It is a well-known fact that whether an aqueous solution is acidic, neutral, or basic depends on the hydronium-ion concentration.

- pH provides needed quantitative information by expressing the degree of activity of an acid or base in terms of its hydrogen ion activity.

  pH = -log[H+]

The pH value of a substance is directly related to the ratio of hydrogen ion [H+] and hydroxyl ion [OH-] concentrations.

- If the H+ concentration is greater than the OH-, the material is acidic; i.e., the pH value is less than 7.
- If the OHconcentration is greater than its H+, the material is basic, with a pH value greater than 7.
- If equal numbers of H+ and OHions are present, the material is neutral, with a pH of 7.

Calculate: a. the pH and pOH of a juice solution in which [$H O_3^+$] is 5.0×10^{-3} M

b. the [$H O_3$ +] and[OH^-] of human blood at pH = 7.40 Solution:

a. pH = -log[H+] or pH = -log [$H O_3^+$]

pH = -log [5.0×10^{-3} M] =

pH =3 -log 5.0 =2.3

pH + pOH + =14

pOH = 14- pH , pOH = 14 - 2.3 = 11.7

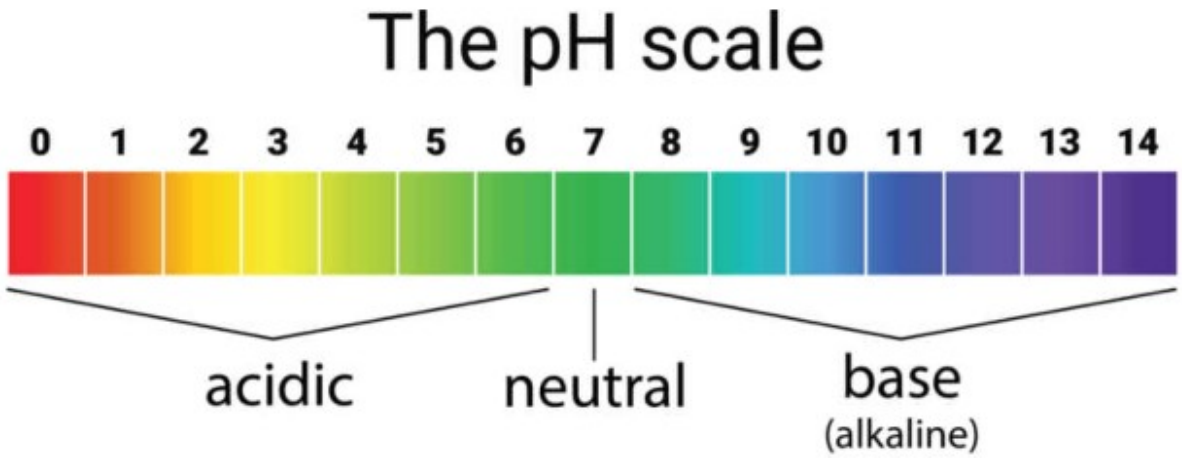
b. pH = 7.40,

- pH + pOH =14
- pOH = 14- pH ,
- pOH =14- 7.40
- pOH = 6.6

a. pOH = 6.6 and pH = 7.40,

- pH = -log[H+] or pH = -log [$H O_3^+$]

- and pOH =-log [OH^-]
- 7.40= -log[H+],
- antilog(7.40) = [H+],
- [H+]= 4.0 x 10^{-8}M
- pOH = 6.6 then pOH =-log [OH^-]
- pOH =-log [OH^-]
- then 6.6 = -log [OH^-]= antilog(6.6) =
- [OH^-] = 2.51 X 10^{-7} M



What is difference between litmus indicator and pH paper indicator?

Ans- Litmus paper is an indicator used to tell if a substance is an acid or a base. The colour of the paper matches up with the numbers on the pH scale to indicate what kind of substance is being tested. For example, Vinegar is an acid and measures 2.4 on the pH scale. pH of acids and bases can be roughly calculated with the help of pH scale while for accurate values we use pH meters.

How pH is related to Hydrogen ion concentration?

