

1. Details of Module and its structure

Module Detail	
Subject Name	Chemistry
Course Name	Chemistry 01 (Class XI, Semester 01)
Module Name/Title	Equilibrium: Part 3
Module Id	kech_10703
Pre-requisites	Ionization, equilibrium, solutions, acids and bases
Objectives	<p>After going through the contents of this module the learner will be able to:</p> <ul style="list-style-type: none">• Classify substances as acids or bases according to Arrhenius, Bronsted-Lowry and Lewis concepts;• Classify acids and bases as weak or strong in terms of their ionization constants;• Explain ioniation of water and its dual role as acid and base;• Explain pH scale for representing hydrogen ion concentration.• Apply the pH scale to day to day problems.
Keywords	Ionic equilibrium, concepts of acids and bases, Arrhenius, Bronsted-Lowry, Lewis, ionization constant, pH scale

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1. Ionic Equilibrium in Solutions

It is well known that the aqueous solution of sugar does not conduct electricity. However, when common salt (sodium chloride) is added to water it conducts electricity. Also, the conductance of electricity increases with an increase in concentration of common salt. Michael Faraday classified the substances into two categories based on their ability to conduct electricity. One category of substances conduct electricity in their aqueous solutions and are called electrolytes while the other do not and are thus, referred to as non-electrolytes. There are numerous equilibria that involve ions. In the following sections we will study the equilibria involving ions.

Faraday classified electrolytes into strong and weak electrolytes. Strong electrolytes on dissolution in water are ionized almost completely, while the weak electrolytes are only partially dissociated. For example, an aqueous solution of sodium chloride is comprised entirely of sodium ions and chloride ions, while that of acetic acid mainly contains unionized acetic acid molecules and only some acetate ions and protons. This is because there is almost 100% ionization in case of sodium chloride as compared to less than 5% ionization of acetic acid which is a weak electrolyte. In the case of strong electrolytes, the dissociation is almost complete and therefore, there is no equilibrium being established. This is represented by a single arrow as shown below.

$\text{NaCl(aq)} \rightarrow \text{Na}^+(\text{aq}) + \text{Cl}^-(\text{aq})$ -----Strong electrolyte; almost 100% ionization

In the case of weak electrolytes, equilibrium is established between ionized and unionized forms and in the equation this condition is represented by the sign \rightleftharpoons as shown in the following equation.

$\text{CH}_3\text{COOH(aq)} \rightleftharpoons \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$ weak electrolytes; less than 5% ionization

In weak electrolytes, equilibrium is established between ions and the unionized molecules. This

type of equilibrium involving ions in aqueous solution is called ionic equilibrium. Acids, bases and salts come under the category of electrolytes and may act as either strong or weak electrolytes.

Acids, Bases and Salts

Acids, bases and salts find widespread occurrence in nature. Hydrochloric acid present in the gastric juice is secreted by the lining of our stomach in a significant amount of 1.2-1.5 L/day and is essential for digestive processes. Acetic acid is known to be the main constituent of vinegar. Lemon and orange juices contain citric and ascorbic acids, and tartaric acid is found in tamarind paste. As most of the acids taste sour, the word “acid” has been derived from a Latin word “acidus” meaning sour.

Acids are known to:

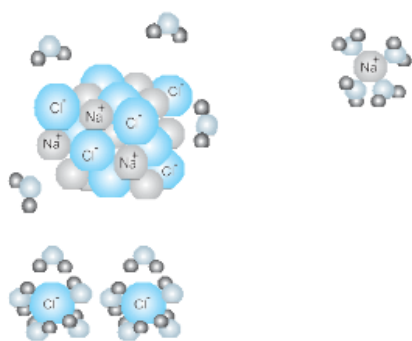
- turn blue litmus paper into red
- taste sour
- liberate dihydrogen on reacting with metals.

Similarly, bases are known to:

- turn red litmus paper blue
- taste bitter
- feel soapy

A common example of a base is washing soda used . When acids and bases are mixed, they react with each other to give salts. Some commonly known examples of salts are sodium chloride, barium sulphate, sodium nitrate. Sodium chloride (common salt) is an important component of our diet and is formed by reaction between hydrochloric acid and sodium hydroxide. It exists in solid state as a cluster of positively charged sodium ions and negatively charged chloride ions which are held together due to electrostatic interactions between oppositely charged species (Fig.1). When sodium chloride is dissolved in water, the electrostatic interactions are reduced and this facilitates the ions to move freely in the solution. Also, they are well-separated due to hydration with water molecules. This is due to the dielectric constant of water which is very high (80).The electrostatic forces between two charges are inversely proportional to dielectric constant of the medium. Water, a universal solvent. Thus,

Fig.1 Dissolution of sodium chloride in water. Na^+ and Cl^- ions are stabilised by their hydration with polar water molecules.



