

# Acids & Bases

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## Objectives

At the end of this, we will be able to-

- Know the concepts of acids and bases.
- Explain the relative strength of acids and bases and different terms in acid-base equilibrium.
- Know fundamentals of acid-base titration, neutralization curves and buffer solutions

## Contents

- Acids & Bases-several concepts
- Strong and weak acids and bases
- Acid-base equilibrium constants
- Self ionization of water
- pH & pOH
- Calculation significance of  $K_a$ ,  $K_b$ , and pH
- Calculation of percent ionization
- Effects of substituents on the strength of acids and bases
- Indicators
- Titration and titration curves
- Buffer solutions & calculation of pH of buffer solutions
- Biological importance of Buffer solutions

# Acids & Bases

Acidic substances are usually identified by their sour taste.

An acid is basically a molecule which can donate an  $H^+$  ion and can remain energetically favorable after a loss of  $H^+$ .

Acids are known to turn blue litmus red.

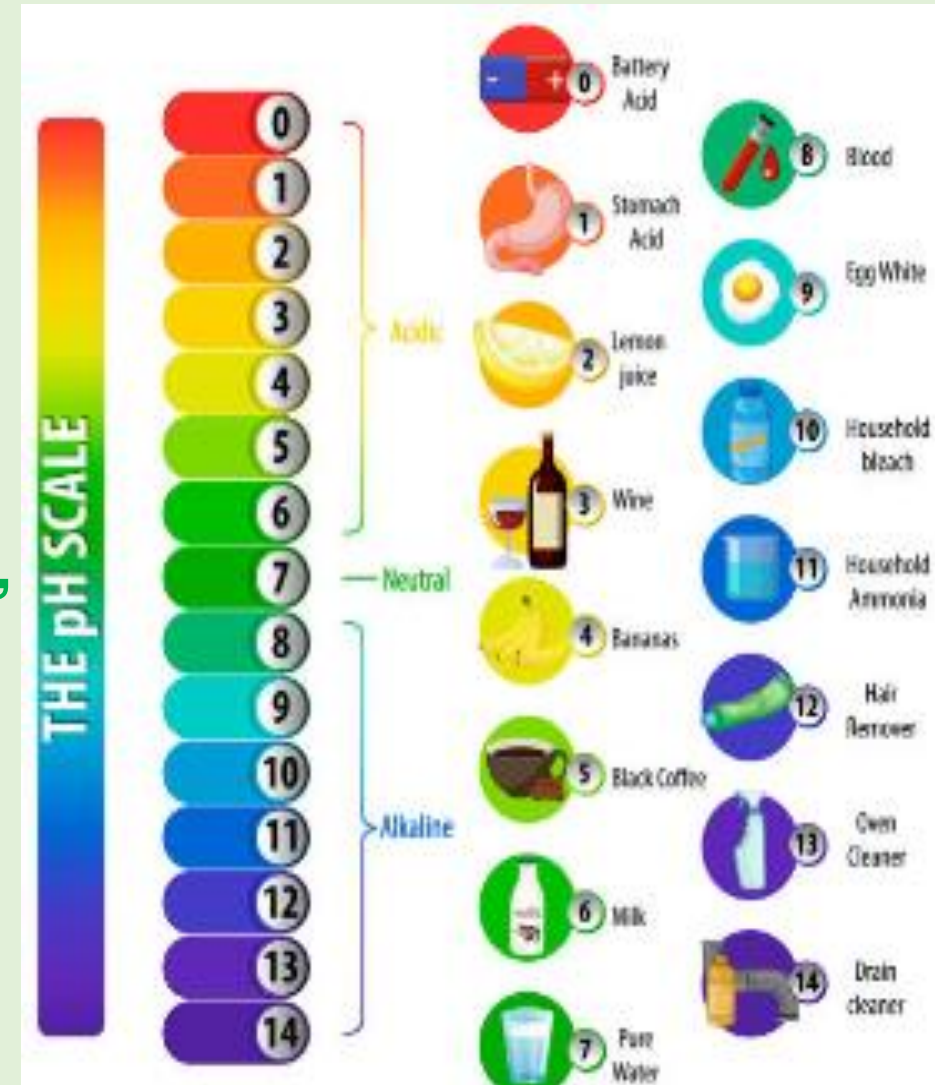
Bases are characterized by a bitter taste and a slippery texture.

A base that can be dissolved in water is referred to as an alkali.

When these substances chemically react with acids, they yield salts.

Bases are known to turn red litmus blue.

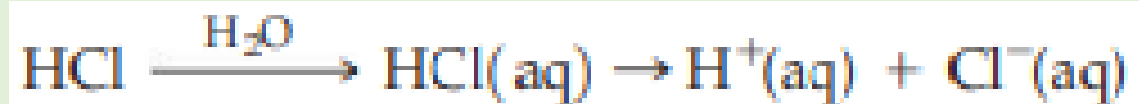
Acids and bases can be defined via three different theories.



# Acids & Bases

## Arrhenius Concept of Acids and Bases

The Swedish scientist Svante August Arrhenius defined acids as substances that increase the  $\text{H}^+$  ion concentration of water when dissolved in it. These protons go on to form hydronium ions ( $\text{H}_3\text{O}^+$ ) by combining with water molecules. Arrhenius proposed that in aqueous solutions, strong electrolytes exist only in the form of ions, whereas weak electrolytes exist partly as ions and partly as molecules. When the acid  $\text{HCl}$  dissolves in water, the  $\text{HCl}$  molecules ionize completely, yielding hydrogen ions, as one of the products.



Similarly, the Arrhenius definition of a base states that bases are the substances that, when dissolved in water, increase the concentration of  $\text{OH}^-$  ions in it. When the base  $\text{NaOH}$  dissolves in water, the and ions  $\text{Na}^+$ , and  $\text{OH}^-$  in the solid become dissociated from one another through the action of  $\text{H}_2\text{O}$  molecules.

