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27

CHAPTER

Acids and Bases

CONTENTS

There are **three concepts of acids and bases** in current use. Each has its own peculiar advantages. The student should understand all the three concepts :

(*a*) Arrhenius concept
(*b*) Bronsted-Lowry concept
(*c*) Lewis concept

ARRHENIUS CONCEPT

Savante Arrhenius (1884) proposed his concept of acids and bases. According to this concept, **an acid is a compound that releases H^+ ions in water; and a base is a compound that releases OH^- ions in water.**

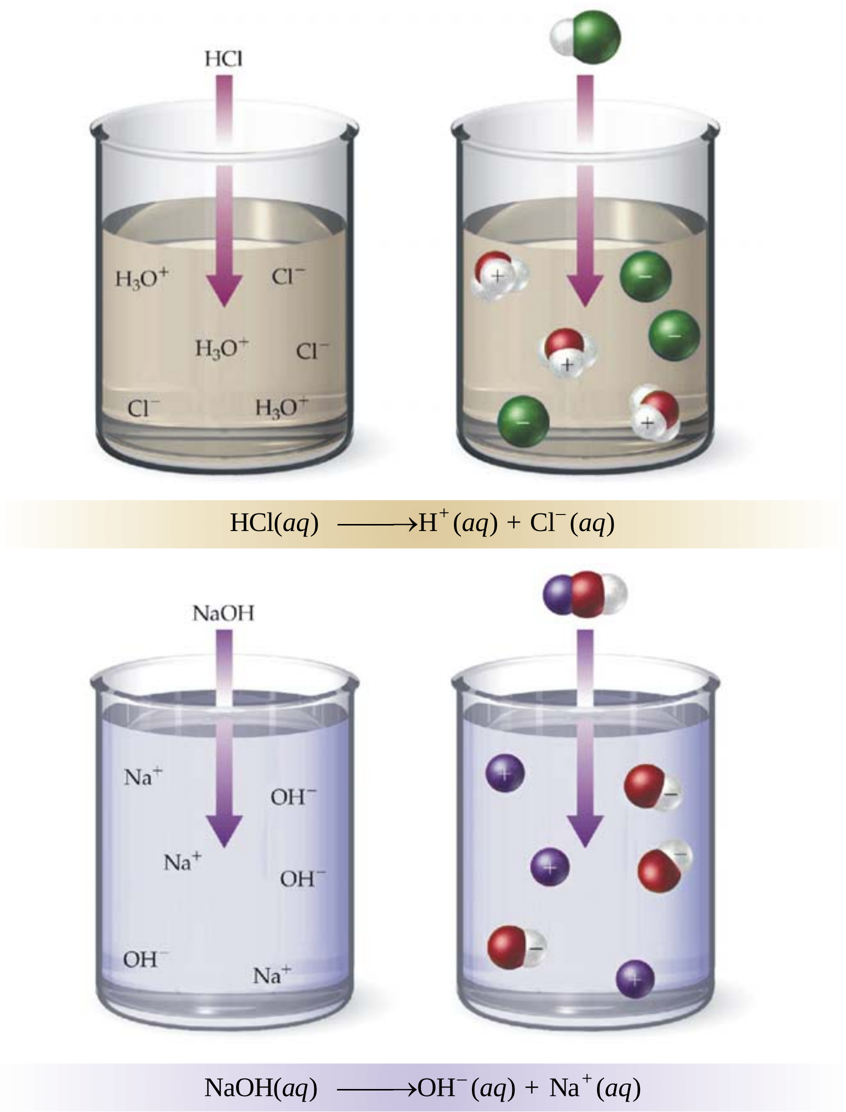
For example, HCl is an Arrhenius acid and NaOH is an Arrhenius base.

$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

$$NaOH(aq) \qquad OH^-(aq) + Na^+(aq)$$

Limitations of Arrhenius Concept

Arrhenius concept of acids and bases proved to be very useful in the study of chemical reactions. However, it has the following limitations :

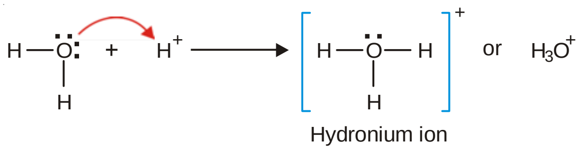


$$HCl(aq) \longrightarrow H^+(aq) + Cl^-(aq)$$

$$NaOH(aq) \longrightarrow OH^-(aq) + Na^+(aq)$$

Figure 27.1
HCl is an Arrhenius acid. NaOH is an Arrhenius base.

(1) **Free H^+ and OH^- ions do not exist in water.** The H^+ and OH^- ions produced by acids and bases respectively do not exist in water in the free state. They are associated with water molecules to form complex ions through hydrogen bonding. Thus the H^+ ion forms a **hydronium ion** :



Similarly, OH^- ion forms the complex $H_3O_2^-$.

Although the hydrogen and hydroxyl ions are associated with water molecule, for simplicity we shall generally write them H^+ and OH^-.

(2) **Limited to water only.** Arrhenius defined acids and bases as compounds producing H^+ and OH^- ions in water only. But a truly general concept of acids and bases should be appropriate to other solvents as well.

(3) **Some bases do not contain OH^-.** Arrhenius base is one that produces OH^- ions in water. Yet there are compounds like ammonia (NH_3) and calcium oxide (CaO) that are bases but contain no OH^- ions in their original formulation.

Arrhenius models of acids and bases, no doubt, proved very helpful in interpreting their action. However on account of its limitations the Arrhenius concept needed to be modified.

BRONSTED–LOWRY CONCEPT

In 1923 J.N. Bronsted and J.M. Lowry independently proposed a broader concept of acids and bases. According to this theory,

an acid is any molecule or ion that can donate a proton (H^+)

a base is any molecule or ion that can accept a proton

For brevity we can say that an acid is a proton donor while a base is a proton acceptor.

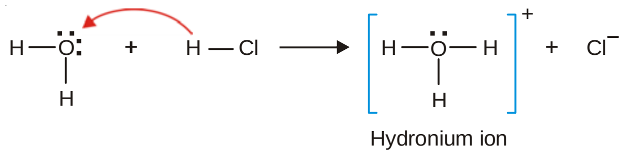
Figure 27.2
A Bronsted acid is a proton donor and a Bronsted base is a proton acceptor.

An acid qualifying Bronsted-Lowry concept is termed a **Bronsted-Lowry acid** or simply **Bronsted acid.**

A base qualifying Bronsted-Lowry concept is termed a **Bronsted-Lowry base** or simply **Bronsted base.**

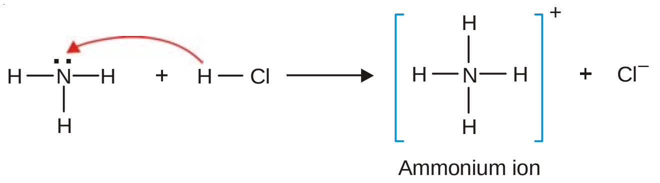
Examples of Bronsted acids and bases

(1) **HCl gas and H_2O.** When dry HCl gas dissolves in water, each HCl molecule donates a proton to a water molecule to produce hydronium ion.



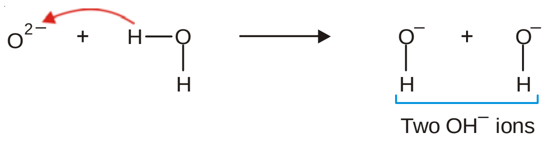
Thus HCl gas is a Bronsted acid and water that accepts a proton is a Bronsted base.

(2) **HCl and Ammonia, NH_3.** HCl gas reacts with ammonia (NH_3) to form solid NH_4Cl.



HCl is a proton donor and hence a Bronsted acid, while NH_3 is a proton acceptor and a Bronsted base.

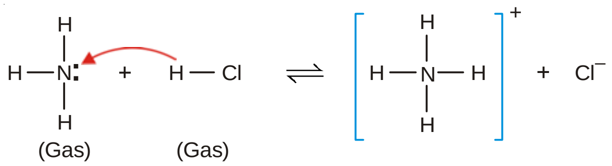
(3) **Calcium oxide and H_2O.** When calcium oxide is dissolved in water, it is converted to calcium hydroxide. Here a water molecule donates a proton to oxide ion, O^{2-}, and is a Bronsted acid. The oxide ion accepts a proton and give $2OH^-$ ions, hence is a Bronsted base.



Bronsted-Lowry concept is superior to Arrhenius concept

(1) **Much wider scope.** Arrhenius concept of acids and bases is restricted to the study of substances which can release H^+ or OH^- ions in water. Bronsted-Lowry concept embraces all molecules and ions that can donate a proton (acids) and those which can accept a proton (bases).

(2) **Not limited to aqueous solutions.** The Bronsted-Lowry model is not limited to aqueous solutions as is the case with Arrhenius model. It can be extended even to the gas phase. For example, gaseous ammonia (a Bronsted base) can react with hydrogen chloride gas (a Bronsted acid) to give ammonium chloride.



Here a proton is donated by HCl to NH_3 as shown above. Note that this is not considered as an acid-base reaction according to Arrhenius concept.

(3) **Release of OH^- not necessary to qualify as a base.** Arrhenius base is a substance that releases OH^- ions in water. On the other hand, Bronsted base is a substance that accepts a proton. Thus liquid ammonia (NH_3) does not produce OH^- ions in water but it is a recognised base. But according to Bronsted-Lowry model, it qualifies as a base since it can accept a proton to form NH_4^+ (an acid).

$$\underset{\text{base}}{NH_3} + H^+ \rightleftharpoons \underset{\text{acid}}{NH_4^+}$$

Conjugate Acid-Base pairs

In an acid-base reaction the acid (HA) gives up its proton (H^+) and produces a new base (A^-). The new base that is related to the original acid is called a **conjugate** (*meaning related*) **base.** Similarly the original base (B^-) after accepting a proton (H^+) gives a new acid (HB) which is called a **conjugate acid.** A hypothetical reaction between the acid HA and the base B^- will illustrate the above definitions.

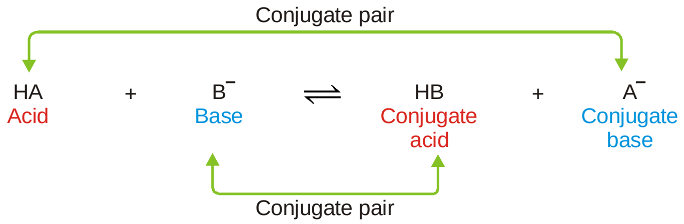
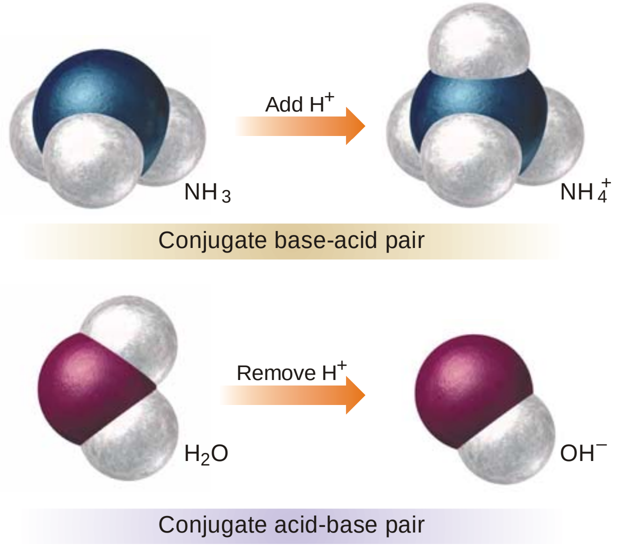


Figure 27.3
Illustration of conjugate pairs.

The acid (HA) and the conjugate base (A^-) that are related to each other by donating and accepting a single proton, are said to constitute a conjugate Acid-Base pair.

It may be noted that in any acid-base reaction, there are two conjugate acid-base pairs, Thus, in the above equation, the two conjugate pairs are : HA and A^-; and HB and B^-.



Examples of Conjugate Acid-base pairs

Let us consider the reaction between HCl (*aq*) and NH_3 (*aq*) which is illustrated below in Fig. 27.4.

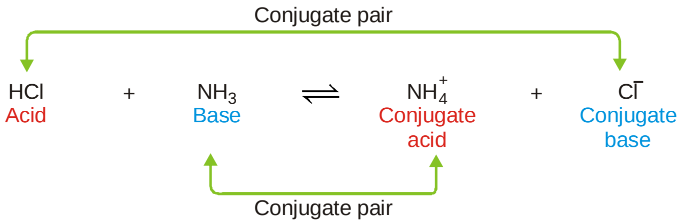


Figure 27.4
In every acid-base reaction involving H^+ transfer, there are two acid-base conjugate pairs.

In this case HCl (acid) and Cl^- (conjugate base) constitute one acid-base conjugate pair. Base NH_3 and the conjugate acid (NH_4^+) comprise the second acid-base conjugate pair.

Now let us consider the reaction between acetic acid and water to form the conjugate base CH_3COO^- and the conjugate acid H_3O^+.

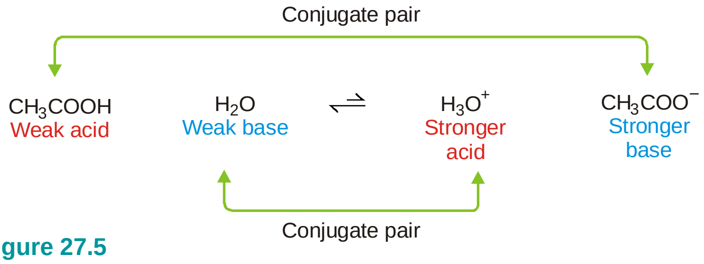


Figure 27.5
A weak acid (CH_3COOH) produces a strong conjugate base (CH_3COO^-); and a weaker base (H_2O) gives a stronger conjugate acid (H_3O^+).