Michael Faraday

(1791–1867)

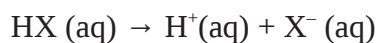
Faraday was born near London into a family of very limited means. At the age of 14 he was an apprentice to a kind bookbinder who allowed Faraday to read the books he was binding. Through a fortunate chance he became laboratory assistant to Davy, and during 1813-4, Faraday accompanied him to the Continent. During this trip he gained much from the experience of coming into contact with many of the leading scientists of the time. In 1825, he succeeded Davy as Director of the Royal Institution laboratories, and in 1833 he also became the first Fullerian Professor of Chemistry. Faraday's first important work was on analytical chemistry. After 1821 much of his work was on electricity and magnetism and different electromagnetic phenomena. His ideas have led to the establishment of modern field theory. He discovered his two laws of electrolysis in 1834. Faraday was a very modest and kind hearted person. He declined all honours and avoided scientific controversies. He preferred to work alone and never had any assistant. He disseminated science in a variety of ways including his Friday evening discourses, which he founded at the Royal Institution. He has been very famous for his Christmas lecture on the 'Chemical History of a Candle'. He published nearly 450 scientific papers.

Comparing, the ionization of hydrochloric acid with that of acetic acid in water we find that

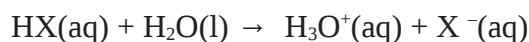
though both of them are polar covalent molecules, former is completely ionized into its constituent ions, while the latter is only partially ionized (< 5%). The extent to which ionization occurs depends upon the strength of the bond and the extent of solvation of ions produced. The terms dissociation and ionization have earlier been used with different meaning. Dissociation refers to the process of separation of ions in water already existing as such in the solid state of the solute, as in sodium chloride. On the other hand, ionization corresponds to a process in which a neutral molecule splits into charged ions in the solution. Here, we shall not distinguish between the two and use the two terms interchangeably.

2. Arrhenius Concept of Acids and Bases

According to Arrhenius theory, acids are substances that dissociates in water to give hydrogen ions $H^+(aq)$ and bases are substances that produce hydroxyl ions $OH^-(aq)$. The ionization of an acid $HX(aq)$ can be represented by the following equations:



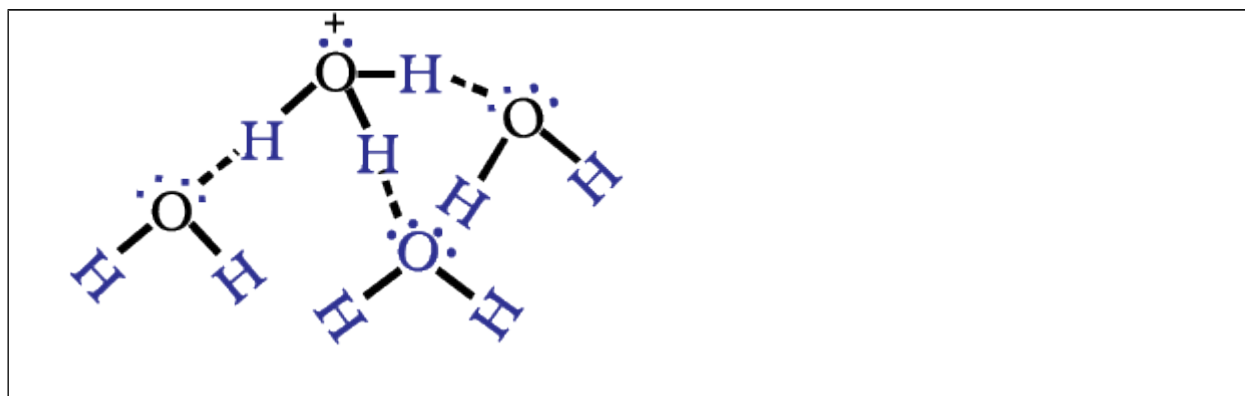
or



A bare proton, H^+ is very reactive and cannot exist freely in aqueous solutions. Thus, it bonds to the oxygen atom of a solvent water molecule to give *trigonal pyramidal hydronium ion*, H_3O^+ $\{[H(H_2O)]^+\}$ (see box). In this chapter we shall use $H^+(aq)$ and $H_3O^+(aq)$ interchangeably to mean the same i.e., a hydrated proton.