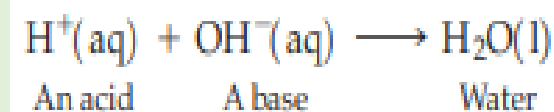


One of the merits of this theory is that it successfully explains the reaction between acids and bases that yield salts and water.

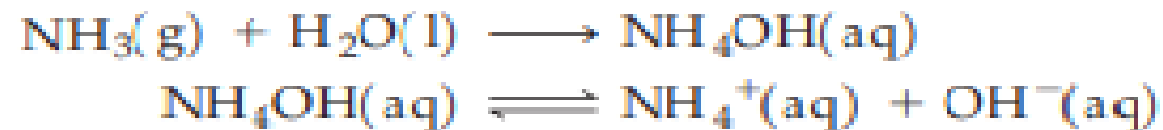
The neutralization reaction of  $\text{HCl}$  and  $\text{NaOH}$  can be represented with the ionic equation,



or net equation



Hypothetical substance,  $\text{NH}_4\text{OH}$



An important limitation of the Arrhenius definitions of acids and bases is that it fails to explain how substances lacking hydroxide ions form basic solutions when dissolved in water, such as  $\text{NH}_3$ ,  $\text{NO}_2^-$  and  $\text{F}^-$

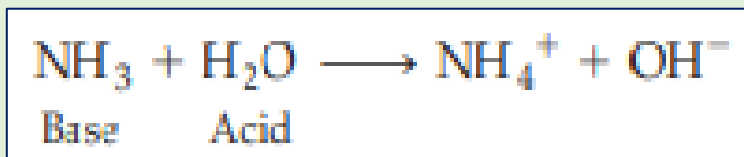
Arrhenius theory is in not recognizing the key role of the solvent in the ionization of a solute.

# Acids & Bases

## Bronsted Lowry Theory of Acids and Bases

The Bronsted-Lowry theory defines an acid as a donor of protons. A base is defined as a proton acceptor (or  $\text{H}^+$  ion acceptor) by this theory. Bronsted acids undergo dissociation to yield protons and therefore increase the concentration of  $\text{H}^+$  ions in the solution. On the other hand, Bronsted bases accept protons from water (the solvent) to yield hydroxide ions.

we can write,



$\text{H}_2\text{O}$  acts as an acid. It gives up a proton  $\text{H}^+$ , which is taken up by a base  $\text{NH}_3$ . As a result of this transfer, the polyatomic ions  $\text{NH}_4^+$  and  $\text{OH}^-$  are formed.

In the reverse reaction,  $\text{NH}_4^+$  is an acid and  $\text{OH}^-$  is a base.



An acid and a base that are related to each other as the pair  $\text{NH}_3/\text{NH}_4^+$  and the  $\text{H}_2\text{O}/\text{OH}^-$  in the reversible reaction, are referred to as a conjugate pairs. Thus, when  $\text{NH}_3$  is a base,  $\text{NH}_4^+$  is the conjugated acid of the base  $\text{NH}_3$ . Similarly, when  $\text{H}_2\text{O}$  is an acid,  $\text{OH}^-$  is the conjugated base of the acid.

The relationship between conjugate pairs

- Acid -  $\text{H}^+$   $\rightarrow$  conjugate base
- Base +  $\text{H}^+$   $\rightarrow$  conjugate acid

Any species that is an acid according to the Arrhenius theory is also an acid according to the Brønsted- Lowry theory; the same is true of bases. Certain species, even though they do not contain the OH group, produce  $\text{OH}^-$  in aqueous solution for example,  $\text{OCl}^-$ . As such, they are Brønsted- Lowry bases.

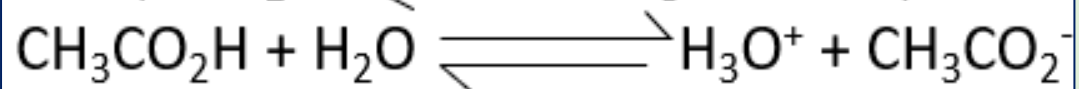
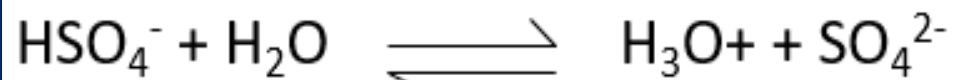
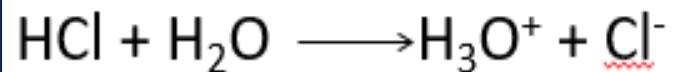
The Brønsted- Lowry theory accounts for substances that can act either as an acid or a base; such substances are said to be amphiprotic. **The Arrhenius theory does not account for the behavior of amphiprotic substances.**

An advantage of the Bronsted-Lowry definition of acids and bases is its ability to explain the acidic or basic nature of ionic species.

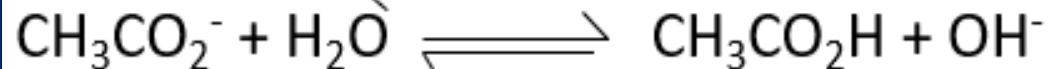
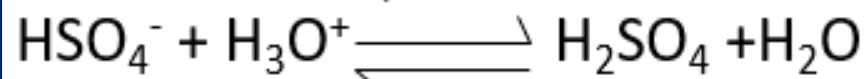
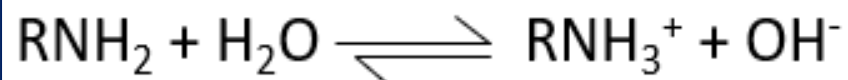
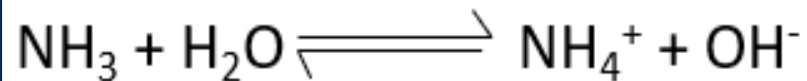
**An important limitation of this theory is that it fails to explain how compounds lacking hydrogen exhibit acidic properties, such as  $\text{BF}_3$  and  $\text{AlCl}_3$ .**