We know that acetic acid is less than 1% ionised in water. Since the equilibrium is displaced toward the left, we can say that : (*i*) CH_3COO^- is a stronger base than H_2O; and (*ii*) H_3O^+ is a stronger acid than CH_3COOH. Thus we can conclude that :

(*a*) **a weak base has strong conjugate acid**

(*b*) **a weak acid has a strong conjugate base**

TABLE 27.1. SOME EXAMPLES OF BRONSTED ACIDS AND BASES

Acid		Base		Conjugate Acid		Conjugate Base
HCl	+	H_2O	$\rightleftharpoons$	H_3O^+	+	Cl^-
HNO_3	+	H_2O	$\rightleftharpoons$	H_3O^+	+	NO_3^-
HCO_3^-	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CO_3^{2-}
CH_3COOH	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CH_3COO^-
HCN	+	H_2O	$\rightleftharpoons$	H_3O^+	+	CN^-
H_2S	+	H_2O	$\rightleftharpoons$	H_3O^+	+	HS^-
H_2O	+	NH_3	$\rightleftharpoons$	NH_4^+	+	OH^-
H_2O	+	CO_3^{2-}	$\rightleftharpoons$	HCO_3^-	+	OH^-
H_2O	+	H_2O	$\rightleftharpoons$	H_3O^+	+	OH^-

Classes of Bronsted acids and bases

There are a variety of **Bronsted acids :**

(1) **Monoprotic acids** which are capable of donating one proton only *e.g.*,

$$HF \longrightarrow H^+ + F^-$$

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

(2) **Polyprotic acids** which are capable of donating two or more protons *e.g.*, H_2SO_4, H_3PO_4, carbonic acid (H_2CO_3), hydrosulphuric acid, etc.

$$H_2S \longrightarrow 2H^+ + S^{2-}$$

$$\begin{array}{l} COOH \\ | \\ COOH \\ \text{oxalic acid} \end{array} \longrightarrow 2H^+ + \begin{array}{l} COO^- \\ | \\ COO^- \\ \text{oxalate ion} \end{array}$$

Similarly, there are **Bronsted bases :**

(1) **Monoprotic bases** which can accept one proton.

$$HS^- + H^+ \longrightarrow H_2S$$

$$H_2O + H^+ \longrightarrow H_3O^+$$

(2) **Polyprotic bases** which can accept two or more protons *e.g.*, anions of diprotic and triprotic acids.

$$SO_4^{2-} + 2H^+ \longrightarrow H_2SO_4$$

$$PO_4^{3-} + 3H^+ \longrightarrow H_3PO_4$$

Amphiprotic substances

Molecules or ions that can behave both as Bronsted acid and base are called amphiprotic substances. For example, with HCl, water acts as a base in accepting a proton from the acid.

$$\underset{\text{acid}}{HCl} + \underset{\text{base}}{H_2O} \longrightarrow H_3O^+ + Cl^-$$

However, water is an acid while donating a proton to ammonia.

$$\underset{\text{base}}{NH_3} + \underset{\text{acid}}{H_2O} \longrightarrow NH_4^+ + OH^-$$

Listed below are some **amphiprotic ions :**

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

$$H_2CO_3 \xleftarrow{+H^+} HCO_3^- \xrightarrow{-H^+} CO_3^{2-}$$

$$HPO_4^- \xleftarrow{+H^+} HPO_4^{2-} \xrightarrow{-H^+} PO_4^{3-}$$

Strength Bronsted acids and bases

The strength of a Bronsted acid depends upon its tendency to donate a proton. The strength of a Bronsted base depends on its ability to accept a proton. For example, HCl is nearly 100% ionised in water. Its reaction with water can be depicted by the equation :

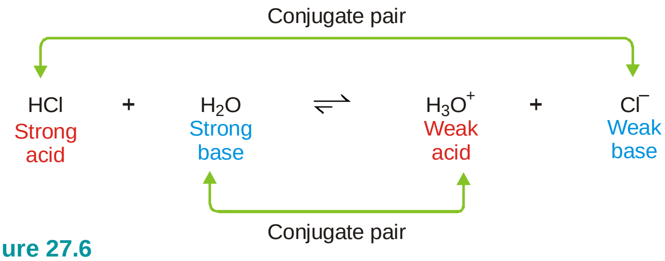


Figure 27.6
A strong acid HCl gives a weak conjugate base (Cl^-); and a strong base (H_2O) gives a weak conjugate acid (H_3O^+).

Since the reaction has proceeded almost completely to the right, it means that HCl has a strong tendency to lose a proton. Also, the base H_2O has a strong ability to accept a proton. The overall situation is that the acid and base on the left are each stronger than the conjugate acid and conjugate base on the right. That is why the equilibrium is displaced to the right. Thus we can conclude that :

a strong acid has a weak conjugate base

a strong base has a weak conjugate acid

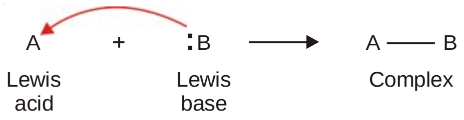
LEWIS CONCEPT OF ACIDS AND BASES

In the early 1930s, G.N. Lewis proposed even a more general model of acids and bases. According to Lewis theory,

an acid is an electron-pair acceptor

a base is an electron-pair donor

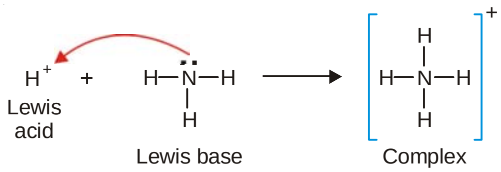
Lewis pictured an acid and base as sharing the electron pair provided by the base. This creates a covalent bond (or coordinate bond) between the **Lewis acid** and the **Lewis base.** The resulting combination is called a **Complex**. If the Lewis acid be denoted by A and the Lewis base by B, then the fundamental equation of the Lewis theory can be written as :



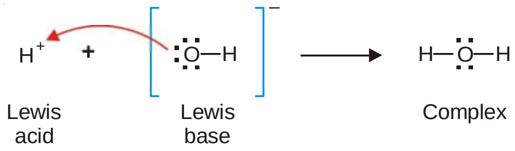
It may be noted that : (1) all cations or molecules short of an electron-pair act as Lewis acids; and (2) all anions or molecules having a lone electron-pair act as Lewis bases.

Examples of Lewis reactions

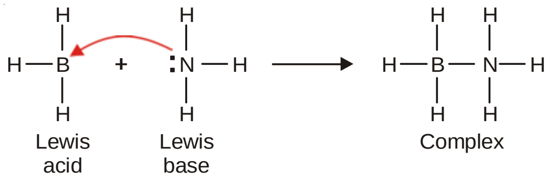
(1) **Between H^+ and NH_3.** Proton (H^+) is a Lewis acid as it can accept an electron-pair. Ammonia molecule (: NH_3) has an electron-pair which it can donate and is a Lewis base. Thus the Lewis reaction between H^+ and NH_3 can be written as :



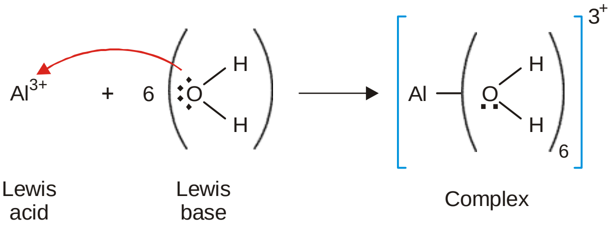
(2) **Between H^+ and OH^-.** A proton (H^+) is an electron-pair acceptor and, therefore, a Lewis acid. The OH^- is an electron-pair donor and hence a Lewis base. Thus Lewis reaction between H^+ and OH^- can be written as :



(3) **Between BF_3 and NH_3.** BF_3 has six valence electrons with B atom which can accept an electron-pair and is a Lewis acid. The N atom of : NH_3 has a lone electron-pair and is a Lewis base. Lewis reaction between BF_3 and NH_3 may be written as :



(4) **Hydration of Al^{3+}.** The hydration of a metal ion such as Al^{3+} is also a Lewis reaction.



Superiority of Lewis model of acids and bases

The useful but limited model of Arrhenius was replaced by a more general model of Bronsted and Lowry. Even a more general model was proposed by Lewis. However, the Bronsted-Lowry model is now used in common practice.

TABLE 27.2. THREE MODELS FOR ACIDS AND BASES

Model	Definition of acid	Definition of base
Arrhenius (1884)	H^+ producer	OH^- producer
Bronsted-Lowry (1923)	H^+ donor	H^+ acceptor
Lewis (1939)	electron-pair acceptor	electron-pair donor

The advantages of the Lewis acid-base model are :

(1) All the Bronsted-Lowry acid base reactions are covered by the Lewis model. It is so because the transfer or gain of a proton is accompanied by the loss or donation of an electron-pair in both types of reactions.

(2) Many reactions which do not involve transfer of a proton *e.g.*,

$$BF_3 + NH_3 \longrightarrow BF_3 - NH_3$$

are also covered by the Lewis theory.

Neutralisation in the Bronsted-Lowry theory

According to Bronsted-Lowry theory, all acid-base neutralisation reactions in aqueous solution can be represented by a single chemical reaction :

$$H_3O^+ + OH^- \longrightarrow 2H_2O$$

This is so because the acid molecule always produces H_3O^+ by donating a proton to a H_2O molecule, and the base molecule always produces OH^- by accepting a proton from another H_2O molecule.

Water can act both as an acid and a base

Water is an amphoteric substance. It can behave either as an acid or a base. One molecule of water transfers a proton to another molecule. There results a hydronium ion (H_3O^+) and a hydroxyl ion (OH^-).

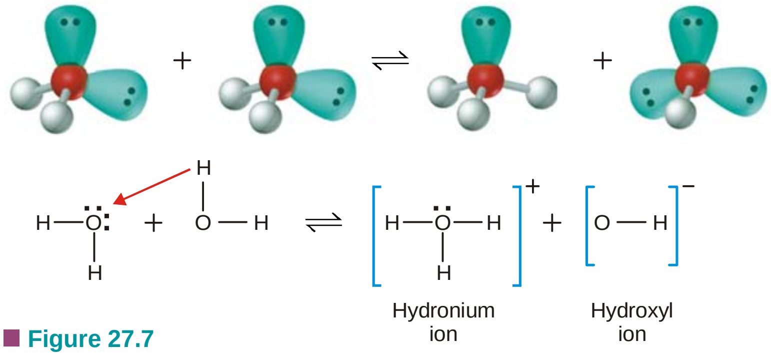


Figure 27.7
Auto-ionisation of water.

In this reaction one molecule of water acts as a Bronsted acid and the other as a Bronsted base.

The above reaction in which water molecules interact to produce a hydronium ion and a OH^- ion is called **auto-ionisation of water.** It may be written as

$$2H_2O \rightleftharpoons H_3O^+ + OH^-$$

That auto-ionisation actually occurs was proved by Friedrich Kohlrausch (1840-1910). He found that even the purest water conducts electricity to a very small extent which was due to the generation of H_3O^+ and OH^- ions in water by ionisation.

Water auto-ionisation is most fundamental to our study of acids and bases. Obviously, H^+ ions are associated with water to give hydronium ions (H_3O^+). But for simplicity we shall generally write the dissociation equilibrium of water as

$$H_2O \rightleftharpoons H^+ + OH^-$$

RELATIVE STRENGTH OF ACIDS

The strength of an acid depends on its ability to transfer its proton (H^+) to a base to form its conjugate base. When a monoprotic acid (HA) dissolves in water, it transfers its proton to water (a Bronsted base) to form hydronium ion (H_3O^+) and a conjugate base.

$$HA + H_2O \rightleftharpoons H_3O^+ + \underset{\text{conjugate base}}{A^-} \qquad ...(1)$$

For simplifying our discussion, we take

$$H_3O^+ = H^+$$

Thus we can write the equilibrium reaction (1) as

$$HA + H_2O \rightleftharpoons H^+ + A^- \qquad ...(2)$$

This equation represents the dissociation of the acid HA into H^+ ion and A^- ion.

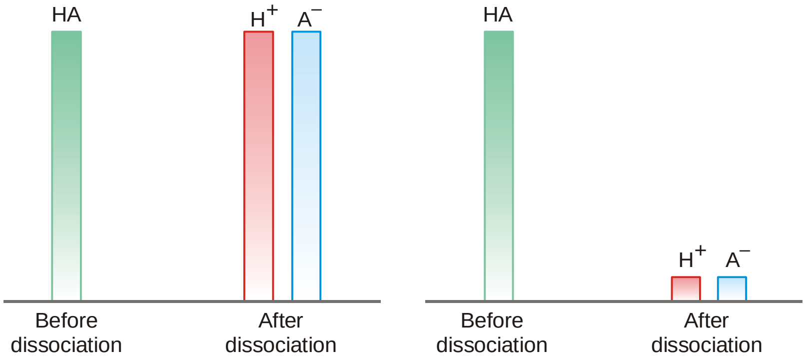
Applying the Law of Mass action to the acid dissociation equilibrium, we can write

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad ...(3)$$

where K_a is called the **acid dissociation constant.** In dilute solution of the acid (HA) we note that the concentration of liquid water remains essentially constant. Therefore, the terms included in the equilibrium expression (3).

The strength of an acid is defined as the concentration of H^+ ions in its aqueous solution at a given temperature.

From the equilibrium (3), it is evident that the concentration of H^+ ions, $[H^+]$, depends on the value of K_a. **Therefore, the value of K_a for a particular acid is a measure of its acid strength or acidity.**



Strong acid (a) Weak acid (b)

Figure 27.8

Graphical extent of concentrations of H^+ and A^- in aqueous solution compared to original concentration of HA for : (*a*) a strong acid; and (*b*) a weak acid.

TABLE 27.3. VALUES OF K_a FOR SOME COMMON MONOPROTIC ACIDS

Formula	Name	K_a
HSO_4^-	Hydrogen sulphate Ion	1.2×10^{-2}
$HClO_2$	Chlorous acid	1.2×10^{-2}
$ClCH_2COOH$	Monochloroacetic acid	1.35×10^{-3}
HF	Hydrofluoric acid	7.2×10^{-4}
HNO_2	Nitrous acid	4.0×10^{-4}
CH_3COOH	Acetic acid	1.8×10^{-5}
HOCl	Hypochlorous acid	3.5×10^{-8}
HCN	Hydrocyanic acid	6.2×10^{-10}
NH_4^+	Ammonium ion	5.6×10^{-10}
HOC_6H_5	Phenol	1.6×10^{-10}

↑ Increasing acid strength

In any aqueous solution of a strong acid, practically all the original acid (HA) is dissociated and the value of K_a is large. On the other hand, a weak acid in aqueous solution is dissociated to a very small extent and the value of K_a is also small. Thus in general we can say that **the value of acid dissociation constant is large for a strong acid while it is small for a weak acid.**

The units of K_a are mol/l but are customarily omitted. The strong acids are not listed in the above table because practically all the acid is dissociated and its concentration at equilibrium cannot be measured accurately.

Calculation of Relative strength of Weak acids from K_a

We have seen that for an acid in aqueous solution we have, $HA \rightleftharpoons H^+ + A^-$

and
$$K_a = \frac{[H^+][A^-]}{[HA]}$$

Let C moles per litre be the concentration of the acid and α its degree of dissociation. Then,

$$[H^+] = C\alpha$$
$$[A^-] = C\alpha$$
$$[HA] = C(1-\alpha)$$

Substituting the values in the equilibrium expression we have

$$K_a = \frac{C\alpha \times C\alpha}{C(1-\alpha)}$$
$$= \frac{C\alpha^2}{(1-\alpha)}$$

For weak acids $1-\alpha \simeq 1$. Therefore,

$$K_a = C\alpha^2$$

For two different acids, 1 and 2, let the degree of dissociation be α_1 and α_2; and the dissociation constants K_1 and K_2. Then,

$$\text{for acid 1} \qquad K_1 = C\alpha_1^2 \qquad \text{...(1)}$$
$$\text{for acid 2} \qquad K_2 = C\alpha_2^2 \qquad \text{...(2)}$$

Dividing equation (1) by (2), we get,

$$\frac{\alpha_1}{\alpha_2} = \sqrt{\frac{K_1}{K_2}}$$

Since $[H^+]$ is a measure of acid strength and it depends on the degree of dissociation α, we can write

$$\frac{\text{Strength of acid 1}}{\text{Strength of acid 2}} = \sqrt{\frac{K_1}{K_2}}$$

Evidently, **the ratio** $\sqrt{K_1/K_2}$ **would give us the relative strengths of the two acids.**

SOLVED PROBLEM 1. The dissociation constants of formic acid and acetic acid are 21.4×10^{-5} and 1.81×10^{-5} respectively. Find the relative strengths of the acids.