Hydronium and Hydroxyl Ions

Hydrogen ion by itself is a bare proton with very small size ($\sim 10^{-15}m$ radius) and intense electric field, binds itself with the water molecule at one of the two available lone pairs on it giving H_3O^+ . This species has been detected in many compounds (e.g., $H_3O^+Cl^-$) in the solid state. In aqueous solution the hydronium ion is further hydrated to give species like $H_5O_2^+$, $H_7O_3^+$ and $H_9O_4^+$. Similarly the hydroxyl ion is hydrated to give several ionic species like $H_3O_2^-$, $H_5O_3^-$ and $H_7O_4^-$ etc.



H_3O^+

Similarly, a base molecule like MOH ionizes in aqueous solution according to the equation:



The hydroxyl ion also exists in the hydrated form in the aqueous solution. Arrhenius concept of acid and base, however, suffers from the limitation of being applicable only to aqueous solutions and also, does

not account for the basicity of substances like, ammonia which do not possess a hydroxyl group.



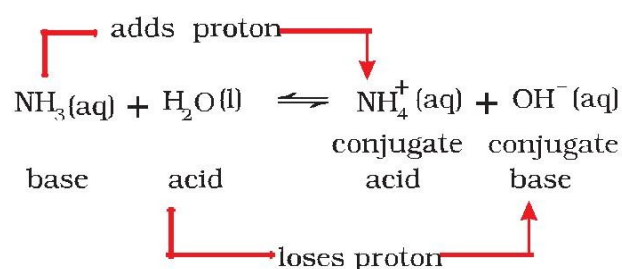
Arrhenius was born near Uppsala, Sweden. He presented his thesis, on the conductivities of electrolyte solutions, to the University of Uppsala in 1884. For the next five years he travelled extensively and visited a number of research centers in Europe. In 1895 he was appointed professor of physics at the newly formed University of Stockholm, serving its rector from 1897 to 1902. From 1905 until his death he was Director of physical chemistry at the Nobel Institute in Stockholm. He continued to work for many years on electrolytic solutions. In 1899 he discussed the temperature dependence of reaction rates on the basis of an equation, now usually known as Arrhenius equation.

He worked in a variety of fields, and made important contributions to immunochemistry, cosmology, the origin of life, and the causes of ice age. He was the first to discuss the green house effect calling by that name. He received Nobel Prize in Chemistry in 1903 for his theory of electrolytic dissociation and its use in the development of chemistry.

3. The Brønsted-Lowry concept of Acids and Bases

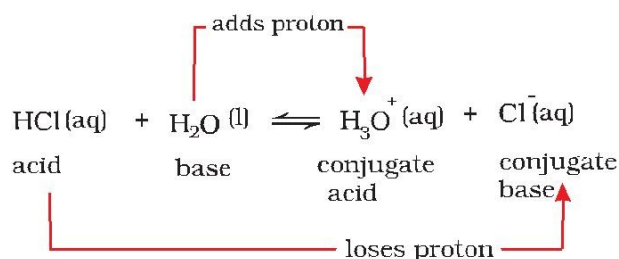
The Danish chemist, Johannes Brønsted and the English chemist, Thomas M. Lowry gave a more general definition of acids and bases. According to Brønsted-Lowry theory, acid is a substance that is capable of donating a hydrogen ion H^+ and bases are substances capable of accepting a hydrogen ion, H^+ . In short, acids are proton donors and bases are proton acceptors.

Consider the example of dissolution of NH_3 in H_2O represented by the following equation:



The basic solution is formed due to the presence of hydroxyl ions. In this reaction, water molecule acts as proton donor and ammonia molecule acts as proton acceptor and are thus, called Lowry-Brønsted acid and base, respectively. In the reverse reaction, H^+ is transferred from NH_4^+ to OH^- . In this case, NH_4^+ acts as a Brønsted acid while OH^- acted as a Brønsted base. The acid-base pair that differs only by one proton is called a **conjugate acid-base pair**. Therefore, OH^- is called the conjugate base of an acid H_2O and NH_4^+ is called conjugate acid of the base NH_3 . If Brønsted acid is a strong acid then **its conjugate base is a weak base and vice-versa**. It may be noted that conjugate acid has one extra proton and each conjugate base has one less proton.