Ans- pH value and H+ ion are inversely proportion to each other. Increase in pH decreases the acidic strength and increase in basic strength. The

strength of acid and base solutions compared in terms of their pH values.

pH MEASUREMENT

pH papers

- A rough indication of pH can be obtained using pH papers or indicators, which change color as pH level varies.
- These indicators have limitations on their accuracy, and can be difficult to interpret correctly in colored or murky samples.

pH meter

- More accurate pH measurements are obtained using a pH meter.
- A pH measurement system consists of four components: a pH measuring electrode, a reference electrode, a high input impedance meter, and a sample of the material to be measured.
- The pH electrode can be thought of as a battery, with a voltage that varies with the pH of the measured solution.
- The pH measuring electrode is a hydrogen ion-sensitive glass bulb, with a millivolt output that varies with changes in the relative hydrogen ion concentration inside and outside the bulb.

chemical dyes

- involves the use of chemical dyes called indicators.
- These substances are generally weak acids/bases and can exist in either of two colored forms, depending on whether or not the molecule is protonated, HIn, or has been deprotonated, In^- .
- In aqueous solution, an equilibrium exists: $HIn \rightleftharpoons H^+ + In$

  First color second color

Depending on what other acidic/basic substances are present in the solution, the equilibrium of the indicator will shift, and one or the other colored form of the indicator will predominate and impart its color to the entire solution.

Indicators commonly change colors over a relatively short pH range (about 2 pH units), and when properly chosen can be used to determine the range of the pH of the solution. A given indicator is useful for determining pH only in the region in which it changes color. Indicators are available for measurement of pH in all ranges of acidity and basicity.

Table: Color changes and pH intervals of some important indicators

Name of indicator	pH interval	Color range
Thymol blue	1.2-2.8	Red to yellow
Orange IV	1.3-3.0	Red to yellow
Methyl orange	3.1-4.4	Red to orange to yellow
Cangp red	3.0-5.0	Blue to red
Bromcresol green	3.8-5.4	Yellow to blue
Methyl red	4.4-6.2	Red to yellow
Bromcresol purple	5.2-6.8	Yellow to purple
Bromthymol blue	6.0-7.6	Yellow to blue
Thymol blue	8.0-9.6	Yellow to blue
Alizarin yellow R	10.0-12.0	Yellow to red
Indigo carmine	12.0-13.0	Blue to yellow

By matching the color of a suitable indicator in a solution of known pH with that in an unknown solution, one can determine the pH of the unknown. The second method for the determination of pH involves an instrument called a pH meter/pH pen. The pH pen is designed so that the reading will directly furnish the pH of the solution. A pH pen gives much more precise measurement of pH than does a typical indicator, and is ordinarily used when an accurate determination of pH is needed.

1.4.2 Measures of the Strength of acids and Bases in Aqueous Solution

The strength of acids and bases depends on a number of factors. Some of

the ways to compare the strengths of acids and bases are

- the concentration of hydrogen and hydroxide ions
- pH and pOH
- percent dissociation, Ka and Kb for the reaction describing its ionization in water

1.4.2.1 Concentration of Hydrogen and Hydroxide ions

By definition a strong acid is one that completely dissociates in water to release proton.

In solutions of the same concentration, stronger acids ionize to a greater extent, and so yield higher concentrations of hydronium ions[H_3O^+] than do weaker acids.

Examples of the strong acids are: hydrochloric acid, HCl , nitric acid,HNO_3 , perchloric acid $HClO_4$, and sulfuric acid, H S_2O_4 .

Each of these acids ionize essentially 100 % in solution. By contrast, however, a weak acid, being less willing to donate its proton, will only partially dissociate in solution. Base strength refers to the ability of a base to accept protons.

A strong base accepts more protons readily than a weak base. A solution of a stronger base will contain a larger concentration of hydroxide ions than a solution of a weaker base if both solutions are of equal concentration. The net direction of an acid-base reaction depends on relative acid and base strengths: a reaction proceeds to the greater extent in the direction in which a stronger acid and stronger base form a weaker acid and weaker base

1.4.2.2 pH and pOH

One way to determine the strength of acids is using the pH values. The acid strength increase with smaller pH value, the concentration of hydroxide

ions in a solution can be expressed in terms of the pOH of the solution. Hence, the strength of bases can also be determined from their pOH values. The strength of base increases with decreasing the pOH value.

1.4.2.3 Percent Ionization

Another measure of the strength of an acid is its percent ionization, which is defined as the proportion of ionized molecules on a percentage basis.

$$Percent\ ionization = \frac{Ionized\ \text{acid concentration at equilibrium}}{Initial\ \text{concentration of acid}}\ \text{x}\ 100\ \%$$

Mathematically

The strength of an acid depends on the percentage of the acid molecules that dissociate in water solution. as with acides, the measure of the strength of a base is its percent ionization, which is defined as the proportion of ionized molecules on a percentage bases. Mathematically:

$$percent\ ionization = \frac{ionized\ base\ concentartion\ at\ equilibrium}{initial\ concentration\ of\ base} \times 100\%$$

The percent ionization increases with base strength.Strong acids and strong bases ionize nearly completely in water. But weak acids and weak bases dissociate partially in water, and their percent of ionization is small