## Examples of Lowry- Bronsted Acids & Bases



### Lowry- Bronsted acids are



### Lowry- Bronsted Bases are



## Relative Strengths of Some Common Brønsted–Lowry Acids and Bases

Acid		Conjugate Base		
	Perchloric acid	$\text{HClO}_4$	Perchlorate ion	$\text{ClO}_4^-$
	Hydroiodic acid	$\text{HI}$	Iodide ion	$\text{I}^-$
	Hydrobromic acid	$\text{HBr}$	Bromide ion	$\text{Br}^-$
	Hydrochloric acid	$\text{HCl}$	Chloride ion	$\text{Cl}^-$
	Sulfuric acid	$\text{H}_2\text{SO}_4$	Hydrogen sulfate ion	$\text{HSO}_4^-$
	Nitric acid	$\text{HNO}_3$	Nitrate ion	$\text{NO}_3^-$
	Hydronium ion <sup>a</sup>	$\text{H}_3\text{O}^+$	Water <sup>a</sup>	$\text{H}_2\text{O}$
	Hydrogen sulfate ion	$\text{HSO}_4^-$	Sulfate ion	$\text{SO}_4^{2-}$
	Nitrous acid	$\text{HNO}_2$	Nitrite ion	$\text{NO}_2^-$
	Acetic acid	$\text{CH}_3\text{COOH}$	Acetate ion	$\text{CH}_3\text{COO}^-$
	Carbonic acid	$\text{H}_2\text{CO}_3$	Hydrogen carbonate ion	$\text{HCO}_3^-$
	Ammonium ion	$\text{NH}_4^+$	Ammonia	$\text{NH}_3$
	Hydrogen carbonate ion	$\text{HCO}_3^-$	Carbonate ion	$\text{CO}_3^{2-}$
	Water	$\text{H}_2\text{O}$	Hydroxide ion	$\text{OH}^-$
	Methanol	$\text{CH}_3\text{OH}$	Methoxide ion	$\text{CH}_3\text{O}^-$
	Ammonia	$\text{NH}_3$	Amide ion	$\text{NH}_2^-$
				



# Lewis Acids and Bases

In 1923, G. N. Lewis proposed an acid base theory closely related to bonding and structure. The Lewis acid base theory is not limited to reactions involving  $\text{H}^+$ , and  $\text{OH}^-$  and it extends acid base concepts to reactions in gases and in solids. It is especially important in describing certain reactions between organic molecules.

A Lewis acid is a species (an atom, ion, or molecule) that is an electron-pair acceptor, and a Lewis base is a species that is an electron-pair donor. A reaction between a Lewis acid (A) and a Lewis base (B) results in the formation of a covalent bond between them. The product of a Lewis acid base reaction is called an adduct (or addition compound). The reaction can be represented as



The formation of a covalent chemical bond by one species donating a pair of electrons to another is called coordination, and the bond joining the Lewis acid and Lewis base is called a coordinate covalent bond.

Lewis acids are species with vacant orbitals that can accommodate electron pairs; Lewis bases are species that have lone-pair electrons available for sharing.

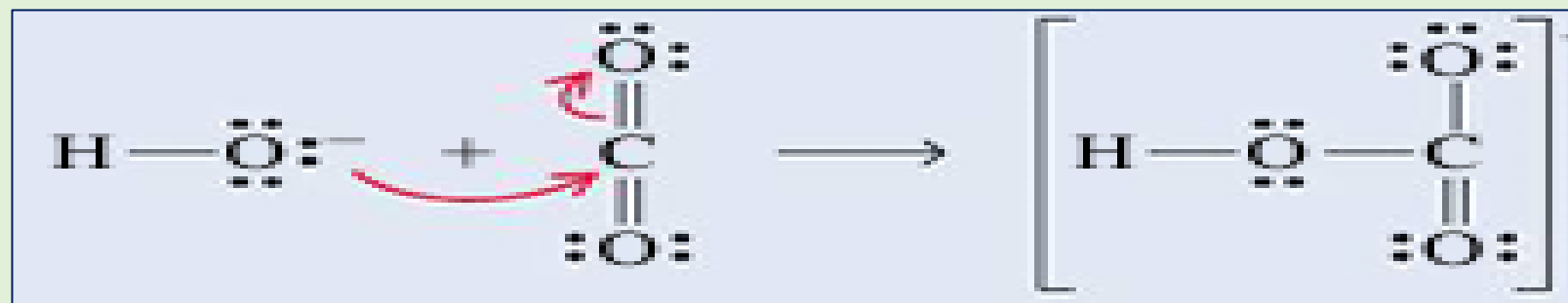
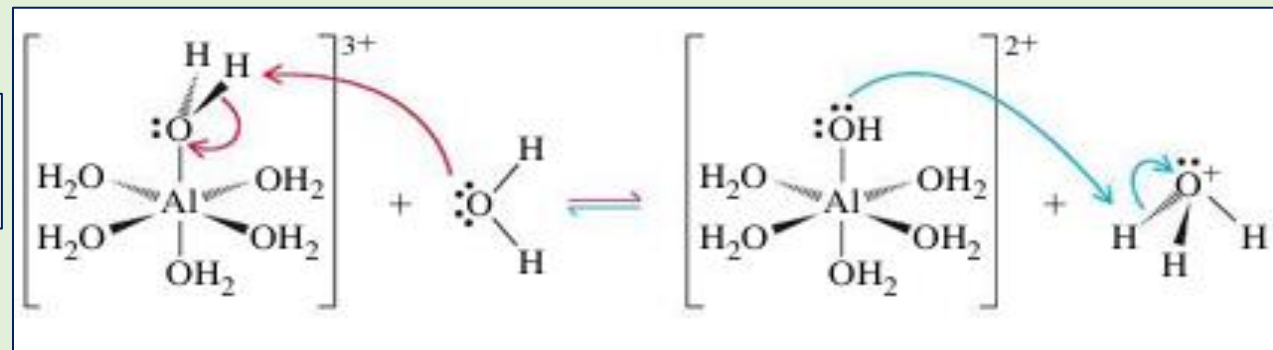
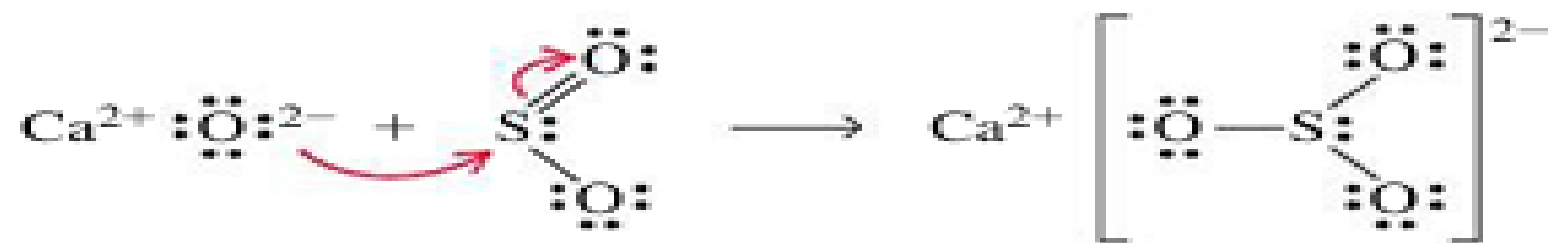
By these definitions,  $\text{OH}^-$  a Brønsted Lowry base, is also a Lewis base because lone-pair electrons are present on the O atom. So too  $\text{NH}_3$  is a Lewis base.