SOLUTION

$$\frac{\text{Strength of HCOOH}}{\text{Strength of CH}_3\text{COOH}} = \sqrt{\frac{K_{HCOOH}}{K_{CH_3COOH}}}$$
$$= \sqrt{\frac{21.4 \times 10^{-5}}{1.81 \times 10^{-5}}}$$
$$= 3.438$$

Thus formic acid is **3.438** times stronger than acetic acid.

SOLVED PROBLEM 2. Two hypothetical acids HA and HB have the dissociation constants 1×10^{-3} and 1×10^{-5} respectively in water at 25°C. Calculate the strength of HA with respect to HB.

SOLUTION

$$\frac{\text{Strength of HA}}{\text{Strength of HB}} = \sqrt{\frac{K_{\text{HA}}}{K_{\text{HB}}}}$$

$$= \sqrt{\frac{1 \times 10^{-3}}{1 \times 10^{-5}}}$$

$$= \mathbf{10}$$

Thus HA is ten times stronger than HB.

RELATIVE STRENGTH OF BASES

According to the Arrhenius concept, a base is a substance which produces OH^- ions in aqueous solution. The basic properties of such a substance are due to these hydroxyl ions. Let us consider a base BOH whose dissociation can be represented as

$$BOH \rightleftharpoons B^+ + OH^- \qquad \text{...(1)}$$

Applying the Law of Mass action to the above equilibrium we can write the equilibrium expression as

$$K_b = \frac{[B^+][OH^-]}{[BOH]} \qquad \text{...(2)}$$

K_b is called the **base dissociation constant or base ionisation constant.**

The strength of a base is defined as the concentration of OH^- ions in its aqueous solution at a given temperature.

From the equilibrium expression (2), it is evident that the concentration of OH^- ions, $[OH^-]$, depends on the value of K_b. Therefore, the value of K_b for a certain base is a measure of its base strength. In the aqueous solution of a strong base, practically all the original base is dissociated and the value of K_b is large. In the case of a weak base, it is dissociated in aqueous solution to a very small extent and the value of K_b is also small.

Calculation of K_b

The equilibrium expression for the dissociation of a base is

$$K_b = \frac{[B^+][OH^-]}{[BOH]}$$

If C is the molar concentration of the base and α its degree of dissociation, the equilibrium concentration of the various species are

$$[BOH] = C(1-\alpha) \text{ mol/l}$$
$$[B^+] = C\alpha \text{ mol/l}$$
$$[OH^-] = C\alpha \text{ mol/l}$$

Substituting the values in the equilibrium expression

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

$$= \frac{\alpha^2 C}{(1-\alpha)}$$

Knowing the values of α and C, K_b can be calculated.

K_b for Bronsted bases

Not all bases conform to the Arrhenius definition of a base. Ammonia (NH_3) and amines are the examples. Bronsted equilibrium for a base in aqueous solution may be written as :

$$\underset{\text{base}}{B} + \underset{\text{acid}}{H_2O} \rightleftharpoons \underset{\substack{\text{conjugate}\\\text{acid}}}{BH^+} + \underset{\substack{\text{conjugate}\\\text{base}}}{OH^-}$$

The equilibrium constant K_b for this general reaction is

$$K_b = \frac{[BH^+]\,[OH^-]}{[B]}$$

The Bronsted equilibrium expression is virtually the same as that of the Arrhenius equilibrium.

The concentration of OH^- ions determines the strength of a Bronsted base.

The values of K_b for some weak bases at 25°C are listed in Table 27.4.

Table 27.4. VALUES OF K_b FOR SOME COMMON WEAK BASES AT 25°C

Formula	Name	K_b
NH_3	Ammonia	1.8×10^{-5}
CH_3NH_2	Methylamine	4.38×10^{-4}
$C_2H_5NH_2$	Ethylamine	5.6×10^{-4}
$C_6H_5NH_2$	Aniline	3.8×10^{-10}
C_5H_5N	Pyridine	1.7×10^{-9}

THE pH OF SOLUTIONS

A knowledge of the concentration of hydrogen ions (more specifically hydronium ions) is of the greatest importance in chemistry. Hydrogen ion concentrations are typically quite small numbers. Therefore, chemists report the hydrogen ion concentration of a solution in terms of pH. It is defined as **the negative of the base-10 logarithm (log) of the H^+ concentration.** Mathematically it may be expressed as

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

where $[H^+]$ is the concentration of hydrogen ions in moles per litre.

Alternative and more useful forms of pH definition are :

$$\mathbf{pH = \log \frac{1}{[H^+]}}$$

and $$\mathbf{[H^+] = 10^{-pH}}$$

The pH concept is very convenient for expressing hydrogen ion concentration. It was introduced by Sorensen in 1909. It is now used as a general way of expressing other quantities also, for example,

(*a*) Concentration of OH^- ions in aqueous solution of a base is expressed as

$$p\,[OH^-] = -\log\,[OH^-]$$

(*b*) Equilibrium constant for water is written as

$$pK_w = -\log\,[K_w]$$

For any quantity *X*, we can write

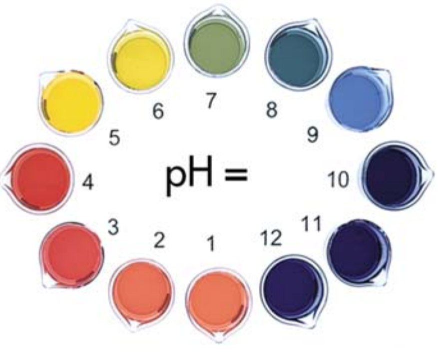
$$pX = -\log X$$

The "**p**" in these expression means **"– log of the quantity"**

MEASUREMENT OF pH

pH can be measured:

☐ by addition of a pH indicator into the solution under study. The indicator colour varies depending on the pH of the solution. Using indicators, qualitative determinations can be made with universal indicators that have broad colour variability over a wide pH range and quantitative determinations can be made using indicators that have strong colour variability over a small pH range. Extremely precise measurements can be made over a wide pH range using indicators that have multiple equilibriums in conjunction with spectrophotometric methods to determine the relative abundance of each pH-dependent component that make up the colour of solution.



Colour Key

☐ by using a pH meter together with pH-selective electrodes (pH glass electrode, hydrogen electrode, quinhydrone electrode, ion sensitive field effect transistor and others).

☐ by using pH paper, indicator paper that turns colour corresponding to a pH on a colour key. pH paper is usually small strips of paper (or a continuous tape that can be torn) that has been soaked in an indicator solution, and is used for approximations.

Substance	**pH**	
Hydrochloric Acid 10M	-1.0	🟥
Battery acid	0.5	🟥
Gastric acid	1.5 – 2.0	🟥
Lemon juice	2.4	🟥
Cola	2.5	🟧
Vinegar	2.9	🟧
Orange or apple juice	3.5	🟧
Beer	4.5	🟨
Acid Rai	<5.0	🟨
Coffee	5.0	🟨
Tea or healthy skin	5.5	🟨

Substance	**pH**	
Milk	6.5	🟩
Pure Water	7.0	🟩
Healthy human saliva	6.5 – 7.4	🟩
Blood	7.34 – 7.45	🟦
Seawater	7.7 – 8.3	🟦
Hand soap	9.0 – 10.0	🟦
Household ammonia	11.5	🟦
Bleach	12.5	🟦
Household lye	13.5	🟦
Caustic Soda	13.9	⬛

As the pH scale is logarithmic, it doesn’t start at zero. Thus the most acidic of liquids encountered can have a pH of as low as **5**. The most alkaline typically has pH of **14**.

The *Hydrangea macrophylla* blossoms in pink or blue, depending on soil pH. In acidic soils, the flowers are blue; in alkaline soils, the flowers are pink.

The measurement of pH

The pH of a given solution can be measured with the help of an apparatus called **pH meter.** This consists of a *voltameter* connected to two electrodes (Fig. 27.9).

(*a*) **a standard electrode** of known potential; and

(*b*) **a special electrode** (the probe) enclosed in a glass membrane that allows migration of H^+ ions. The glass case contains a reference solution of dilute HCl.

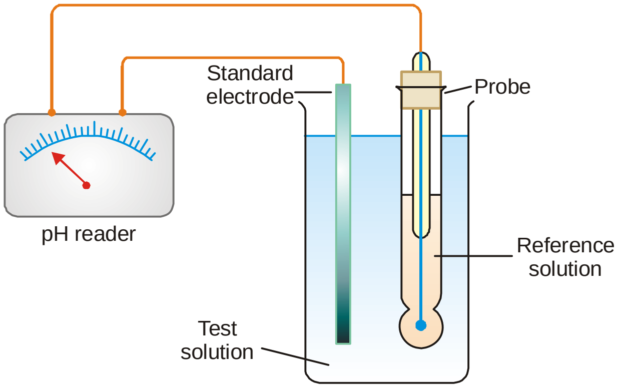


Figure 27.9
A pH meter.

The two electrodes are dipped in the solution to be tested. If this solution has a different pH from the solution in the probe, an electrical potential results. Thus the potential between the standard electrode and the glass electrode varies with the pH of the solution under test. This potential is recorded by an inbuilt potentiometer of the pH meter. The potentiometer reading is automatically converted electrically to a direct reading of the pH of the unknown solution. Knowing the pH of the solution its hydrogen ion concentration can be calculated.

pH Scale

In order to express the hydrogen ion concentration or acidity of a solution, a pH scale was evolved. The pH is defined as

$$\text{pH} = -\log [\text{H}^+] \qquad \text{or} \qquad [\text{H}^+] = 10^{-\text{pH}}$$

The hydrogen ion concentration of different acidic solutions were determined experimentally. These were converted to pH values using the above relations. Then these pH values were computed on a scale taking water as the reference substance. **The scale on which pH values are computed is called the pH scale.**

Water dissociates to H^+ and OH^- ions to a very small degree so that we have the equilibrium.

$$\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^- \qquad \text{...(1)}$$

We can write the equilibrium expression as

$$K = \frac{[\text{H}^+]\,[\text{OH}^-]}{[\text{H}_2\text{O}]} \qquad \text{...(2)}$$

Since water is so little dissociated, the concentration of undissociated molecules, $[H_2O]$, is presumed to be constant. Therefore from expression (2) we can write

$$[\text{H}^+]\,[\text{OH}^-] = K\,[\text{H}_2\text{O}] = K_w = \text{a constant.} \qquad \text{...(3)}$$

where K_w is called the **water dissociation constant or the water ionisation constant.**

When the concentrations of H^+ and OH^- ions in water are expressed in mole per litre, the value of

K_w found experimentally is 1.0×10^{-14}. From the equation (1) it is obvious that one molecule of water dissociates to give one H^+ ion and one OH^- ion. This means that the concentration of H^+ and OH^- ions in pure water is equal. Using the expression (3), we have

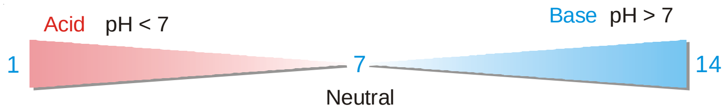
$$[H^+]\,[OH^-] = \sqrt{K_w} = \sqrt{1.0 \times 10^{-14}}$$

or $$[H^+] = [OH^-] = 1.0 \times 10^{-7}\ \text{mol/l}$$

Thus the H^+ ion and OH^- ion concentrations in pure water are both 10^{-7} mol l^{-1} at 25°C and it is said to be neutral. In acidic solution, however, the concentration of H^+ ions must be greater than 10^{-7} mol l^{-1}. Similarly in a basic solution, the concentration of OH^- ions must be greater than 10^{-7} mol l^{-1}. Thus we can state :

neutral solution	$[H^+] = [OH^-]$
acidic solution	$[H^+] > [OH^-]$
basic solution	$[H^+] < [OH^-]$

Expressing the $[H^+]$ in terms of pH for the different solutions cited above, we get what we call the **pH scale.** On this scale (Fig. 27.9) the values range from 0 to 14. Since pH is defined as – log $[H^+]$ and the hydrogen ion concentration of water is 10^{-7}, the pH of water is 7. **All solutions having pH less than 7 are acidic and those with pH greater than 7 are basic.**



As shown by the pH scale, pH decreases with the increase of $[H^+]$. **The lower the pH, higher is the $[H^+]$ or acidity.**

NUMERICAL PROBLEMS BASED ON pH

To understand the pH concept fully, one must have a good exercise in the related numerical problems. Here we will review and discuss certain useful relations that the student is expected to know.

How to calculate $[H^+]$ and $[OH^-]$ from K_w. In any aqueous solution, the product of $[H^+]$ and $[OH^-]$ is always equal to K_w. This is so irrespective of the solute and relative concentrations of H^+ and OH^- ions. However, the value of K_w depends on temperature. At 25°C it is 1.0×10^{-14}. Thus,

$$[H^+]\,[OH^-] = 1.0 \times 10^{-14}$$

Each of $[H^+]$ and $[OH^-]$ in pure water at 25°C is 10^{-7}. The concentration of H^+ and OH^- ions are expressed in gram moles per litre.

The concentration of H^+ and OH^- ions can be calculated from the expressions :

$$[H^+] = \frac{K_w}{[OH^-]}$$

$$[OH^-] = \frac{K_w}{[H^+]}$$

Relation between pH and pOH

We have already stated that pH concept can also be used to express small quantities as $[OH^-]$ and K_w. Thus we have

$$\text{pOH} = -\log\,[OH^-]$$
$$\text{p}K_w = -\log\,k_w$$

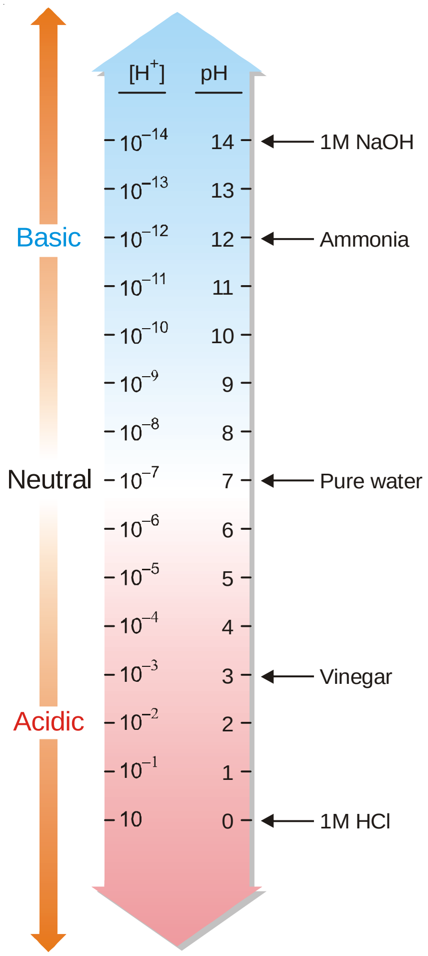
Let us consider the log form of the expression

$$
\begin{aligned}
& & K_w &= [H^+][OH^-]\\
\text{That is,} & & \log K_w &= \log [H^+] + \log [OH^-]\\
\text{or} & & -\log K_w &= -\log [H^+] - \log [OH^-]\\
\text{Thus} & & pK_w &= pH + pOH\\
\text{Since} & & K_w &= 1.0 \times 10^{-14}\\
& & pK_w &= -\log (1.0 \times 10^{-14}) = 14.00
\end{aligned}
$$

Hence, for any aqueous solution at 25°C, pH and pOH add up to 14.00. That is,

$$\mathbf{pH + pOH = 14.00}$$

In general, the pH problems may be of the following types :



■ **Figure 27.10**
pH Scale and pH values of some common substances.