Consider the example of ionization of hydrochloric acid in water. $HCl(aq)$ acts as an acid by donating a proton to H_2O molecule which acts as a base.



It can be seen in the above equation, that water acts as a base because it accepts the proton. The species H_3O^+ is produced when water accepts a proton from HCl . Therefore, Cl^- is a conjugate base of HCl and HCl is the

conjugate acid of base Cl^- . Similarly, H_2O is a conjugate base of an acid H_3O^+ and H_3O^+ is a conjugate acid of base H_2O .

It is interesting to observe the dual role of water as an acid and a base. In case of reaction with HCl water acts as a base while in case of ammonia it acts as an acid by donating a proton.

Problem 1

What will be the conjugate bases for the following Brønsted acids: HF , H_2SO_4 and HCO_3^- ?

Solution

The conjugate bases should have one proton less in each case and therefore the corresponding conjugate bases are: F^- , HSO_4^- and CO_3^{2-} respectively.

Problem 2

Write the conjugate acids for the following Brønsted bases: NH_2^- , NH_3 and HCOO^- .

Solution

The conjugate acid should have one extra proton in each case and therefore the corresponding conjugate acids are: NH_3 , NH_4^+ and HCOOH respectively.

Problem 3

The species H_2O , HCO_3^- , HSO_4^- and NH_3 can act both as Brønsted acids and bases. For each case, give the corresponding conjugate acid and conjugate base.

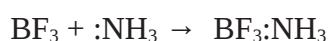
Solution

The answer is given in the following Table:

Species	Conjugate acid	Conjugate base
H_2O	H_3O^+	OH^-
HCO_3^-	H_2CO_3	CO_3^{2-}
HSO_4^-	H_2SO_4	SO_4^{2-}
NH_3	NH_4^+	NH_2^-

4. Lewis concept of Acids and Bases

G.N. Lewis in 1923 defined an acid as a species which accepts electron pair and base which donates an electron pair. As far as bases are concerned, there is not much difference between Brönsted-Lowry and Lewis concepts, as the base provides a lone pair in both the cases. However, in Lewis concept many acids do not have proton. A typical example is reaction of electron deficient species BF_3 with NH_3 . BF_3 does not have a proton but still acts as an acid and reacts with NH_3 by accepting its lone pair of electrons. The reaction can be represented by,



Electron deficient species like AlCl_3 , Co^{3+} , Mg^{2+} , etc., can act as Lewis acids while species like H_2O , NH_3 , OH^- etc., which can donate a pair of electrons, can act as Lewis bases.

Problem 4

Classify the following species into Lewis acids and Lewis bases and show how these act as such:

- (a) OH^- (b) F^- (c) H^+ (d) BCl_3
- 3

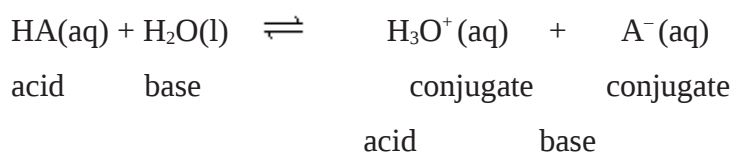
Solution

- (a) Hydroxyl ion is a Lewis base as it can donate an electron lone pair (:OH^-).
- (b) Fluoride ion acts as a Lewis base as it can donate any one of its four electron lone pairs.
- (c) A proton is a Lewis acid as it can accept a lone pair of electrons from bases like hydroxyl ion and fluoride ion.
- (d) BCl_3 acts as a Lewis acid as it can accept a lone pair of electrons from species like ammonia or amine molecules.