$\text{HCl}$ , conversely, is not a Lewis acid: It is not an electron-pair acceptor. We can think of  $\text{HCl}$  as producing  $\text{H}^+$ , however, and  $\text{H}^+$  is a Lewis acid. forms a coordinate covalent bond with an available electron pair.

Species with an incomplete valence shell are Lewis acids. When the Lewis acid forms a coordinate covalent bond with a Lewis base, the octet is completed. A good example of octet completion is the reaction of  $\text{BF}_3$  and  $\text{NH}_3$ .



# Lewis Acids and Bases -Examples





# Acids & Bases

A strong acid is an acid that is totally ionized in aqueous solution forming hydrated hydrogen ions,  $\text{H}_3\text{O}^+$ .

For example, hydrochloric acid,  $\text{HCl}$  (an), is a strong acid. Strong Acids:  $\text{HCl}$ ,  $\text{HBr}$ ,  $\text{HI}$ ,  $\text{HClO}_4$ ,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  - plus a few rare ones (e.g.  $\text{H}_2\text{SeO}_4$ ).



The ionization of  $\text{HCl}$  in dilute aqueous solutions goes essentially to completion. The self-ionization of water occurs only to a very slight extent. As a result, in calculating  $[\text{H}_3\text{O}^+]$  in an aqueous solution of a strong acid, the strong acid is the only significant source of  $[\text{H}_3\text{O}^+]$ . The contribution due to the self-ionization of water can generally be ignored unless the solution is extremely dilute.



An weak acid is an acid that is only very slightly ionized in aqueous solution.

For example, ethanoic acid is an weak acid. A  $0.1 \text{ mol dm}^{-3}$  solution of ethanoic acid is only 1.3% ionized.

A strong base is totally ionized in aqueous solution forming hydroxide ions,  $\text{OH}^-$ .

For example, sodium hydroxide is a strong base.



Strong Bases:  $\text{MOH}$  and  $\text{M(OH)}_2$ , where  $\text{M} = \text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Rb}^+$ ,  $\text{Cs}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Sr}^{2+}$ ,  $\text{Ba}^{2+}$ . The common strong bases are ionic hydroxides. When these bases dissolve in water,  $\text{H}_2\text{O}$  molecules completely dissociate the cations and anions ( $\text{OH}^-$ ) of the base from each other. The self-ionization of water, because it occurs to so very limited an extent, is an insignificant source of  $\text{OH}^-$ . This means that in calculating  $[\text{OH}^-]$  in an aqueous solution of a strong base, the strong base is the only significant source of  $\text{OH}^-$  unless the solution is extremely dilute.

A weak base is protonated to only a small degree in solution and so only forms a small proportion of hydroxide ions.

For example, ammonia is a weak base:



The Common Strong Acids and Strong Bases

Acids	Bases
$\text{HCl}$	$\text{LiOH}$
$\text{HBr}$	$\text{NaOH}$
$\text{HI}$	$\text{KOH}$
$\text{HClO}_4$	$\text{RbOH}$
$\text{HNO}_3$	$\text{CsOH}$
$\text{H}_2\text{SO}_4^a$	$\text{Mg(OH)}_2$
	$\text{Ca(OH)}_2$
	$\text{Sr(OH)}_2$
	$\text{Ba(OH)}_2$

# Acid & Base Equilibrium Constant (Acid dissociation constant, $K_a$ )

A weak acid is in equilibrium with its conjugate base in aqueous solution.

Consider a weak acid, HA;  $\text{HA} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{A}^-$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

The expression for equilibrium constant (acid dissociation constant,  $K_a$ ) is

$[\text{H}_2\text{O}]$  is not included in this expression as the concentration of water, in aqueous solutions, is constant. The true expression of the equilibrium constant includes  $[\text{H}_2\text{O}]$ .

$$K_{\text{true}} = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

1 dm<sup>3</sup> of water has a mass of 1000g. It contains  $1000\text{g}/18.0\text{g mol}^{-1} = 55.6$  mol. Thus, concentration of water in an aqueous solution is 55.6 mol dm<sup>-3</sup>. This is constant for all aqueous equilibria involving weak acids.

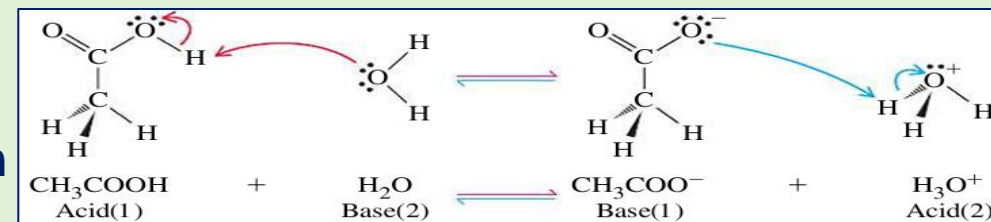
Therefore, its value can be incorporated into the equilibrium expression.