TYPE 1. Interpreting the pH

SOLVED PROBLEM 1. The hydrogen ion concentration of a fruit juice is 3.3×10^{-2} M. What is the pH of the juice ? Is it acidic or basic ?

SOLUTION

The definition of pH is

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

We are given $[H^+] = 3.3 \times 10^{-2}$

Substituting into the definition of pH, we get

$$
\begin{aligned}
pH &= -\log (3.3 \times 10^{-2})\\
&= -(-1.48)\\
&= \mathbf{1.48}
\end{aligned}
$$

Since the pH is less than 7.00 the **solution is acidic**.

SOLVED PROBLEM 2. If a solution has a pH of 7.41, determine its H^+ concentration.

SOLUTION

$$
\begin{aligned}
\text{Since} & & pH &= -\log [H^+]\\
& & -pH &= \log [H^+]
\end{aligned}
$$

Now $[H^+]$ can be calculated by taking antilog of – pH :

$$[H^+] = \text{antilog} (-pH)$$

In this case,

$$[H^+] = \text{antilog} (-7.41) = 10^{-7.41}$$

Therefore, the $[H^+]$ of the given solution is $\mathbf{3.9 \times 10^{-8}}$ **M**

TYPE 2. Calculating OH^- from pH

SOLVED PROBLEM. If a solution has a pH of 5.50 at 25°C, calculate its $[OH^-]$.

SOLUTION

We know that :

$$
\begin{aligned}
pH + pOH &= 14.00\\
pOH &= 14.00 - pH = 14.00 - 5.50 = 8.50
\end{aligned}
$$

Then $\quad \text{pOH} = -\log[\text{OH}^-] = 8.50$

$\log[\text{OH}] = -8.50$

$[\text{OH}^-] = \text{antilog}(-8.50)$

$= \mathbf{3.2 \times 10^{-9}\ M}$

TYPE 3. Calculating the pH of a strong acid

SOLVED PROBLEM 1. Calculate the pH of 0.001 M HCl.

SOLUTION

HCl is a strong acid and it is completely dissociated in aqueous solution.

$$\underset{0.001\text{M}}{\text{HCl}} \rightleftharpoons \underset{0.001\text{M}}{\text{H}^+} + \text{Cl}^-$$

For every molecule of HCl, there is one H^+. Therefore,

$[\text{H}^+] = [\text{HCl}]$

or $\quad [\text{H}^+] = 0.001\ \text{M}$

$\therefore \quad \text{pH} = -\log(0.001)$

$= -\log(1 \times 10^{-3})$

$= -\log 1 + 3\log 10$

$= 0 + 3 = 3$

Therefore, the pH of 0.001 M HCl is **3**.

SOLVED PROBLEM 2. The pH of a solution of HCl is 2. Find out the amount of acid present in a litre of the solution.

SOLUTION

$\text{pH} = 2$

$-\log[\text{H}^+] = 2$ (*By definition*)

The dissociation of HCl takes place according to the equation :

$$\text{HCl} \longrightarrow \text{H}^+ + \text{Cl}^-$$

One molecule of HCl gives one ion of H^+. Therefore,

$[\text{H}^+] = [\text{HCl}] = 10^{-2}\ \text{M}$

$\therefore$ Amount of HCl in one litre $= 10^{-2} \times \text{mol mass of HCl}$

$= 10^{-2} \times 36.5$

$= \mathbf{0.365\ gl^{-1}}$

TYPE 4. Calculating the pH of a Strong base

SOLVED PROBLEM 1. Determine the pH of 0.10 M NaOH solution.

SOLUTION

NaOH is a strong base and it is completely dissociated in aqueous solution.

$$\underset{0.10\text{M}}{\text{NaOH}} \rightleftharpoons \text{Na}^+ + \underset{0.10\text{M}}{\text{OH}^-}$$

Therefore the concentration of OH^- ions is equal to that of the undissociated NaOH.

$[\text{OH}^-] = [\text{NaOH}] = 0.10\ \text{M}$

$[H^+]$ can be calculated by applying the expression by substituting the value of $K_w = 1 \times 10^{-14}$ and of $[OH^-]$

$$[\text{H}^+] = \frac{K_w}{[\text{OH}^-]} = \frac{1 \times 10^{-14}}{0.10} = \frac{1 \times 10^{-14}}{10^{-1}} = 10^{-13}\ \text{M}$$

By definition

$$\text{pH} = -\log [H^+] = -\log^{-13}$$
$$= 13$$

Therefore the pH of 0.10 M NaOH is **13**.

SOLVED PROBLEM 2. Calculate the pH of a 0.020 M $Ba(OH)_2$ solution.

SOLUTION

Barium hydroxide dissociates according to the equation

$$Ba(OH)_2 \rightleftharpoons Ba^{2+} + 2OH^-$$

One molecule of barium hydroxide dissociates to give two OH^- ions. Therefore we have

$$[OH^-] = 0.40 \text{ M}$$

The pOH of the solution is, therefore,

$$\text{pOH} = -\log 0.040 = 1.40$$

We have that $\text{pH} + \text{pOH} = 14.00$

$\therefore$ $\text{pH} = 14.00 - 1.40 = 12.60$

The pH of 0.020 M $Ba(OH)_2$ solution is **12.60**.

TYPE 5. Calculating pH of a Weak acid

SOLVED PROBLEM 1. Calculate the pH of 0.1 M CH_3COOH. The dissociation constant of acetic acid is 1.8×10^{-5}.

SOLUTION

Acetic acid dissociates in aqueous solution as

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

The K_a for acetic acid is stated as

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = 1.8 \times 10^{-5} \qquad ...(1)$$

One molecule of CH_3COOH dissociates to form one H^+ and one CH_3COO^-. Thus,

$$[H^+] = [CH_3COO^-]$$

If x be the concentration of H^+ ion at equilibrium, the various concentrations at the equilibrium may be written as

$$[CH_3COOH] = 0.10 - x$$
$$[H^+] = x$$
$$[CH_3COO^-] = x$$

Since the value of x is negligible relative to 0.10, $(0.10 - x)$ is approximately equal to 0.10.

Substituting the values in (1), we have

$$K_a = \frac{x \times x}{0.10} = 1.8 \times 10^{-5}$$

Solving for x,

$$\frac{x^2}{0.10} = 1.8 \times 10^{-5}$$

or $x^2 = (1.0 \times 10^{-1})(1.8 \times 10^{-5}) = 1.8 \times 10^{-6}$

$$x = \sqrt{1.8 \times 10^{-6}} = 1.34 \times 10^{-3} \text{ M}$$

Thus the hydrogen concentration $[H^+]$ of 0.1 M CH_3COOH is 1.34×10^{-3} M

$$\begin{aligned} pH &= -\log[H^+] = -\log(1.34 \times 10^{-3}) \\ &= +3 - \log 1.34 \\ &= 2.87 \end{aligned}$$

Thus the pH of 0.1 M CH_3COOH solution is **2.87**.

SOLVED PROBLEM 2. Find out the pH of a 0.002 M acetic acid solution if it is 2.3% ionised at this dilution.

SOLUTION

The dissociation equation for acetic acid is

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

If the dissociation is 2.3%, it means that 2.3 × 0.002 molecules dissociated and generated 2.3 × 0.002 ions of H^+.

$$\begin{aligned} [H^+] &= 0.002 \times 0.023 \\ \therefore \quad &= 0.000046 \\ pH &= -\log[H^+] \\ &= -\log(0.000046) = -\log(4.6 \times 10^{-5}) \\ &= +5 - \log 4.6 \\ &= +5 - 0.6628 \\ &= \mathbf{4.3372} \end{aligned}$$

TYPE 6. Calculating pH of a Weak base

SOLVED PROBLEM. Calculate the pH of 0.1 M NH_3 solution. The ionisation constant, K_b, for NH_3 is 1.8×10^{-5}.

SOLUTION

The equilibrium reaction is

$$\underset{0.10-x}{NH_3} + H_2O \rightleftharpoons \underset{x}{NH_4^+} + \underset{x}{OH^-}$$

We assume $[OH^-] = x$ when equilibrium is reached. Thus we can write the equilibrium expression as

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = \frac{x^2}{0.10 - x}$$

Since x is insignificant relative to 0.1, we can write

$$K_b = \frac{x^2}{0.10}$$

Solving for x,

$$x = \sqrt{0.10 \times K_b} \quad \textit{where} \quad K_b = 1.8 \times 10^{-5}$$

$$x = \sqrt{0.10 \times (1.8 \times 10^{-5})} = 1.34 \times 10^{-3} \text{ M}$$

Since $x = [OH^-]$, we have

$$pOH = -\log(1.34 \times 10^{-3}) = 2.87$$

We know that

$$\text{pH} + \text{pOH} = 14.00$$

$$\therefore \quad \text{pH} = 14.00 - 2.87 = 11.13$$

Thus the pH of 0.1 M NH_3 solution is **11.1**.

TYPE 7. Calculating pH of aqueous Sulphuric acid

SOLVED PROBLEM. Calculate the pH of 0.100 M H_2SO_4 at 25°C. K_{a_1} is large and $K_{a_2} = 0.012$ M.

SOLUTION

Sulphuric acid ionises in two steps,

$$H_2SO_4 \longrightarrow H^+ + HSO_4^- \qquad ...(1)$$

$$\underset{\text{weak acid}}{HSO_4^-} \rightleftharpoons H^+ + SO_4^{2-} \qquad ...(2)$$

The pH of aqueous solution of H_2SO_4 depends on the total hydrogen ion concentration with both ionisation steps taken into account.

First Ionisation Step

The first ionisation is complete and it results in a hydrogen ion concentration of the acid, 0.100 M.

$\therefore$ pH due to step (1) is = 1.0

Second Ionisation Step

The second ionisation step adds to the hydrogen ion concentration slightly. Therefore, the overall pH of the solution will be slightly less than 1.

In step (2), HSO_4^- is treated as a weak acid. The initial concentration of HSO_4^- is 0.100 M. If x concentration is ionised at equilibrium, the concentrations at this point are :

$$[H^+] = 0.100\,\text{M} + x$$

$$[SO_4^{2-}] = x$$

$$[HSO_4^-] = 0.100\,\text{M} - x$$

Since K_{a_2} is not very small, x cannot be ignored. Thus, the ionisation constant expression is

$$K_{a_2} = \frac{[SO_4^{2-}]\,[H^+]}{[HSO_4^-]} = \frac{x \times (0.100\,\text{M} + x)}{0.100\,\text{M} - x}$$

Substituting K_{a_2} and rearranging we get

$$x^2 + (0.112\,\text{M})\,x - 0.0012\,\text{M}^2 = 0$$

Solving for x using the quadratic formula

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

$$= \frac{-0.112 + \sqrt{(0.112)^2 + 4 \times 0.0012}}{2} = 0.010\,\text{M}$$

$$= \frac{-0.112 - \sqrt{(0.112)^2 + 4 \times 0.0012}}{2} = -0.122\,\text{M}$$

Since the $[H^+]$ at equilibrium is $0.100 - x$, these two solutions are

$$[H^+] = 0.110 \quad \text{or} \quad -0.022\,\text{M}$$

The second solution makes no sense and can be discarded. Thus,

$$\text{pH} = -\log 0.110 = \mathbf{0.96}$$

This is slightly lower than 1.0 as expected.

ACID RAIN

Acid Rain, form of air pollution in which airborne acids produced by electric utility plants and other sources fall to Earth in distant regions. The corrosive nature of acid rain causes widespread damage to the environment. The problem begins with the production of sulphur dioxide and nitrogen oxides from the burning of fossil fuels, such as coal, natural gas, and oil, and from certain kinds of manufacturing. Sulphur dioxide and nitrogen oxides react with water and other chemicals in the air to form sulphuric acid, nitric acid, and other pollutants. These acid pollutants reach high into the atmosphere, travel with the wind for hundreds of miles, and eventually return to the ground by way of rain, snow, or fog, and as invisible "dry" forms.

Damaged by acid rain

Damage from acid rain has been widespread in eastern North America and throughout Europe, and in Japan, China, and Southeast Asia. Acid rain leaches nutrients from soils, slows the growth of trees, and makes lakes uninhabitable for fish and other wildlife. In cities, acid pollutants corrode almost everything they touch, accelerating natural wear and tear on structures such as buildings and statues. Acids combine with other chemicals to form urban smog, which attacks the lungs, causing illness and premature deaths.

WHAT IS A BUFFER SOLUTION ?

It is often necessary to maintain a certain pH of a solution in laboratory and industrial processes. This is achieved with the help of **buffer solutions, buffer systems or simply buffers.**

A buffer solution is one which maintains its pH fairly constant even upon the addition of small amounts of acid or base.

In other words, a buffer solution resists (or buffers) a change in its pH. That is, we can add a small amount of an acid or base to a buffer solution and the pH will change very little. Two common types of buffer solutions are :

(1) a weak acid together with a salt of the same acid with a strong base. These are called **Acid**

buffers *e.g.*, $CH_3COOH + CH_3COONa$.

(2) a weak base and its salt with a strong acid. These are called **Basic buffers.** *e.g.*, $NH_4OH + NH_4Cl$.

Let us illustrate buffer action by taking example of a common buffer system consisting of solution of acetic acid and sodium acetate (CH_3COOH/CH_3COONa).

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

$$CH_3COONa \longrightarrow Na^+ + CH_3COO^-$$

since the salt is completely ionised, it provides the common ions CH_3COO^- in excess. The common ion effect suppresses the ionisation of acetic acid. This reduces the concentration of H^+ ions which means that pH of the solution is raised. Thus, a 0.1 M acetic acid solution has a pH of 2.87 but a solution of 0.1 M acetic acid and 0.1 M sodium acetate has a pH of 4.74 (Fig. 27.11). Thus 4.74 is the pH of the buffer. On addition of 0.01 mole NaOH the pH changes from 4.74 to 4.83, while on the addition of 0.01 mole HCl the pH changes from 4.74 to 4.66. Obviously the buffer solution maintains fairly constant pH and the changes in pH could be described as marginal.