5. Ionization of Acids and Bases

Arrhenius concept of acids and bases becomes useful in case of ionization of acids and bases as mostly ionizations in chemical and biological systems occur in aqueous medium. Strong acids like perchloric acid (HClO_4), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) are termed *strong* because they are almost

completely dissociated into their constituent ions in an aqueous medium, thereby acting as proton (H^+) donors. Similarly, strong bases like lithium hydroxide (LiOH), sodium hydroxide (NaOH), potassium hydroxide (KOH), caesium hydroxide (CsOH) and barium hydroxide $Ba(OH)_2$ are almost completely dissociated into ions in an aqueous medium giving hydroxyl ions, OH^- . According to Arrhenius concept they are strong acids and bases as they are able to completely dissociate and produce H_3O^+ and OH^- ions respectively in the medium. Alternatively, the strength of an acid or base may also be gauged in terms of Brønsted-Lowry concept of acids and bases, wherein a strong acid means a good proton donor and a strong base implies a good proton acceptor. Consider the acid-base dissociation equilibrium of a weak acid HA,

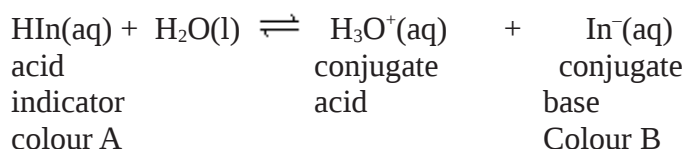


In section 3, we saw that acid (or base) dissociation equilibrium is dynamic involving a transfer of proton in forward and reverse directions. Now, the question arises that if the equilibrium is dynamic then with passage of time which direction is favoured? What is the driving force behind it? In order to answer these questions we shall deal into the issue of comparing the strengths of the two acids (or bases) involved in the dissociation equilibrium. Consider the two acids HA and H_3O^+ present in the above mentioned acid-dissociation equilibrium. We have to see which amongst them is a stronger proton donor. Whichever exceeds in its tendency of donating a proton over the other shall be termed as the stronger acid and the equilibrium will shift in the direction of weaker acid. Say, if HA is a stronger acid than H_3O^+ , then HA will donate protons and not H_3O^+ , and the solution will mainly contain A^- and H_3O^+ ions. The equilibrium moves in the direction of formation of weaker acid and weaker base because **the stronger acid donates a proton to the stronger base**.

It follows that as a strong acid dissociates completely in water, the resulting base formed would be very weak i.e., **strong acids have very weak conjugate bases**. Strong acids like perchloric acid ($HClO_4$), hydrochloric acid (HCl), hydrobromic acid (HBr), hydroiodic acid (HI), nitric acid (HNO_3) and sulphuric acid (H_2SO_4) will give conjugate base ions ClO_4^- , Cl^- , Br^- , I^- , NO_3^- and HSO_4^- , which are much weaker bases than H_2O . Similarly a very strong base would give a very weak conjugate acid. On the other hand, a weak acid say HA is only partially dissociated in aqueous medium and thus, the solution mainly contains undissociated HA molecules. Typical weak acids are nitrous acid (HNO_2), hydrofluoric acid (HF) and acetic acid (CH_3COOH). It should be noted that the weak acids have very strong conjugate bases. For example, NH_2^- , O^{2-} and

H^- are very good proton acceptors and thus, much stronger bases than H_2O .

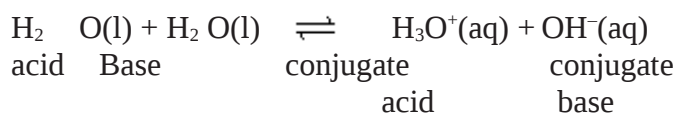
Certain water soluble organic compounds like phenolphthalein and bromothymol blue behave as weak acids and exhibit different colours in their acid (HIn) and conjugate base (In^-) forms.



Such compounds are useful as indicators in acid-base titrations, and finding out H^+ ion concentration.

6. The Ionization Constant of Water and its Ionic Product

Some substances like water are unique in their ability of acting both as an acid and a base. We have seen this in case of water in section 3. In presence of an acid, HA it accepts a proton and acts as the base while in the presence of a base, B^- it acts as an acid by donating a proton. In pure water, one H_2O molecule donates proton and acts as an acid and another water molecules accepts a proton and acts as a base at the same time. The following equilibrium exists:



The dissociation constant is represented by,

$$K = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]} \quad (1)$$

The concentration of water is omitted from the denominator as water is a pure liquid and its concentration remains constant. $[\text{H}_2\text{O}]$ is incorporated within the equilibrium constant to give a new constant, K_w , which is called the **ionic product of water**.

$$K_w = [\text{H}^+][\text{OH}^-] \quad (2)$$

The concentration of H^+ has been found out experimentally as 1.0×10^{-7} M at 298 K. And, as dissociation of water produces equal number of H^+ and OH^- ions, the concentration of hydroxyl ions, $[\text{OH}^-] = [\text{H}^+] = 1.0 \times 10^{-7}$ M. Thus, the value of K_w at 298K,

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = (1 \times 10^{-7})^2 = 1 \times 10^{-14} \text{ M}^2 \quad (3)$$

The value of K_w is temperature dependent as it is an equilibrium constant.