Thus,  $K_a = K_{\text{true}} \times 55.6$

$$K_{\text{true}} \times 55.6 = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

As for example, The ionization of acetic acid can be expressed as  
Here, acetate ion,  $\text{CH}_3\text{COO}^-$  is the conjugate base of the acid  $\text{CH}_3\text{COOH}$ .  $\text{H}_2\text{O}$  acts as a base. Its conjugate acid is the hydronium ion  $\text{H}_3\text{O}^+$ . Thus, ionization of  $\text{CH}_3\text{COOH}$  can be expressed can be described as-

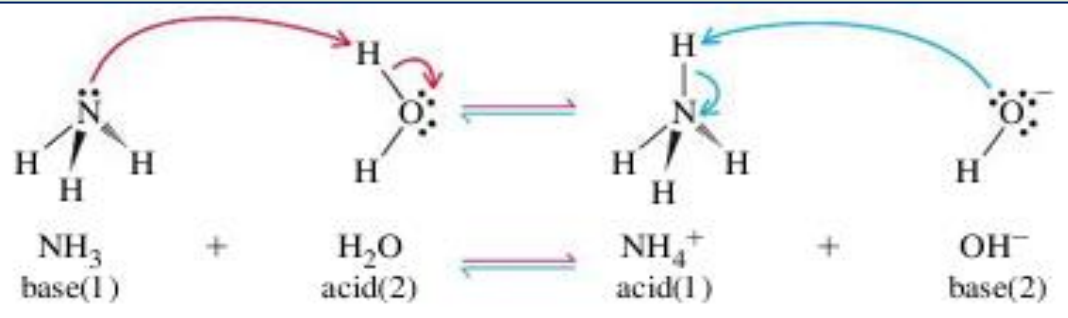
$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = 1.8 \times 10^{-5}$$



Here, the equilibrium constant  $K_a$  is called the acid ionization constant of acetic acid.

# Acid & Base Equilibrium Constant (Base dissociation constant, $K_b$ )

A weak base is in equilibrium with its conjugate acid in aqueous solution, for example,



The equilibrium constant expression for reaction,

$$K = \frac{a_{\text{NH}_4^+} a_{\text{OH}^-}}{a_{\text{NH}_3} a_{\text{H}_2\text{O}}}$$

In an aqueous solution the activities of  $\text{NH}_3$ ,  $\text{NH}_4^+$ , and  $\text{OH}^-$  are approximately equal to  $[\text{NH}_3]$ ,  $[\text{NH}_4^+]$ , and  $[\text{OH}^-]$  respectively, the expression can be written as The equilibrium constant  $K_b$  is called the base ionization constant.

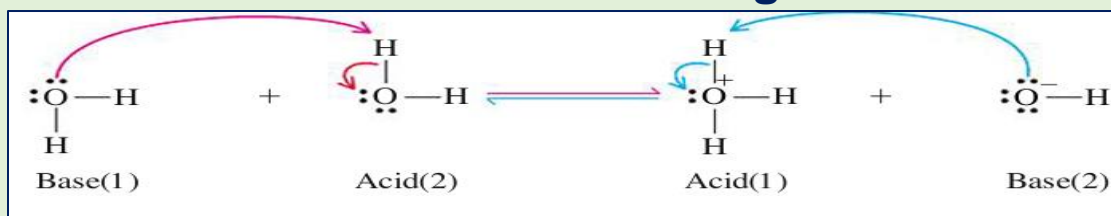
$$K = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5} = K_b$$

As with weak acids,  $[\text{H}_2\text{O}]$  is omitted from the expression because its value is constant in aqueous equilibria involving weak bases.

# Self Ionization of Water

Even when it is pure, water contains a very low concentration of ions that can be detected in precise electrical conductivity measurements. The ions form as a result of the amphoteric nature of water; some water molecules donate protons and others accept protons. In the self-ionization (or autoionization) of water, for each  $\text{H}_2\text{O}$  molecule that acts as an acid, another  $\text{H}_2\text{O}$  molecule acts as a base, and hydronium  $\text{H}_3\text{O}^+$  and hydroxide  $\text{OH}^-$  ions are formed. The reaction is reversible, and in the reverse reaction,  $\text{H}_3\text{O}^+$  releases a proton to  $\text{OH}^-$ .

The reverse reaction is far more significant than the forward reaction. Equilibrium is displaced far to the left.



In reaction acid, (1) and base(2) are much stronger than are acid(2) and base(1).

For the self-ionization of water, we can write-

$[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  are equal in pure water. At  $25^\circ\text{C}$  in pure water:

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

The equilibrium condition for the self-ionization of water is called the ion product of water. It is symbolized as  $K_w$ . At  $25^\circ\text{C}$ ,

$$[\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

Since  $K_w$  is an equilibrium constant, the product of the concentrations of the hydronium and hydroxide ions must always equal  $10^{-14}$ . If the concentration of  $\text{H}_3\text{O}^+$  is increased by the addition of an acid, then the concentration of  $\text{OH}^-$  must decrease to maintain the value of  $K_w$ . If the concentration of  $\text{OH}^-$  is increased by the addition of a base, then the concentration of  $\text{H}_3\text{O}^+$  must decrease. The above equation connects the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  and applies to all aqueous solutions, not just to pure water. For an acidic solution containing  $1.0 \times 10^{-3} \text{ mol dm}^{-3}$  of  $\text{H}^+(\text{aq.})$  ions,  $[\text{OH}^-] = 1.0 \times 10^{-14} / 1.0 \times 10^{-3} = 1.0 \times 10^{-11} \text{ mol dm}^{-3}$

# pH & pOH

In 1909, the Danish biochemist Søren Sørensen proposed the term pH to refer to the 'potential of hydrogen ion'. He defined pH as the negative of the logarithm of  $[H^+]$ . Restated in terms of  $[H_3O^+]$ ,  $pH = -\log[H_3O^+]$