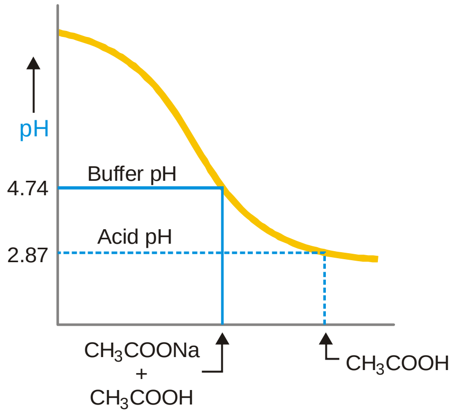


Figure 27.11
The buffer solution (CH_3COOH/CH_3COONa) has a higher pH than the acid itself.

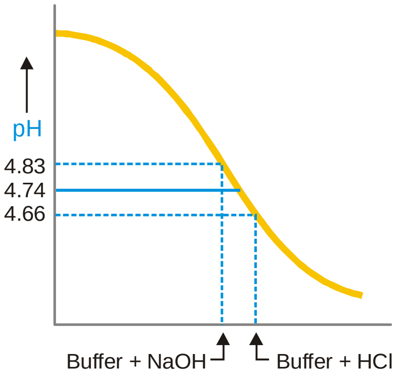


Figure 27.12
The pH of buffer changes only slightly upon addition of an acid (0.01 moles) or base (0.01 mole NaOH).

HOW A BUFFER OPERATES ?

We have already stated that a buffer solution containing equimolar amounts (0.10 M) of acetic acid and sodium acetate has pH 4.74. Now we proceed to discuss how the addition of a small amount of HCl or NaOH to the buffer solution affects its pH.

The pH of the buffer is governed by the equilibrium

$$CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \qquad ...(1)$$

The buffer solution has a large excess of CH_3COO^- ions produced by complete ionisation of sodium acetate,

$$CH_3COONa \longrightarrow CH_3COO^- + Na^+ \qquad ...(2)$$

(1) **Addition of HCl.** Upon the addition of HCl, the increase of H^+ ions is counteracted by association with the excess of acetate ions to form unionised CH_3COOH. Thus the added H^+ ions are neutralised and the pH of the buffer solution remains virtually unchanged. However owing to the increased concentration of CH_3COOH, the equilibrium (1) shifts slightly to the right to increase H^+ ions. This explains the marginal increase of pH of the buffer solution on addition of HCl (Fig. 27.12)

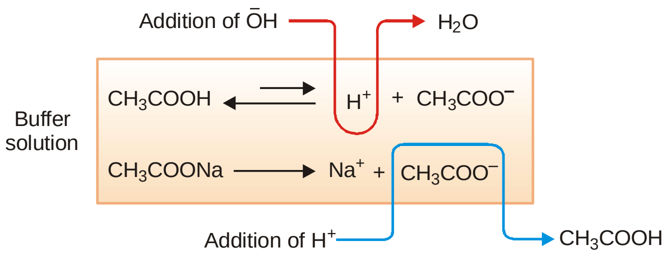


Figure 27.13
Mechanism of Buffer action of an acid buffer.

(2) **Addition of NaOH.** When NaOH is added to the buffer solution, the additional OH^- ions combine with H^+ ions of the buffer to form water molecules. As a result the equilibrium (1) shifts to the right to produce more and more H^+ ions till practically all the excess OH^- ions are neutralised and the original buffer pH restored. However, a new equilibrium system is set up in which $[CH_3COOH]$ is lower than it was in the original buffer. Consequently $[H^+]$ is also slightly less and pH slightly higher than the buffer pH values (Fig. 27.13).

Operation of a Basic buffer as NH_4OH/NH_4Cl can also be explained on the same lines as of an acid buffer (Fig. 27.14) upon addition of HCl the H^+ ions combine with OH^- ions of the buffer to form water molecules. The equilibrium,

$$NH_4OH \rightleftharpoons NH_4^+ + OH^-$$

is shifted to the right till all the additional H^+ ions are neutralised and the original buffer pH restored. When NaOH is added to the buffer solution, OH^- ions associate with excess of NH_4^+ ions to form unassociated NH_4OH. Thus the pH of the buffer is maintained approximately constant.

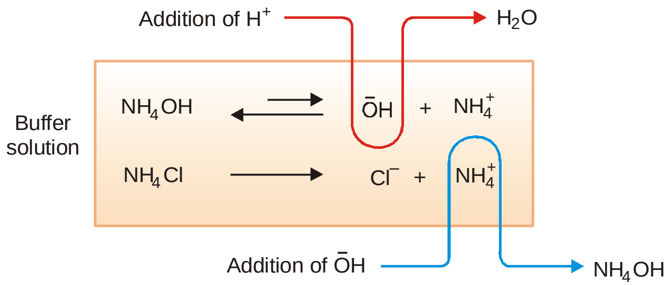


Figure 27.14
Mechanism of Buffer action of a basic buffer.

CALCULATION OF THE pH OF BUFFER SOLUTIONS

The pH of an acid buffer can be calculated from the dissociation constant, K_a, of the weak acid and the concentrations of the acid and the salt used.

The dissociation expression of the weak acid, HA, may be represented as

$$HA \rightleftharpoons H^+ + A^-$$

and $$K_a = \frac{[H^+][A^-]}{[HA]}$$

or $$[H^+] = K_a \times \frac{[HA]}{[A^-]} \qquad ...(1)$$

The weak acid is only slightly dissociated and its dissociation is further depressed by the addition of the salt (Na^+A^-) which provides A^- ions (Common ion effect). As a result the equilibrium concentration of the unionised acid is nearly equal to the initial concentration of the acid. The equilibrium concentration $[A^-]$ is presumed to be equal to the initial concentration of the salt added since it is completely dissociated. Thus we can write the equation (1) as

$$[H^+] = K_a \times \frac{[\text{acid}]}{[\text{salt}]} \qquad \text{...(2)}$$

where [acid] is the initial concentration of the added acid and [salt] that of the salt used.

Taking negative logs of both sides of the equation (2), we have

$$-\log[H^+] = -\log K_a - \log\frac{[\text{acid}]}{[\text{salt}]} \qquad \text{...(3)}$$

But $\quad -\log[H^+] = \text{pH} \quad$ and $\quad \log K_a = \text{p}K_a$

Thus from (3) we have

$$\text{pH} = \text{p}K_a - \log\frac{[\text{acid}]}{[\text{salt}]} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

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

This relationship is called the **Henderson-Hasselbalch equation** or simply **Henderson equation.**

In a similar way, the Henderson-Hasselbalch equation for a basic buffer can be derived. This can be stated as :

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

Significance of the Henderson-Hasselbalch equation

With its help :

(1) The pH of a buffer solution can be calculated from the initial concentrations of the weak acid and the salt provided K_a is given.

However, the Henderson-Hasselbalch equation for a basic buffer will give pOH and its pH can be calculated as (14 – pOH).

(2) The dissociation constant of a weak acid (or weak base) can be determined by measuring the pH of a buffer solution containing equimolar concentrations of the acid (or base) and the salt.

$$\text{pH} = \text{p}K_a + \log\frac{[\text{salt}]}{[\text{acid}]}$$

Since $\quad [\text{salt}] = [\text{acid}], \quad \log\frac{[\text{salt}]}{[\text{acid}]} = \log 1 = 0$

$\therefore \quad \text{p}K_a = \text{pH}$

The measured pH, therefore, gives the value of $\text{p}K_a$ of the weak acid.

Likewise we can find the $\text{p}K_b$ of a weak base by determining the pH of equimolar basic buffer.

(3) A buffer solution of desired pH can be prepared by adjusting the concentrations of the salt and the acid added for the buffer.

It is noteworthy that buffer solution are most effective when the concentrations of the weak acid (or weak base) and the salt are about equal. This means that pH is close to the value of $\text{p}K_a$ of the acid (or $\text{p}K_b$ of the base).

NUMERICAL PROBLEMS BASED ON BUFFERS

The numerical problems pertaining to buffer solutions may be classified into the following types:

TYPE 1. Calculation of pH of Acid Buffers

SOLVED PROBLEM 1. Find the pH of a buffer solution containing 0.20 mole per litre CH_3COONa and 0.15 mole per litre CH_3COOH. K_a for acetic acid is 1.8×10^{-5}.

SOLUTION

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

$$pK_a = -\log(1.8 \times 10^{-5}) = 4.7447$$

$$\text{pH} = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]} \qquad \textit{(Henderson-Hasselbalch equation)}$$

$$= 4.7447 + \log\frac{0.20}{0.15}$$

$$= 4.7447 + \log\frac{4}{3}$$

$$= 4.7447 + 0.6021 - 0.4771$$

$$= \mathbf{4.8697}$$

ALTERNATIVE SOLUTION

The equilibrium equation for dissociation of acetic acid is

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

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

Since CH_3COOH is feebly dissociated in the presence of CH_3COOH^- ions (Common ion effect), $[CH_3COOH]$ is the same as of acid taken initially. Again $[CH_3COOH^-]$ is equal to the initial concentration of the salt CH_3COONa as it is completely dissociated. Thus we have

$$K_a = \frac{[H^+] \times 0.20}{0.15} = 1.8 \times 10^{-5}$$

or

$$[H^+] = \frac{(1.8 \times 10^{-5}) \times 0.15}{0.20} = 1.35 \times 10^{-5}$$

$$\text{pH} = -\log(H^+)$$

$$= -\log(1.35 \times 10^{-5})$$

$$= 5 - 0.1303$$

$$= \mathbf{4.8697}$$

SOLVED PROBLEM 2. Estimate the pH at 25°C containing 0.10 M sodium acetate and 0.03 M acetic acid pK_a for $CH_3COOH = 4.57$.

SOLUTION

$$\text{pH} = pK_a + \log\frac{[\text{salt}]}{[\text{acid}]} \qquad \textit{(Henderson-Hasselbalch equation)}$$

$$= 4.57 + \log\frac{0.10}{0.03}$$

$$= 4.57 + 0.52 = \mathbf{5.09}$$

SOLVED PROBLEM 3. Calculate the pH of a buffer solution that is 0.250 M in formic acid, HCOOH, and 0.100 M in sodium formate, HCOONa. K_a for formic acid is 1.8×10^{-4}.

SOLUTION

$$K_a = 1.8 \times 10^{-4}$$

$$pK_a = -\log (1.8 \times 10^{-4})$$

$$= 4 - \log 1.8 = 3.7447$$

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} \qquad \textit{(Henderson-Hasselbalch equation)}$$

$$= 3.7447 + \log \frac{[0.100]}{[0.250]}$$

$$= 3.7447 - 0.3979 = \mathbf{3.3468}$$

ALTERNATIVE SOLUTION

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$

$$K_a = \frac{[H^+][HCOO^-]}{[HCOOH]}$$

or
$$[H^+] = \frac{K_a [HCOOH]}{[HCOO^-]}$$

Since HCOOH is weakly ionised in the presence of $HCOO^-$, the [HCOOH] at equilibrium is equal to its initial concentration. Again, HCOONa is fully ionised and hence the concentration of $HCOO^-$ ions is the same as that of the salt taken.

Substituting values in the above expression

$$[H^+] = \frac{1.8 \times 10^{-4} \times 0.250}{0.100} = 4.5 \times 10^{-4}\ M$$

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

$$= -\log (4.5 \times 10^{-4})$$

$$= 4 - \log 4.5$$

$$= 4 - 0.6532$$

$$= 3.3468$$

$$\therefore \quad pH = \mathbf{3.3468}$$

SOLVED PROBLEM 4. The K_a of propionic acid is 1.34×10^{-5}. What is the pH of a solution containing 0.5 M propionic acid, C_2H_5COOH, and 0.5 sodium propionate, C_2H_5COONa. What happens to the pH of this solution when volume is doubled by the addition of water ?

SOLUTION

The pH of solution can be calculated by substituting the given values in the Henderson-Hasselbalch equation.

$$pK_a = 1.34 \times 10^{-5}$$

$$pK_a = -\log K_a = -\log 1.34 \times 10^{-5} = 4.87$$

$$pH = pK_a + \log \frac{[\text{salt}]}{[\text{acid}]} \qquad \textit{(Henderson-Hasselbalch equation)}$$

$$= 4.87 + \log \frac{0.5}{0.5}$$

$$= 4.87 + 0$$

$$= \mathbf{4.87}$$

ALTERNATIVE SOLUTION

The equation for the dissociation of propionic acid is

$$C_2H_5COOH \rightleftharpoons C_2H_5COO^- + H^+$$

$$K_a = \frac{[C_2H_5COO^-]\,[H^+]}{[C_2H_5COOH]} = \frac{0.5 \times [H^+]}{0.5} = [H^+]$$

$$\therefore \quad -\log [H^+] = -\log K_a \quad \text{or} \quad pH = pK_a$$

$$pH = \mathbf{4.87}$$

When the volume of the solution is doubled, there will be no change in pH of the solution because the ratio [salt] / [acid] remains the same.

TYPE 2. Calculation of pH of Basic or Alkaline Buffers

Henderson-Hasselbalch equation for basic buffers is first used to determine the value of pOH.

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

where K_b is the dissociation constant of the base.

We know that,

$$pH + pOH^+ = 14.00$$

$$pH = 14.00 - pOH$$

The rest of the procedure followed is the same as for calculating the pH of acid buffers.

SOLVED PROBLEM 1. A buffer solution contains 0.015 mole of ammonium hydroxide and 0.025 mole of ammonium chloride. Calculate the pH value of the solution. Dissociation constant of NH_4OH at the room temperature is 1.80×10^{-5}.

SOLUTION

In this case,

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

But

$$pK_b = -\log K_b$$

$$= -\log (1.80 \times 10^{-5})$$

$$= 4.7447$$

$$\therefore \quad pOH = 4.7447 + \log \frac{0.025}{0.015}$$

$$= 4.7447 + 0.2218$$

$$= 4.9665$$

Since

$$pH + pOH = 14$$

$$\therefore \quad pH = 14 - 4.9665$$

$$= \mathbf{9.0335}$$

SOLVED PROBLEM 2. A buffer solution contains 0.25 M NH_3 and 0.40 M NH_4Cl. Calculate the pH of the solution. K_b for ammonia = 1.8×10^{-5}.

SOLUTION

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

$$K_b = \frac{[NH_4^+]\;[OH^-]}{[NH_3]}$$

or
$$[OH^-] = \frac{K_b \times [NH_3]}{[NH_4^+]}$$
$$= \frac{1.8 \times 10^{-5} \times 0.25}{0.40} = 1.125 \times 10^{-5}$$
$$\text{pOH} = -\log(1.125 \times 10^{-5}) = 4.945$$
$$\text{pH} = 14.00 - 4.945 = \mathbf{9.055}$$

This problem can also be solved with the help of Henderson-Hasselbalch equation.