The density of pure water is 1000 g / L and its molar mass is 18.0 g /mol. From this, the molarity of pure water can be given as,

$$[\text{H}_2\text{O}] = (1000 \text{ g /L}) (1 \text{ mol}/18.0 \text{ g}) = 55.55 \text{ M.}$$

Therefore, the ratio of dissociated water to that of undissociated water can be given as,

$$10^{-7} / (55.55) = 1.8 \times 10^{-9} \text{ or } \sim 2 \text{ in } 10^{-9} \text{ (thus, equilibrium lies mainly towards undissociated water)}$$

We can distinguish acidic, neutral and basic aqueous solutions by the relative values of the H_3O^+ and OH^- concentrations:

$$\text{Acidic: } [\text{H}_3\text{O}^+] > [\text{OH}^-]$$

$$\text{Neutral: } [\text{H}_3\text{O}^+] = [\text{OH}^-]$$

$$\text{Basic : } [\text{H}_3\text{O}^+] < [\text{OH}^-]$$

7. The pH Scale

Hydronium ion concentration in molarity is more conveniently expressed on a logarithmic scale known as the **pH scale**. The pH of a solution is defined as the negative logarithm to base 10 of the activity (a_{H^+}) of hydrogen ion. In dilute solutions ($< 0.01 \text{ M}$), activity of hydrogen ion (H^+) is equal in magnitude to molarity represented by $[\text{H}^+]$. It should be noted that activity has no units and is defined as:

$$a_{\text{H}^+} = [\text{H}^+] / \text{mol L}^{-1}$$

From the definition of pH, the following can be written,

$$\text{pH} = -\log a_{\text{H}^+} = -\log [\text{H}^+] \text{ Thus, an acidic solution of HCl } (10^{-2} \text{ M}) \text{ will have a pH} = 2.$$

Similarly, a basic solution of NaOH having $[\text{OH}^-] = 10^{-4} \text{ M}$ and $[\text{H}_3\text{O}^+] = 10^{-10} \text{ M}$ will have a pH = 10. At 25 °C, pure water has a concentration of hydrogen ions, $[\text{H}^+] = 10^{-7} \text{ M}$. Hence, the pH of pure water is given as: $\text{pH} = -\log(10^{-7}) = 7$

Acidic solutions possess a concentration of hydrogen ions, $[H^+] > 10^{-7}$ M, while basic solutions possess a concentration of hydrogen ions, $[H^+] < 10^{-7}$ M. Thus, we can summarise that

Acidic solution has $pH < 7$

Basic solution has $pH > 7$

Neutral solution has $pH = 7$

Now again, consider the equation (3) at 298 K

$$K_w = [H_3O^+] [OH^-] = 10^{-14}$$

Taking negative logarithm on both sides of equation, we obtain

$$\begin{aligned} &= -\log \{[H_3O^+] \\ &-\log K_w [OH^-]\} \\ &= -\log [H_3O^+] - \log \\ & \quad [OH^-] \\ &= -\log 10^{-14} \\ pH + pOH &= 14 \quad (4) \end{aligned}$$

Note that although K_w may change with temperature the variations in pH with temperature are so small that we often ignore it.

pK_w is a very important quantity for aqueous solutions and controls the relative concentrations of hydrogen and hydroxyl ions as their product is a constant. It should be noted that as the pH scale is logarithmic, a change in pH by just one unit also means change in $[H^+]$ by a factor of 10. Similarly, when the hydrogen ion concentration, $[H^+]$ changes by a factor of 100, the value of pH changes by 2 units. Now you can realise why the change in pH with temperature is often ignored.

Measurement of pH of a solution is very essential as its value should be known when dealing with biological and cosmetic applications. The pH of a solution can be found roughly with the help of pH paper that has different colour in solutions of different pH. Now-a-days pH paper is available with four strips on it. The different strips have different colours (Fig. 2) at the same pH. The pH in the range of 1-14 can be determined with an accuracy of ~ 0.5 using pH paper.