The quantity pOH can be defined as  $pOH = -\log[OH^-]$

A useful expression can be derived by taking the negative logarithm of  $K_w$  expression (written for 25 °C) and introducing the symbol  $pK_w$

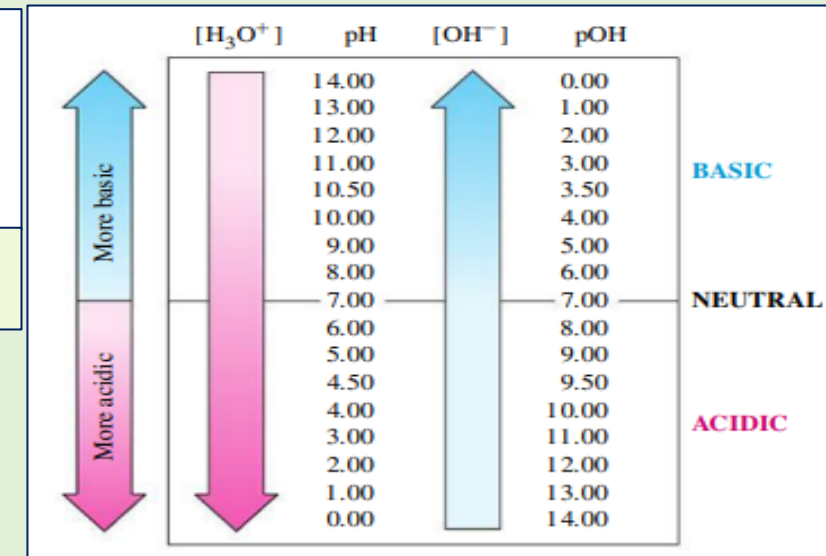
$$K_w = [H_3O^+][OH^-] = 1.0 \times 10^{-14}$$

$$-\log K_w = -(\log[H_3O^+][OH^-]) = -\log(1.0 \times 10^{-14})$$

$$pK_w = -(\log[H_3O^+] + \log[OH^-]) = -(-14.00)$$

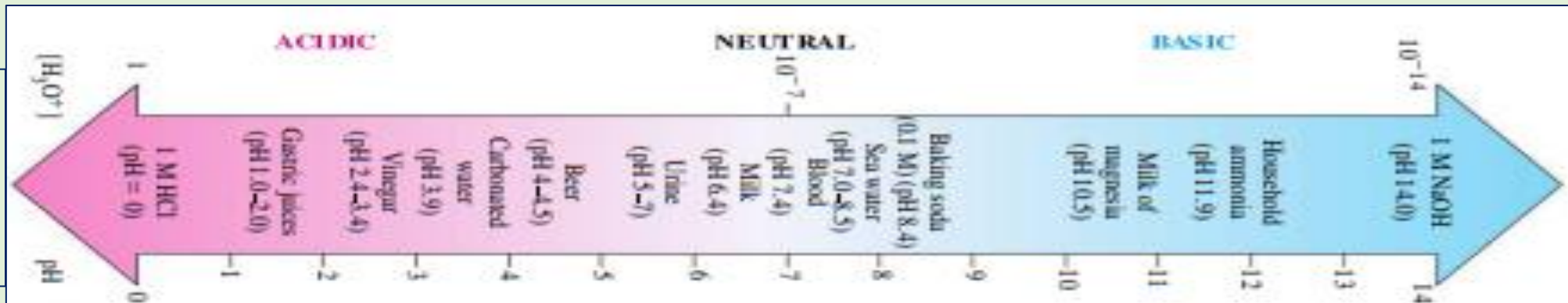
$$= -\log[H_3O^+] - \log[OH^-] = 14.00$$

$$pK_w = pH + pOH = 14.00$$



An aqueous solution with  $[H_3O^+] = [OH^-]$  is said to be neutral. In pure water at 25 °C,  $[H_3O^+] = [OH^-] = 1 \times 10^{-7} \text{ M}$  and  $pH = 7.00$ . Thus at 25 °C, all aqueous solutions with  $pH = 7.00$  are neutral. If the pH is less than 7.00, the solution is acidic; if the pH is greater than 7.00, the solution is basic, or alkaline.

The hydrogen ion concentration can be calculated from the pH, using the expression:  $[H^+] = 10^{-pH}$



## Calculate in an extremely dilute solution of a strong acid?

The pH of a solution as dilute as  $1 \times 10^{-8}$  M HCl. We would write  $[\text{H}_3\text{O}^+] = 1 \times 10^{-8}$  M and  $\text{pH} = 8$ .

But how can a solution of a strong acid, no matter how dilute, have a pH greater than 7?

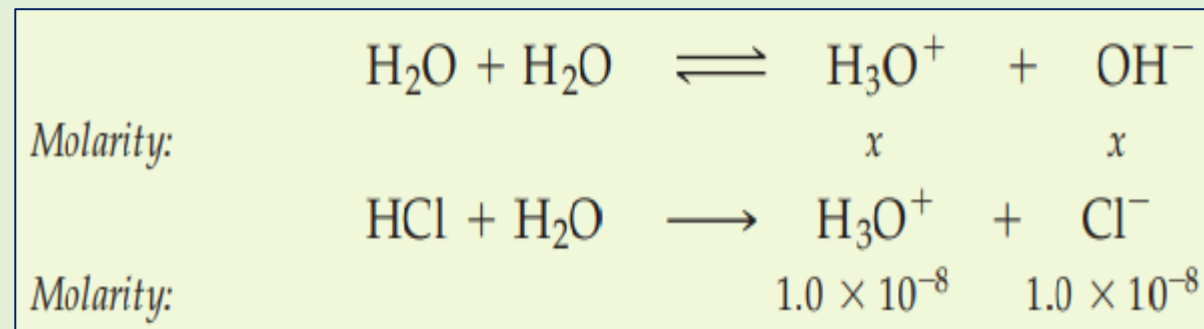
The difficulty is that at this extreme dilution, we must consider two sources of  $[\text{H}_3\text{O}^+]$ . The sources of  $[\text{H}_3\text{O}^+]$  and the ion concentrations from both sources are indicated as follows:

Thus,  $K_w$  expression for this solution,

$$[\text{H}_3\text{O}^+][\text{OH}^-] = (x + 1.0 \times 10^{-8})x = 1.0 \times 10^{-14}$$

This expression rearranges to the quadratic form-

$$x^2 + (1.0 \times 10^{-8})x - (1.0 \times 10^{-14}) = 0$$



The solution to this equation is  $x = 9.5 \times 10^{-8}$  M. Therefore, we combine  $[\text{H}_3\text{O}^+]$  from both sources to get  $[\text{H}_3\text{O}^+] = (9.5 \times 10^{-8})\text{M} + (1.0 \times 10^{-8})\text{M} = 1.05 \times 10^{-7}$  M,  $\text{pH} = 6.98$ . From this result, we conclude that the pH is slightly less than 7, as expected for a very dilute acid, and that the self-ionization of water contributes nearly ten times as much hydronium ion to the solution as does the strong acid.



# Ionization Constants of Some Weak Acids & Bases In Water at 25 °C

Ionization Equilibrium				Ionization Constant $K$	pK
Acid				$K_a =$	$pK_a =$
Iodic acid	$\text{HIO}_3 + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{IO}_3^-$	$1.6 \times 10^{-1}$	0.80
Chlorous acid	$\text{HClO}_2 + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{ClO}_2^-$	$1.1 \times 10^{-2}$	1.96
Chloroacetic acid	$\text{ClCH}_2\text{COOH} + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{ClCH}_2\text{COO}^-$	$1.4 \times 10^{-3}$	2.85
Nitrous acid	$\text{HNO}_2 + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{NO}_2^-$	$7.2 \times 10^{-4}$	3.14
Hydrofluoric acid	$\text{HF} + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{F}^-$	$6.6 \times 10^{-4}$	3.18
Formic acid	$\text{HCOOH} + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{HCOO}^-$	$1.8 \times 10^{-4}$	3.74
Benzoic acid	$\text{C}_6\text{H}_5\text{COOH} + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{C}_6\text{H}_5\text{COO}^-$	$6.3 \times 10^{-5}$	4.20
Hydrazoic acid	$\text{HN}_3 + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{N}_3^-$	$1.9 \times 10^{-5}$	4.72
Acetic acid	$\text{CH}_3\text{COOH} + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$	$1.8 \times 10^{-5}$	4.74
Hypochlorous acid	$\text{HOCl} + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{OCl}^-$	$2.9 \times 10^{-8}$	7.54
Hydrocyanic acid	$\text{HCN} + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{CN}^-$	$6.2 \times 10^{-10}$	9.21
Phenol	$\text{HOC}_6\text{H}_5 + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{C}_6\text{H}_5\text{O}^-$	$1.0 \times 10^{-10}$	10.00
Hydrogen peroxide	$\text{H}_2\text{O}_2 + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{H}_3\text{O}^+ + \text{HO}_2^-$	$1.8 \times 10^{-12}$	11.74
Base				$K_b =$	$pK_b =$
Diethylamine	$(\text{C}_2\text{H}_5)_2\text{NH} + \text{H}_2\text{O}$	$\rightleftharpoons$	$(\text{C}_2\text{H}_5)_2\text{NH}_2^+ + \text{OH}^-$	$6.9 \times 10^{-4}$	3.16
Ethylamine	$\text{C}_2\text{H}_5\text{NH}_2 + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{C}_2\text{H}_5\text{NH}_3^+ + \text{OH}^-$	$4.3 \times 10^{-4}$	3.37
Ammonia	$\text{NH}_3 + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{NH}_4^+ + \text{OH}^-$	$1.8 \times 10^{-5}$	4.74
Hydroxylamine	$\text{HONH}_2 + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{HONH}_3^+ + \text{OH}^-$	$9.1 \times 10^{-9}$	8.04
Pyridine	$\text{C}_5\text{H}_5\text{N} + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{C}_5\text{H}_5\text{NH}^+ + \text{OH}^-$	$1.5 \times 10^{-9}$	8.82
Aniline	$\text{C}_6\text{H}_5\text{NH}_2 + \text{H}_2\text{O}$	$\rightleftharpoons$	$\text{C}_6\text{H}_5\text{NH}_3^+ + \text{OH}^-$	$7.4 \times 10^{-10}$	9.13

↑  
Acid strength

↑  
Base strength



# Calculation of $K_a$ from pH

A solution of ethanoic acid of concentration  $0.100 \text{ mol dm}^{-3}$  has a pH of 2.88. Calculate the value of  $K_a$ .



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{CO}_2^-]}{[\text{CH}_3\text{CO}_2\text{H}]}$$

The concentrations  $[\text{H}_3\text{O}^+]$  and  $[\text{CH}_3\text{CO}_2^-]$  are equal.

$[\text{CH}_3\text{CO}_2\text{H}] = 0.100 \text{ mol dm}^{-3}$ . in fact  $[\text{CH}_3\text{CO}_2\text{H}]$  is slightly less than  $0.100 \text{ mol dm}^{-3}$  because some molecules have dissociated. For most weak electrolytes, the difference can be neglected.

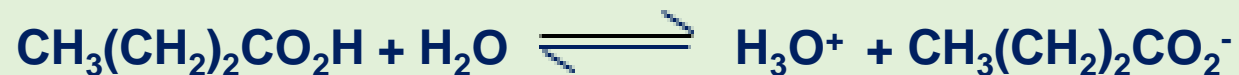
Since,  $\text{pH} = 2.88$ ,  $[\text{H}_3\text{O}^+] = 10^{-2.88} = 1.32 \times 10^{-3} \text{ mol dm}^{-3}$ .

$$\begin{aligned} K_a &= (1.32 \times 10^{-3} \text{ mol dm}^{-3})^2 / 0.100 \text{ mol dm}^{-3} - 1.32 \times 10^{-3} \text{ mol dm}^{-3} \\ &= 1.76 \times 10^{-5} \text{ mol dm}^{-3} \end{aligned}$$

$$\text{p}K_a = -\lg K_a = 4.75.$$

## Calculation of pH from $K_a$

Calculate the pH of a  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$  solution of butanoic acid, for which  $K_a = 1.51 \times 10^{-5} \text{ mol dm}^{-3}$ .