TYPE 3. Calculation of pH of buffer solution after addition of HCl or NaOH

The pH of a buffered solution changes upon the addition of a strong acid or strong base. The changed pH can be calculated as follows:

(1) **When HCl is added.** Let the buffer contain *a* mole/litre of weak acid HA and *b* mole/litre of the salt $Na^+ A^-$. That is,

$$\underset{a}{HA} \rightleftharpoons H^+ + \underset{b}{A^-}$$

If *x* mole of HCl/litre is added, it forms *x* mole/litre of H^+ ions. These combine with (*x* mole) A^- ions and the equilibrium is pushed to the left to form *x* mole undissociated acid. In other words, the concentration of A^- ions is decreased by *x* mole/litre and that of HA is increased by *x* mole/litre.

$$\underset{(a+x)}{HA} \rightleftharpoons H^+ + \underset{(b-x)}{A^-}$$

Thus we can write the equilibrium expression for the buffer solution with changed concentration as

$$K_a = \frac{[H^+][A^-]}{[HA]} = \frac{[H^+](b-x)}{(a+x)}$$

or
$$[H^+] = \frac{K_a(a+x)}{(b-x)}$$

Knowing the value of K_a, $[H^+]$ of the buffer can be calculated and

$$\text{pH} = -\log[H^+] = -\log\frac{K_a(a+x)}{(b-x)}$$

(2) **When NaOH is added.** If *x* mole/litre of NaOH is added, it produces *x* mole/litre OH^- ions. Thus combine with *x* mole/litre H^+ ions of the buffer to form water. The equilibrium

$$HA \rightleftharpoons H^+ + A^-$$

is thus shifted to the right till *x* mole/litre H^+ ions are produced that are needed to neutralise the added OH^- ions. The net result is that *x* mole/litre HA dissociates to yield *x* mole/litre A^- ions. Hence, the concentration of HA is decreased by *x* mole/litre and the concentration of A^- is increased by *x* mole/litre.

$$\underset{(a-x)}{HA} \rightleftharpoons H^+ + \underset{(b+x)}{A^-}$$

We can now write the following expression for the new equilibrium with changed concentration as

$$K_a = \frac{[H^+](b+x)}{(a-x)}$$

or
$$[H^+] = \frac{K_a(a-x)}{(b+x)}$$
$$\text{pH} = -\log[H^+] = -\log\frac{K_a(a-x)}{(b+x)}$$

The pH of a buffer after the addition of HCl or NaOH can also be calculated with the help of Henderson-Haselbalch equation. It may be noted that **any volume changes caused in these additions are ignored.**

SOLVED PROBLEM 1. The pH of a buffer solution containing 0.5 mole/litre of CH_3COOH and 0.5 mole/litre CH_3COONa has been found to be 4.76. What will be the pH of this solution after 0.1 mole/litre HCl has been added to the buffer ? Assume that the volume is unchanged. $K_a = 1.75 \times 10^{-5}$.

SOLUTION

The concentrations of each of CH_3COOH and CH_3COO^- for the initial equilibrium

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

are 0.5 mole/litre. This is so because the acid is very slightly dissociated and CH_3COONa strongly so.

When 0.1 mole/litre acid is added, 0.1 mole/litre H^+ ions are produced. The equilibrium is pushed in the reverse direction to form 0.1 mole/litre CH_3COOH. Thereby, the concentration of CH_3COOH is increased by 0.1 mole/litre and that of CH_3COO^- ion is decreased by 0.1 mole/litre.

Thus the concentration of the acid and salt when the new equilibrium is set up after the addition of HCl, are :

$$[CH_3COOH] = (0.5 + 0.1) = 0.6 \text{ mole/litre}$$
$$[CH_3COO^-] = (0.5 - 0.1) = 0.4 \text{ mole/litre}$$

The equilibrium expression for the equilibrium can, now, be written as

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+] \times 0.4}{0.6}$$

or
$$[H^+] = \frac{K_a \times 0.6}{0.4} = \frac{1.75 \times 10^{-5} \times 0.6}{0.4} = 2.63 \times 10^{-5}$$

∴
$$pH = -\log(2.63 \times 10^{-5}) = \mathbf{4.58}$$

SOLVED PROBLEM 2. A litre of solution containing 0.1 mole of CH_3COOH and 0.1 mole of CH_3COONa provides a buffer of pH 4.74. Calculate the pH of solution after the addition of 0.02 mole NaOH. $K_a = 1.8 \times 10^{-5}$.

SOLUTION

0.02 mole NaOH yields 0.02 mole of OH^- ions. These combine with 0.02 mole H^+ ions to form H_2O and the equilibrium

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

is shifted to the right (Le Chatelier's principle). Thereby 0.02 mole of CH_3COOH dissociates to form 0.02 mole H^+ needed to neutralise OH^- ions and also 0.02 mole of CH_3COO^- ions. Hence the concentration of CH_3COOH is decreased by 0.02 mole/litre and that of CH_3COO^- ions is increased by 0.02 mole/litre.

$$\underset{(0.1-0.02)}{CH_3COOH} \rightleftharpoons H^+ + \underset{(0.1+0.02)}{CH_3COO^-}$$

Thus the concentrations in mole/litre when the new equilibrium is set up are

$$[CH_3COOH] = 0.1 - 0.02 = 0.08$$
$$[CH_3COO^-] = 0.1 + 0.02 = 0.12$$

The equilibrium expression may now be written as :

$$K_a = \frac{[H^+][CH_3COO^-]}{[CH_3COOH]} = \frac{[H^+] \times 0.12}{0.08} = 1.8 \times 10^{-5}$$

or
$$[H^+] = \frac{1.8 \times 10^{-5} \times 0.08}{0.12} = 1.2 \times 10^{-5}$$

$$pH = -\log[H^+] = -\log(1.2 \times 10^{-5}) = \mathbf{4.92}$$

TYPE 4. To obtain a buffer of given pH

Here we first find the $[H^+]$ corresponding to the required pH. Then we apply the equilibrium expression.

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

or
$$[H^+] = K_a \times \frac{[HA]}{[A^-]}$$

Knowing the values of $[H^+]$, $[HA]$ and K_a, we can calculate the ratio $[HA]/[A^-]$ or $[A^-]$ from the above expression.

SOLVED PROBLEM 1. A chemist needs a buffered solution of propanoic acid, CH_3CH_2COOH, and its salt, CH_3CH_2COONa. Calculate the ratio $[CH_3CH_2COOH]/[CH_3CH_2COONa]$ required to yield a pH of 4.30. K_a for propanoic acid is 1.3×10^{-5}.

SOLUTION

A pH of 4.30 corresponds to

$$[H^+] = 10^{-4.30} = \text{antilog}(-4.30) = 5.0 \times 10^{-5}\ M$$

$$CH_3CH_2COOH \rightleftharpoons CH_3CH_2COO^- + H^+$$

$$K_a = \frac{[CH_3CH_2COO^-][H^+]}{[CH_3CH_2COOH]}$$

or
$$[H^+] = K_a \frac{[CH_3CH_2COOH]}{[CH_3CH_2COO^-]} = 5.0 \times 10^{-5}$$

$$\therefore \quad \frac{[CH_3CH_2COOH]}{[CH_3CH_2COO^-]} = \frac{5.0 \times 10^{-5}}{K_a} = \frac{5.0 \times 10^{-5}}{1.3 \times 10^{-5}} = \mathbf{3.8}$$

SOLVED PROBLEM 2. Calculate the concentration of sodium formate, HCOONa, that must be present in a 0.10 M solution of formic acid to produce a pH of 3.80. K_a for formic acid is 1.8×10^{-4}.

SOLUTION

A pH of 3.80 corresponds to

$$\begin{aligned}[H^+] = 10^{-3.80} = \text{antilog}(-3.80) &= \text{antilog}(-4 + 0.20) \\ &= 0.0001585 \\ &= 1.585 \times 10^{-4}\end{aligned}$$

$$HCOOH \rightleftharpoons H^+ + HCOO^-$$

$$K_a = \frac{[H^+][HCOO^-]}{HCOOH}$$

$$[HCOO^-] = \frac{K_a[HCOOH]}{[H^+]}$$

Substituting the values
$$[HCOO^-] = \frac{1.8 \times 10^{-4} \times 0.10}{1.585 \times 10^{-4}}$$

$$= \mathbf{0.113\ M}$$

SOLVED PROBLEM 3. A chemistry student desires to prepare one litre of a solution buffered at pH 9.00. How many grams of ammonium chloride have to be added to one litre of 0.20 M NH_3 to make such a buffer. pK_b value of ammonia is 4.75 in the equation

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

SOLUTION

The equilibrium expression is

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

Henderson-Hasselbalch equation may be used with convenience.

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

Since $\quad pH + pOH = 14$

$$pOH = 14 - 9 = 5$$

$\therefore$ $\quad 5 = 4.74 + \log\dfrac{[salt]}{0.20}$

Thus $\quad \log\dfrac{[salt]}{0.20} = 5 - 4.74 = 0.26$

$$\frac{[salt]}{0.20} = 10^{0.26} = 1.8$$

$$[salt] = 1.8 \times 0.20 = \mathbf{0.36\ M}$$

Thus the concentration of NH_4Cl in the buffer must be 0.36 M for the buffer to hold a pH of 9.00. The amount of NH_4Cl per litre = 0.36 × 53.5 = **19.26 g**

ACID–BASE INDICATORS

In an acid-base titration the base solution can be added gradually from a burette into an acid solution contained in a receiver flask. When the amount of the base added equals the amount of the acid in the flask, the **equivalence point** or the **end-point** is reached. The end-point of a titration is shown by colour change of an indicator previously added to the acid solution in the receiver flask.

An acid-base indicator is an organic dye that signals the end-point by a visual change in colour.

Phenolphthalein and methyl orange are two common examples of acid-base indicators. Phenolphthalein is pink in base solution and colourless in acid solution. Thus when added to the acid solution in the receiver flask, it shows no colour. As the added base is in slight excess, it becomes pink. Thus phenolphthalein signals the end-point by a colour change from colourless to pink. Similarly methyl orange indicates the end-point by a colour change from red (in acid) to yellow (in base).

pH range of indicators

Most indicators do not change colour at a particular pH. They do so over a range of pH from two to three units. This is called the **pH range** which is different for various indicators.

TABLE 27.5. pH RANGES OF SOME ACID-BASE INDICATORS

Indicator	Colour change (acid-base)		pH range
Methyl orange	red-orange	🟥 → 🟧	3.1 – 4.4
Methyl red	red-yellow	🟥 → 🟨	4.4 – 6.0
Litmus	red-blue	🟥 → 🟦	5.0 – 8.0
Bromothymol blue	yellow-blue	🟨 → 🟦	6.0 – 7.6
Phenolphthalein	colourless-pink	⬜ → 🟪	8.3 – 10.0

pH curves and Indicator range

During an acid-base titration the pH of the solution in the receiver flask changes with the addition of the titrant from the burette. A plot of pH against the volume of the solution being added is known as **pH curve** or **titration curve.** For illustration, the pH curve produced by titration of HCl solution with NaOH solution is shown in Fig. 27.15. As NaOH is added, the pH of the solution increases slowly at first, then rapidly in the vicinity of the equivalence point and again slowly. The equivalence point lies in the middle of the vertical portion of the curve (pH = 7). It must be clearly understood that equivalence point is the theoretical end-point of a titration. The end-point of a titration determined by a colour change of the indicator in titration solution is the experimental estimate of the equivalence point.

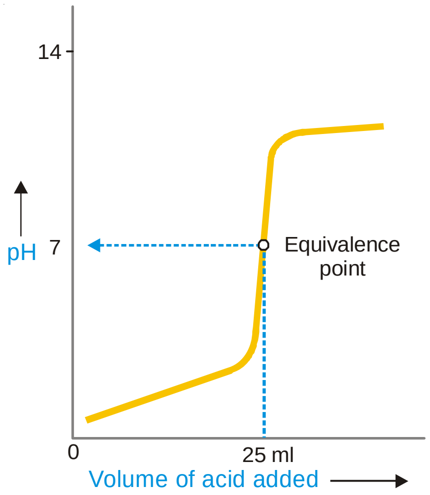


Figure 27.15
pH curve for titration of a strong base with strong acid.

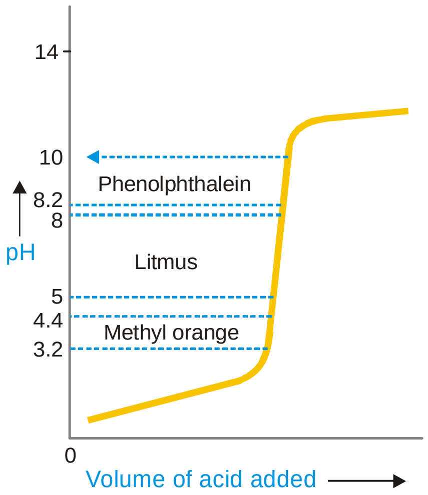


Figure 27.16
Indicator ranges for phenolphthalein, litmus and methyl orange.

The titration curve in Fig. 27.15. Shows that it remains vertical around the equivalence point. From a study of this part of the curve, it is evident that the volume of litre used at the experimental end-point will be very nearly the same as for the equivalence point provided that : (*i*) the indicator used has a small pH range and; (*ii*) the range wholly falls on the vertical portion of the curve.

Thus, **a suitable indicator for a given titration may be defined as one which has as narrow a pH range as possible that lies entirely on the upright part of the titration curve.** For example, as shown in Fig. 27.16, phenolphthalein, litmus and methyl orange may be used as indicators for acid-base titrations.

CHOICE OF A SUITABLE INDICATOR

The choice of a suitable indicator for a particular acid-base titration depends on the nature of the acid and the base involved in the titration. We may have the titration of :

(*a*) a strong acid with a strong base
(*b*) a weak acid with a strong base
(*c*) a strong acid with a weak base
(*d*) a weak acid with weak base

Which indicator is suitable for a given titration, can be found by examining the titration curve of that titration. We have already discussed that a suitable indicator is one which has a small pH range that falls wholly on the upright portion of the titration curve.

All the pH curves given in Fig. 27.17 refer to addition of 0.1 M monoacid base to 25 ml of 0.1 M of monobasic acid. The equivalence point in all cases is at pH 7 when all the acid has been neutralised by the base to form a salt. If the titration is performed so that acid is added to the base, the pH curve is the mirror image of that shown.

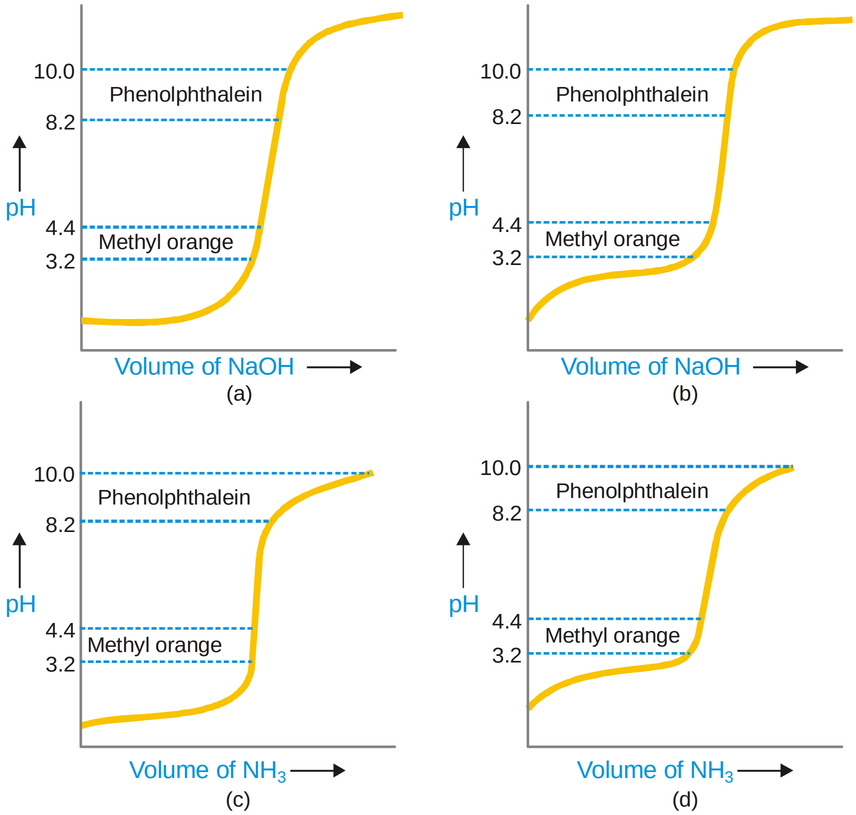


Figure 27.17

To find a suitable indicator from a study of the pH curves for :
(*a*) a strong acid and strong base; (*b*) weak acid and strong base;
(*c*) strong acid and weak base; (*d*) a weak acid and weak base.