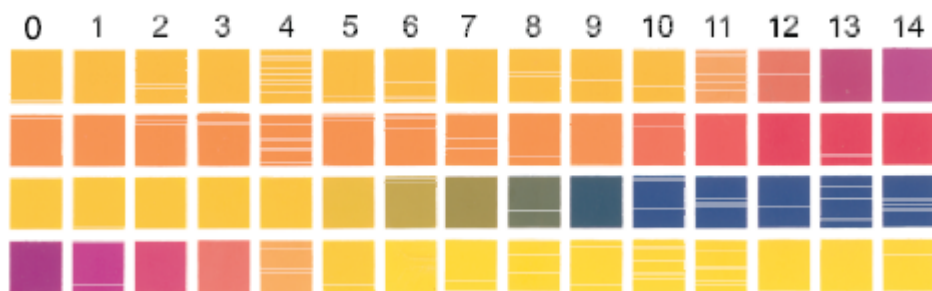


Fig. 2 pH-paper with four strips that may have different colours at the same pH

For greater accuracy pH meters are used. pH meter is a device that measures the pH-dependent electrical potential of the test solution within 0.001 precision. pH meters of the size of a writing pen

are now available in the market. The pH of some very common substances are given in Table 1.

Table 1 The pH of Some Common Substances

Name of the Fluid	pH	Name of the Fluid	pH
Saturated solution of NaOH	~15	Black Coffee	5.0
0.1 M NaOH solution	13	Tomato juice	~4.2
Lime water	10.5	Soft drinks and vinegar	~3.0
Milk of magnesia	10	Lemon juice	~2.2
Egg white, sea water	7.8	Gastric juice	~1.2
Human blood	7.4	1M HCl solution	~0
Milk	6.8	Concentrated HCl	~-1.0
Human Saliva	6.4		

Problem 5

The concentration of hydrogen ion in a sample of soft drink is $3.8 \times 10^{-3}M$. What is its pH ?

Solution

$$pH = -\log[3.8 \times 10^{-3}]$$

$$= -\{\log[3.8] + \log[10^{-3}]\}$$

$$= -\{(0.58) + (-3.0)\} = -\{-2.42\} = 2.42$$

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

Problem 6

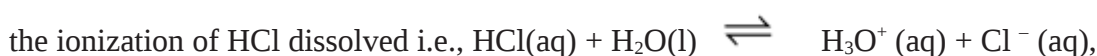
Calculate pH of a 1.0×10^{-8} M solution of HCl.

Solution



$$K_w = [\text{OH}^-][\text{H}_3\text{O}^+] = 10^{-14}$$

Let, $x = [\text{OH}^-] = [\text{H}_3\text{O}^+]$ from H_2O . The H_3O^+ concentration is generated (i) from



and (ii) from ionization of H_2O . In these very dilute solutions, both sources of H_3O^+ must be considered:

$$[\text{H}_3\text{O}^+] = 10^{-8} + x$$

$$K_w = (10^{-8} + x)(x) = 10^{-14} \text{ or } x^2 + 10^{-8}x - 10^{-14} = 0 \quad [\text{OH}^-] = x = 9.5 \times 10^{-8}$$

So, $\text{pOH} = 7.02$ and $\text{pH} = 6.98$

8. Summary

All substances that conduct electricity in aqueous solutions are called **electrolytes**. Acids, bases and salts are electrolytes and the conduction of electricity by their aqueous solutions is due to anions and cations produced by the **dissociation or ionization of electrolytes** in aqueous solution. The strong electrolytes are completely dissociated. In weak electrolytes there is equilibrium between the ions and the unionized electrolyte molecules. According to **Arrhenius**, **acids** give hydrogen ions while bases produce hydroxyl ions in their aqueous solutions. **Brönsted-Lowry** on the other hand, defined an acid as a proton donor and a base as a proton acceptor. When a Brönsted-Lowry acid reacts with a base, it produces its conjugate base and a conjugate acid corresponding to the base with which it reacts. Thus a **conjugate pair of acid-base** differs only by one proton. **Lewis** further generalised the definition of an acid as an electron pair acceptor and a base as an electron pair donor. The expressions for ionization (equilibrium) constants of weak acids (K_a) and weak bases (K_b) are developed using Arrhenius definition. The degree of ionization and its dependence on concentration and common ion are discussed. The **pH scale** ($\text{pH} = -\log[\text{H}^+]$) for the hydrogen ion concentration (activity) has been introduced and extended to other quantities ($\text{pOH} = -\log[\text{OH}^-]$).