Titrating a Strong acid with a Strong base

Figure 27.17 (*a*) depicts the titration curve when NaOH is added gradually to HCl. It shows that the pH of the titration solution rises extremely slowly in the beginning. In the vicinity of the equivalence point, the pH rises dramatically and the curve becomes vertical. Beyond this, the curve becomes almost flat that shows a slight rise of pH when only excess base is present in the titration solution.

The vertical portion of the curve extends from pH 3 to pH 7. The pH ranges of methyl orange (3.1– 4.4), and phenolphthalein (8.30 – 10.0) are fairly narrow and fall on the vertical curve. **Thus both methyl orange and phenolphthalein are suitable indicators** for strong acid/strong base titrations. Litmus with an exceptionally wide pH range (4.5 – 8.3) is seldom used. Its colour does not change sharply from red to blue but goes through various shades of purple.

Titrating a Weak acid with a Strong base

Figure 27.17 (*b*) represents the titration curve when NaOH (strong base) is added to acetic acid (weak acid). The pH curve rises slowly in the beginning but near the equilibrium point, the pH changes abruptly from 6 to 11 and the curve becomes vertical. Beyond this the shape of the titration curve is similar to that for strong acid/strong base.

Phenolphthalein has pH range 8.3 – 10.0 that falls on the vertical part of the titration curve as marked in the figure. The pH range of methyl orange (3.1 – 4.4), on the other hand, does not fall on the vertical curve. Thus if methyl orange is used as indicator, the experimental end-point will be reached earlier than the equivalence point. Therefore for weak acid-strong base titration **Phenolphthalein is a suitable indicator, while methyl orange is not.**

Titrating a Strong acid with a Weak base

The titration curve for HCl (strong acid) with NH_4OH (weak base) is shown in Fig. 27. 17 (*c*). As NH_4OH is added, the pH of the titration solution increases gradually. Around the equivalence point, a sharp rise in pH occurs approximately from 3 to 8, when the curve becomes vertical. The pH range of methyl orange (3.1 – 4.4) and that of methyl red (4.4 – 6.0) falls on the vertical portion of the titration curve. Evidently, **methyl orange and methyl red are suitable indicators for strong acid/weak base titrations.**

Titrating a acid with a Weak base

The titration curve for acetic acid (weak acid) with NH_4OH (weak base) is shown in Fig. 27.17 (*d*). The pH of the titration solution rises gradually and there is no sharp change in pH around the equivalence point. The vertical portion is missing in the titration curve. Under these conditions, all indicators change colour only gradually and **no indicator is suitable.**

THEORIES OF ACID-BASE INDICATORS

An acid-base indicator is an organic substance used for the detection of equivalence point or neutral point in an acid-base titration. An indicator has one colour in acid solution and entirely different in basic solution. The end-point of the titration is shown by a colour change of the indicator. Two theories have been put forward to explain the indicator action in acid-base titrations :

(1) The Ostwald's theory

(2) The Quinonoid theory

We will discuss these with reference to two commonly used indicators, namely, methyl orange and phenolphthalein.

The Ostwald's theory

According to this theory :

(1) an acid-base indicator is a weak organic acid (HIn) or a weak organic base (InOH), where the letter In stands for a complex orange group. Methyl orange and phenolphthalein are both weak acids.

(2) the unionised indicator, HIn, has a colour different from the In^- ions produced by the ionisation of the indicator in aqueous solution.

(3) the degree of ionisation of the indicator determines the visible colour of the indicator solution.

How an acid-base indicator works

Let us explain the indicator action by taking example of methyl orange. Methyl orange is a weak acid and gives the following ionisation equilibrium in solution.

$$\underset{\text{red}}{\text{HIn}} \rightleftharpoons H^+ + \underset{\text{yellow}}{\text{In}^-}$$

In accordance with the law of mass action,

$$K_{\text{in}} = \frac{[H^+][In^-]}{[HIn]} \qquad ...(1)$$

where K_{in} is the dissociation constant of the indicator and is called the **Indicator constant.**

The anion In^- is yellow and the nonionised form HIn^- is red. If an acid is added to the solution, the hydrogen ion concentration, $[H^+]$, in the equilibrium expression (1) increases. To maintain K_{in} constant, the equilibrium shifts to the left. Thereby the concentration of $[In^-]$ is reduced and the concentration of [HIn] increases so that the solution is red. On the other hand, upon addition of a base to the solution, H^+ ions are removed as H_2O by reacting with OH^- ions of the base. This shifts the equilibrium to the right, resulting in the increase of In^- ions that are yellow. Thus in acid solution the unionised HIn molecules predominate and the solution is pink, while in basic solution In^- ions are in excess and the solution is yellow.

Relation of Indicator colour to pH

The indicator solution contains both the yellow In^- and the red HIn molecules. The actual colour shade of the indicator depends on the ratio of concentration of In^- and HIn present in solution. From the equilibrium constant expression (1) we can write

$$[H^+] = K_{in}\frac{[In^-]}{[HIn]} \qquad ...(2)$$

If $[H^+]$ is large, the concentration of In^- ions is also large and the colour is yellow. When $[H^+]$ is small, [HIn] is large and the solution is red. At the equivalence point, [In] = [HIn] and the colour is orange (red + yellow). Obviously the **indicator colour is controlled by hydrogen ion concentration or pH of the solution.**

Taking logarithms and using definition of pH and K_{in}, the expression (2) can be converted to the Henderson-Hasselbalch equation.

$$pH = pK_{in} + \log\frac{[In^-]}{[HIn]} \qquad ...(3)$$

At the equivalence point, $[In^-]$ = [HIn] and methyl orange in solution is orange. Then,

$$pH = pK_{in}$$

The numerical value of the indicator constant K_{in} for methyl orange is 3.6 and the pH of the orange solution is, therefore, about 4. As the values of K_{in} for the various indicators are different, they will have intermediate intense colours (**middle tint**) at different pH values. When a base is added to an acid solution in a titration, the colour change of the indicator is gradual. It just becomes visible to the human eye when $[In^-]/[HIn] = \frac{1}{10}$ and pH calculated from equation (3) is 3.1. The colour of the indicator continues to change till $[In^-]$ / [HIn] = 10 when pH is 4.4. The pH range between 3.1 (red) and 4.4 (yellow) is called the **colour change interval** of methyl orange. The visible indicator colour change takes place between these pH values.

Indicator action of Phenolphthalein

It can be explained as in case of methyl orange. It is a weak acid and exists as the following equilibrium in solution,

$$\underset{\text{colourless}}{HIn} \rightleftharpoons H^+ + \underset{\text{pink}}{In^-}$$

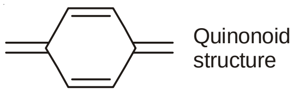
HIn molecules are colourless, while In^- ions are pink. Thus in acid solution, phenolphthalein is colourless and in basic solution it is pink. The value of K_{in} = 9.6 and the pH of the intermediate intense pink tint is also 9.6. The colour change interval of phenolphthalein is 8.1 – 10.0.

Quinonoid theory of Indicator colour change

The Ostwald's theory takes care of the quantitative aspect of indicator action adequately. The Quinonoid theory, on the other hand, tells us the cause of colour change of an indicator in acid-base solutions. It lays down that :

(1) the unionised HIn molecule and the anion In^- are tautomeric forms of the indicator which is an organic dye.

(2) one tautomeric form possesses the quinonoid structural unit and is called the **quinonoid form.**

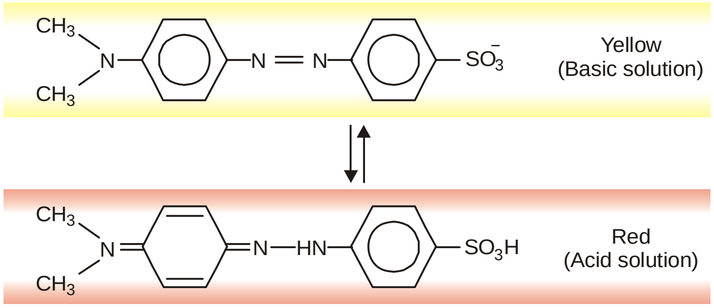


It has a deep colour. The other form has a lesser colouring group, say, –N = N – and or simply benzene rings and is called the **benzenoid form.** This form has a light colour or no colour.

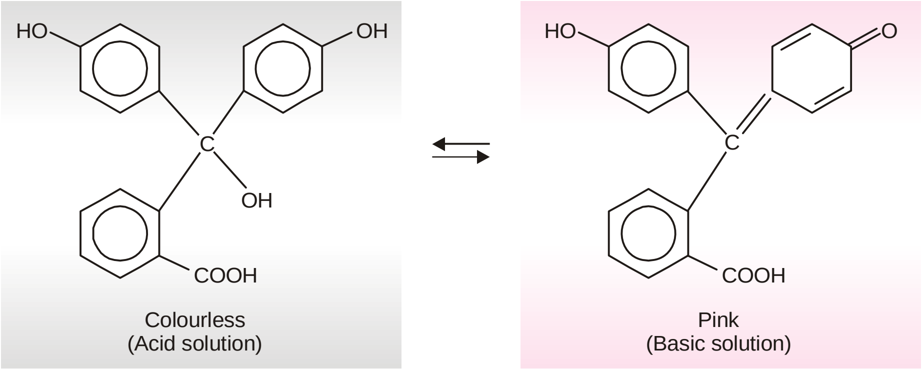
(3) the colour change of the indicator occurs when one tautomeric form is transformed into the other due to change of pH of the solution.

Let us illustrate the Quinonoid theory by taking example of methyl orange and phenolphthalein.

Methyl Orange. The red quinonoid form of methyl orange exists in acid solution. It is converted to yellow benzenoid form when pH alters to the basic side.



Phenolphthalein. Phenolphthalein exists in two tautomeric forms : (*i*) the benzenoid form which is yellow and present in basic solution; and (*ii*) the quinonoid form which is pink and present in acid solution.



EXAMINATION QUESTIONS

1. Define or explain the following terms :

(*a*) Arrhenius acids	(*b*) Arrhenius bases
(*c*) Bronsted acids	(*d*) Bronsted bases
(*e*) Lewis acids	(*f*) Lewis bases
(*g*) pH of solutions	(*h*) Buffer solution

2. (*a*) What are strong and weak electrolytes?

(*b*) Define pH of a solution. Calculate pH of 0.085 N monobasic acid which dissociates 25%.

Answer. (*b*) 1.67

3. (*a*) Derive Henderson's equation to calculate the pH of a buffer solution.

(*b*) Calculate the pH of a 0.1M acetic acid when it is half neutralised by NaOH solution ($K_a = 1.7 \times 10^{-5}$)

Answer. (*b*) 4.7695

4. (*a*) Compare the Lewis theory of acids and bases with the Bronsted-Lowry concept.

(*b*) What are conjugate acid-base pairs? Give two examples.

5. Derive an expression connecting dissociation constant of a weak monobasic acid and its degree of dissociation.

6. State and explain Lowry-Bronsted theory and Lewis theory of acids and bases. In what way Lewis acid differs from Bronsted acid?

7. Calculate the pH of the buffer solution containing 0.04 M NH_4Cl and 0.02 M NH_4OH. K_b for NH_4OH is 1.8×10^{-5}.

Answer. 8.9543

8. A buffer solution is prepared by mixing 3 g of acetic acid and 1.30 g of sodium acetate (CH_3COONa $3H_2O$) and making the total volume to one litre. Calculate the pH of the buffer ($K_a = 1.8 \times 10^{-5}$; H = 1; C = 12; O = 16; Na = 23)

Answer. 5.4437

9. Calculate the degree of hydrolysis of ammonium acetate. The dissociation constant of NH_4OH is 1.8×10^{-5} and that of acetic acid is 1.8×10^{-5} and $K_w = 1.0 \times 10^{-14}$.

Answer. 0.55×10^{-2}

10. Calculate the pH of solution having hydrogen ion concentration 2.5×10^{-3} M.

Answer. 2.6020

11. (*a*) Calculate the pH of 0.01 M NH_4OH solution. Dissociation constant of NH_4OH is 1.8×10^{-5}.

(*b*) Draw and explain strong acid-strong base pH neutralisation curve. Why weak acid-weak base titration is difficult to carry out?

Answer. (*a*) 10.6275

12. Do you expect the pH of pure water at 100°C to be less than 7, or more than 7. Explain your answer. (*Nagpur BSc, 2000*)

13. Why phenolphthalein is not a suitable indicator for the titration of ammonium hydroxide with HCl. Explain. (*Madras BSc, 2000*)

14. What are buffers and how is their buffer capacity measured? (*Guru Nanak Dev BSc, 2000*)

15. Why a solution of NaCl does not act as buffer? (*Himachal Pradesh BSc, 2000*)

16. Show that the degree of hydrolysis of a salt of weak acid and weak base is independent of concentration of the solution. (*Guru Nanak Dev BSc, 2000*)

17. How will you explain the buffer action of aqueous solution of ammonium acetate? (*Punjabi BSc, 2000*)

18. (*a*) What is a Buffer solution? Give examples.

(*b*) Explain the buffer action of an acidic buffer. (*Madurai BSc, 2000*)

19. Explain how does a buffer solution work? (*Kathmandu BSc, 2001*)

20. What are acids and bases? Explain the different theories of acids and bases. (*Kathmandu BSc, 2001*)

21. (*a*) Discuss the Bronsted-Lowry concept and Lewis concept of acids and bases.

(*b*) Write three methods for determining the strength of acids. (*Arunachal BSc, 2002*)

22. Explain : The second dissociation constant of a dibasic acid is always greater than its first dissociation constant. (*Delhi BSc, 2002*)

23. (*a*) Define Lewis acids and Lewis bases. Give one example of each.

(*b*) What do you understand by conjugate acids and bases in the following reactions :

(*i*) $NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$

(*ii*) $HNO_3 + H_2O \rightleftharpoons H_3O^+ + NO_3^-$

(*c*) Calculate the pH of a solution having hydrogen ion concentration 2.5×10^{-3} M.

Answer. 2.6 (*Arunachal BSc, 2002*)

24. What are buffer solutions? Derive Henderson's equation. (*Purvanchal BSc, 2002*)

25. Explain with an example why pH of a buffer solution does not change significantly on small addition of acids or bases. (*Guru Nanak Dev BSc, 2002*)

26. Derive the following equations :

(*i*) $$\text{pH} = \text{p}K_a + \log\frac{[\text{Salt}]}{[\text{Acid}]}$$

(*ii*) $$\text{pH} = \left[-\frac{1}{2}(\log K_w + \log K_a - \log C)\right]$$ (*Panjab BSc, 2003*)

27. (*a*) Explain the buffer action of a mixture of ammonium hydroxide and ammonium chloride solution.

(*b*) The pH scale ranges from 0–14. Explain. (*Kalyani BSc, 2003*)

28. A solution is found to contain 0.63 g of nitric acid per 100 ml of the solution. If the acid is completely dissociated, calculate the pH of the solution.

Answer. 1 (*Delhi BSc, 2003*)

29. What is meant by buffer capacity? What is its value when 0.01 mole of NaOH is added to 9 buffer solution to change its pH value from 4.745 to 4.832?

Answer. 0.11494 (*Sambalpur BSc, 2003*)

30. Calculate the pH of 0.01 M solution of acetic acid. K_a for CH_3COOH is 1.8×10^{-5} at 25°C.

Answer. 3.3725 (*Delhi BSc, 2003*)

31. The buffer solution of pH = 5 is to be prepared by using acetic acid and sodium acetate. Calculate the ratio [Salt] : [Acid] that must be used. $K_a = 1.8 \times 10^{-5}$.

Answer. 0.5691 (*Goa BSc, 2003*)

32. (*a*) What do you understand by a buffer solution? Give examples of such solutions.

(*b*) Given the dissociation constant of acetic acid at 25°C as 1.8×10^{-5}, calculate the pH of a solution containing 0.185 g mol acetic acid and 3.015 g mol sodium acetate per litre.

Answer. (*b*) 5.956 (*Dibrugarh BSc, 2004*)

33. What is a buffer solution? Calculate the pH of 0.001 M HCl and 0.01 M NaOH.

Answer. 3; 12 (*Agra BSc, 2004*)

34. An aqueous solution of aniline of concentration 0.24 M is prepared. What concentration of sodium hydroxide is needed in this solution so that anilinium ion concentration remains at 1×10^{-8} M ?

(K_a for $C_6H_5NH_3^+ = 2.4 \times 10^{-5}$)

Answer. 1×10^{-2} (*Punjabi BSc, 2005*)

35. Calculate the *pH* of the following solution :

(i) 0.0002 M HCl

(ii) 0.1 M NH_4OH ($K_b = 1.8 \times 10^{-5}$)

Answer. (i) 3.6990 ; (ii) 11.13 (*Madurai BSc, 2005*)

36. Calculate the *pH* of a solution made by mixing 50 ml of 0.01 M $Ba(OH)_2$ solution with 50 ml of water.

Answer. 12 (*Mysore BSc, 2005*)

37. What is the pH of 0.50 M aqueous NaCN solution ? pK_b of CN^- is 4.70`

Answer. 11.5 (*Baroda BSc, 2006*)

38. Calculate the hydrogen ion concentration in a sample of blood having *pH* = 7.4.

Answer. 3.98×10^{-8} M (*Kerala BSc, 2006*)

MULTIPLE CHOICE QUESTIONS

1. An acid is a compound that gives H^+ ions in water and a base is a compound that gives OH^- ions in water. This concept was given by

(*a*) Arrhenius
(*b*) Lewis
(*c*) Bronsted
(*d*) Lowry

Answer. (*a*)

2. Which one of the following is the limitation of Arrhenius concept?

(*a*) free H^+ and OH^- ions do not exist in water
(*b*) this concept is limited to water only
(*c*) some bases do not contain OH^- ions
(*d*) all of these

Answer. (*d*)

3. According to Bronsted-Lowry concept, an acid is a substance that

(*a*) accepts a proton
(*b*) releases a proton
(*c*) accepts an electron pair
(*d*) releases an electron pair

Answer. (*b*)

4. A substance accepts a proton. According to Bronsted-Lowry concept it is

(*a*) an acid
(*b*) a base
(*c*) a neutral substance
(*d*) amphoteric

Answer. (*b*)

5. In the following reaction

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

the species that acts as a Bronsted base is

(*a*) H_2O
(*b*) HCl
(*c*) H_3O^+
(*d*) Cl^-

Answer. (*b*)

6. When calcium oxide is dissolved in water, following reaction takes place

$O^{2-} + H_2O \rightarrow 2OH^-$

The Bronsted acid is

(*a*) O^{2-}
(*b*) H_2O
(*c*) OH^-
(*d*) none of these

Answer. (*b*)

7. In the following hypothetical reaction

$HA + B^- \rightleftharpoons HB + A^-$

The conjugate base of the acid HA is

(*a*) B^-
(*b*) HA
(*c*) A^-
(*d*) none of these

Answer. (*c*)

8. In the reaction between NH_3 and HCl

$HCl + NH_3 \rightleftharpoons NH_4^+ + Cl^-$

the conjugate acid of NH_3 is

(*a*) HCl
(*b*) NH_4^+
(*c*) Cl^-
(*d*) none of these

Answer. (*b*)

9. A weak base has _______ conjugate acid and a weak acid has a _______ conjugate base

(*a*) strong, strong
(*b*) weak, strong
(*c*) strong, weak
(*d*) weak, weak

Answer. (*a*)

10. Molecules or ions that can behave both as Bronsted acid and base are called

(*a*) monoprotic acids
(*b*) polyprotic acids
(*c*) amphiprotic substances
(*d*) polyprotic bases

Answer. (*c*)

11. HCO_3^- is an example of

(*a*) conjugate acid
(*b*) conjugate base
(*c*) amphiprotic ion
(*d*) amphoteric ion

Answer. (*c*)

12. The strength of a Bronsted acid depends upon its tendency to _______ a proton

(*a*) gain
(*b*) donate
(*c*) react with
(*d*) none of these

Answer. (*b*)

13. According to Lewis concept an acid is _______ acceptor

(*a*) proton
(*b*) base
(*c*) electron
(*d*) electron pair

Answer. (*d*)

14. All cations and molecules that are short of an electron pair act as _______

(*a*) Lewis acids
(*b*) Lewis bases
(*c*) Bronsted acid
(*d*) Bronsted bases

Answer. (*a*)

15. According to Lewis concept, a reaction between an acid and a base is the transfer of

(*a*) a proton from acid to base
(*b*) OH^- ion from bases to acid
(*c*) electron pair from acid to base
(*d*) electron pair from base to acid

Answer. (*d*)

16. The auto-ionisation of water can be represented by

(*a*) $H_2O \rightleftharpoons H^+ + OH^-$
(*b*) $H_2O + H^+ \rightleftharpoons H_3O^+ + OH^-$
(*c*) $H_2O + H_2O \rightleftharpoons H_3O^+ + OH^-$
(*d*) $H_2O + HA \rightleftharpoons H_3O^+ + A^-$

Answer. (*c*)

17. The strength of an acid depends upon

(*a*) the concentration of H^+ ions in aqueous solution
(*b*) the concentration of electrons pairs in aqueous solution
(*c*) the tendency to release the electron pair
(*d*) the tendency to gain the electron pair

Answer. (*a*)

18. The dissociation constant of an acid HA is given by

(*a*) $K_a = \dfrac{[H^+][A^-]}{[HA]}$
(*b*) $K_a = \dfrac{[H^+]^2[A^-]^2}{[HA]}$
(*c*) $K_a = \dfrac{[H^+][A]^2}{[HA]}$
(*d*) $K_a = \dfrac{[H^+]^2[A]}{[HA]}$

Answer. (*a*)

19. For a weak acid with α as its degree of dissociation, the value of dissociation constant is given by (*C* is concentration of acid in moles per litre)

(*a*) $K_a = C\alpha$
(*b*) $K_a = C\alpha^2$
(*c*) $K_a = C^2\alpha$
(*d*) $K_a = C^2\alpha^2$

Answer. (*b*)

20. The strength of a base depends upon the

(*a*) concentration of H^+ ions in aqueous solution

(*b*) concentration of OH^- ions in aqueous solution
(*c*) concentration of electron pairs in aqueous solution
(*d*) concentration of the base

Answer. (*b*)

21. The dissociation constant K_b for a base BOH is given by the expression

(*a*) $K_b = \frac{[B^+][H^+]}{[BOH]}$ (*b*) $K_b = \frac{[B^+][OH^-]}{[BOH]}$
(*c*) $K_b = \frac{[B^+][OH^-]^2}{[BOH]}$ (*d*) $K_b = \frac{[B^+]^2[OH^-]}{[BOH]}$

Answer. (*b*)

22. Which is correct about pH?

(*a*) $pH = -\log [H^+]$ (*b*) $pH = \log \frac{1}{[H^+]}$
(*c*) $pH = 10^{-pH}$ (*d*) all of these

Answer. (*d*)

23. The concept of pH was introduced by

(*a*) Arrhenius (*b*) Bronsted
(*c*) Lewis (*d*) Sorensen

Answer. (*d*)

24. Which of the following is correct?

(*a*) $pH - pOH = 14$ (*b*) $pH + pOH = 7$
(*c*) $pH - pOH = 0$ (*d*) $pH + pOH = 14$

Answer. (*d*)

25. The pH of 0.001 M HCl is

(*a*) 0.001 (*b*) 10^{-3}
(*c*) 3 (*d*) –3

Answer. (*c*)

26. The pH of a solution of HCl is 1. The amount of acid present in one litre of the solution will be

(*a*) 3.65 g lit^{-1} (*b*) 0.365 g lit^{-1}
(*c*) 36.5 g lit^{-1} (*d*) 1.0 g lit^{-1}

Answer. (*a*)

27. The pH of 0.1 M NaOH solution will be

(*a*) 1 (*b*) 0.1
(*c*) 13 (*d*) 14

Answer. (*c*)

28. The pOH of 0.1 M KOH is

(*a*) 0.1 (*b*) 1.0
(*c*) –1.0 (*d*) 13

Answer. (*b*)

29. The fraction of total molecules which is ionised in a solution of an electrolyte is known as

(*a*) dissociation constant (*b*) mole fraction of the electrolyte
(*c*) degree of dissociation (*d*) electrolyte constant

Answer. (*c*)

30. Acetic acid is a weak electrolyte because

(*a*) its molecular mass is high (*b*) it exists as dimer

(*c*) it is highly unstable
(*d*) it has low ionisation

Answer. (*d*)

31. The strength of an acid depends on the
(*a*) number of H atoms present in its molecule
(*b*) concentration of protons given by it on ionisation
(*c*) concentration of water
(*d*) concentration of acid

Answer. (*b*)

32. Which of the following does not act as Bronsted acid?
(*a*) $CH_3\ COO^-$
(*b*) NH_4^+
(*c*) HCO_3^-
(*d*) HSO_3^-

Answer. (*a*)

33. The pH of a solution is 3, the hydrogen ion concentration is mole lit^{-1} is
(*a*) 1×10^{-1}
(*b*) 2×10^{-1}
(*c*) 1×10^{-3}
(*d*) 3×10^{-2}

Answer. (*c*)

34. The pOH and pH of 0.1 M aqueous HCl will be
(*a*) 13, 1
(*b*) 1, 13
(*c*) 14, 0
(*d*) 0, 14

Answer. (*a*)

35. The pH of a solution increases from 1 to 2. The concentration of H^+ ions
(*a*) decreases
(*b*) increases
(*c*) remains the same
(*d*) becomes zero

Answer. (*a*)

36. On the addition of a small amount of an acid or a base, the pH value of a buffer solution ________
(*a*) increases
(*b*) decreases
(*c*) remains unaltered
(*d*) none of these

Answer. (*c*)

37. The Henderson equation for an acidic buffer is
(*a*) $\text{pH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$
(*b*) $\text{pOH} = \text{p}K_a + \log \frac{[\text{salt}]}{[\text{acid}]}$
(*c*) $\text{pH} = \text{p}K_a - \log \frac{[\text{salt}]}{[\text{acid}]}$
(*d*) $\text{pH} = \text{p}K_a - \log \frac{[\text{acid}]^2}{[\text{acid}]}$

Answer. (*a*)

38. For a basic buffer, the Henderson equation is
(*a*) $\text{pH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$
(*b*) $\text{pOH} = \text{p}K_b - \log \frac{[\text{salt}]}{[\text{base}]}$
(*c*) $\text{pOH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$
(*d*) $\text{pH} = \text{p}K_b + \log \frac{[\text{salt}]}{[\text{base}]}$

Answer. (*c*)

39. When a small quantity of HCl is added to a mixture of sodium acetate and acetic acid (equimolar), the pH value
(*a*) increases
(*b*) decreases
(*c*) remains the same
(*d*) increases abruptly

Answer. (*c*)

40. The following equilibrium exists in aqueous solution $CH_3\ COOH \rightleftharpoons H^+ + CH_3COO^-$. When dil HCl is added
(*a*) the equilibrium constant will increase
(*b*) acetate ion concentration decreases

(*c*) acetate ion concentration increases (*d*) the equilibrium constant will decrease

Answer. (*b*)

41. The compound that is not a Lewis acid is

(*a*) BF_3 (*b*) $AlCl_3$

(*c*) $BeCl_2$ (*d*) $BaCl_2$

Answer. (*d*)

42. The ionic product of water will increase if

(*a*) temperature is reduced (*b*) temperature is increased

(*c*) pressure is decreased (*d*) pressure is increased

Answer. (*b*)

43. The solution A has pH equal to 2 and solution B has pH of 4. Which one of the following is true?

(*a*) solution B is 100 times more acidic than solution A

(*b*) solution B is twice more acidic than solution A

(*c*) solution A is twice more acidic than solution B

(*d*) solution A is 100 times more acidic than solution B

Answer. (*d*)

44. The pH of 10^{-10} M solution of NaOH is nearly

(*a*) –10 (*b*) 10

(*c*) 7 (*d*) zero

Answer. (*c*)

45. The pH of a solution is enhanced from 2 to 3. The concentration of H^+ in the new solution

(*a*) is three times the original solution (*b*) is about 1.5 times the original solution

(*c*) decreases 10 times (*d*) increases 10 times

Answer. (*c*)

46. Which of the following is not a buffer solution?

(*a*) $NH_4Cl + NH_4OH$ (*b*) $CH_3COONa + CH_3COOH$

(*c*) $NaOH + HCl$ (*d*) $HCOONa + HCOOH$

Answer. (*c*)

47. Which one of the following statement is correct?

(*a*) $pK_w = 14$ at all temperatures (*b*) $pK_w = pH$ at 0°C

(*c*) pK_w decreases with increase temperature (*d*) pK_w increases with increase in temperature

Answer. (*d*)

48. All nucleophiles are

(*a*) Arrhenius acid (*b*) Bronsted bases

(*c*) Lewis acids (*d*) Lewis bases

Answer. (*d*)

49. The best indicator for titrating HCl with NH_4OH is

(*a*) litmus (*b*) phenolphthalein

(*c*) methyl orange (*d*) phenol red

Answer. (*c*)

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