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_3\text{H}_7\text{CO}_2^-]}{[\text{C}_3\text{H}_7\text{CO}_2\text{H}]}$$

The concentrations  $[\text{H}_3\text{O}^+]$  and  $[\text{C}_3\text{H}_7\text{CO}_2^-]$  are equal.

The concentration of  $[\text{C}_3\text{H}_7\text{CO}_2\text{H}]$  is very little less than  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ . Since the degree of ionization is small, the approximation  $[\text{C}_3\text{H}_7\text{CO}_2\text{H}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$  is made to simplify the calculation. Then

$$[\text{H}_3\text{O}^+]^2 = 1.51 \times 10^{-5} \times 1.0 \times 10^{-2} \text{ mol}^2 \text{ dm}^{-6}$$

$$[\text{H}_3\text{O}^+] = 3.89 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{pH} = 3.42$$

**Validity of approximation:**

$$[\text{H}^+] = 3.89 \times 10^{-4} \text{ mol dm}^{-3}$$

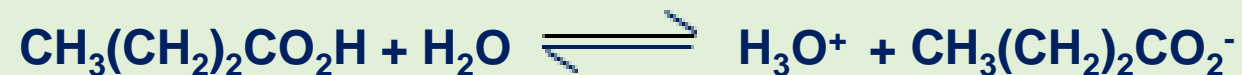
$$[\text{C}_3\text{H}_7\text{CO}_2\text{H}] \text{ of equilibrium} = (1.0 \times 10^{-2}) - (3.89 \times 10^{-4}) = 0.96 \times 10^{-2} \text{ mol dm}^{-3}$$

When, we use this value for  $\text{C}_3\text{H}_7\text{CO}_2\text{H}$ ,  $\text{pH} = 3.42$ .

So, approximation is justified.

## Calculation of pH from $K_a$

Calculate the pH of a  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$  solution of butanoic acid, for which  $K_a = 1.51 \times 10^{-5} \text{ mol dm}^{-3}$ .



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_3\text{H}_7\text{CO}_2^-]}{[\text{C}_3\text{H}_7\text{CO}_2\text{H}]}$$

The concentrations  $[\text{H}_3\text{O}^+]$  and  $[\text{C}_3\text{H}_7\text{CO}_2^-]$  are equal.

The concentration of  $[\text{C}_3\text{H}_7\text{CO}_2\text{H}]$  is very little less than  $1.0 \times 10^{-2} \text{ mol dm}^{-3}$ . Since the degree of ionization is small, the approximation  $[\text{C}_3\text{H}_7\text{CO}_2\text{H}] = 1.0 \times 10^{-2} \text{ mol dm}^{-3}$  is made to simplify the calculation. Then

$$[\text{H}_3\text{O}^+]^2 = 1.51 \times 10^{-5} \times 1.0 \times 10^{-2} \text{ mol}^2 \text{ dm}^{-6}$$

$$[\text{H}_3\text{O}^+] = 3.89 \times 10^{-4} \text{ mol dm}^{-3}$$

$$\text{pH} = 3.42$$

**Validity of approximation:**

$$[\text{H}^+] = 3.89 \times 10^{-4} \text{ mol dm}^{-3}$$

$$[\text{C}_3\text{H}_7\text{CO}_2\text{H}] \text{ of equilibrium} = (1.0 \times 10^{-2}) - (3.89 \times 10^{-4}) = 0.96 \times 10^{-2} \text{ mol dm}^{-3}$$

When, we use this value for  $\text{C}_3\text{H}_7\text{CO}_2\text{H}$ ,  $\text{pH} = 3.42$ .

So, approximation is justified.

# Calculation of $K_b$ from pH

If the pH of a  $0.100 \text{ mol dm}^{-3}$  solution of ethylamine is 11.85, what is its base dissociation constant,  $K_b$ ?

When ethylamine dissociates,



$$K_b = \frac{[\text{C}_2\text{H}_5\text{NH}_3^+][\text{OH}^-]}{[\text{C}_2\text{H}_5\text{NH}_2]}$$

Since, pH = 11.85, pOH =  $14.0 - 11.85 = 2.15$

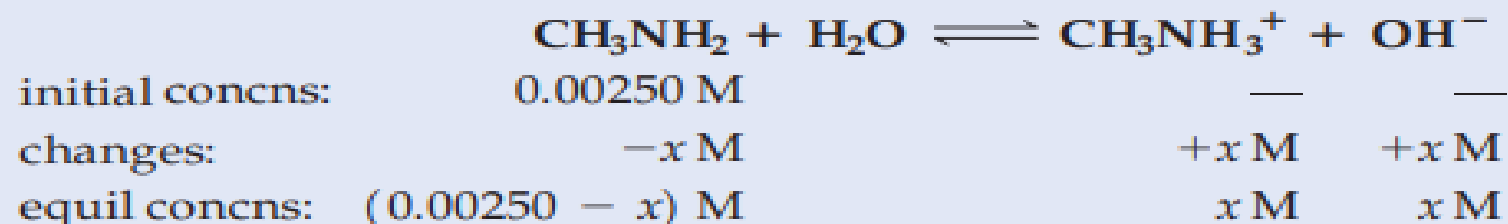
and  $[\text{OH}^-] = 10^{-2.15} = 7.08 \times 10^{-3} \text{ mol dm}^{-3}$

$$\begin{aligned} K_b &= \frac{(7.08 \times 10^{-3} \text{ mol dm}^{-3})^2}{(0.100 - 7.08 \times 10^{-3}) \text{ mol dm}^{-3}} \\ &= 5.39 \times 10^{-4} \text{ mol dm}^{-3} \end{aligned}$$

$$\text{p } K_b = -\log(5.39 \times 10^{-4}) = 3.26$$

# Calculation of pH from $K_b$

What is the pH of a solution that is 0.00250 M For methylamine?  $K_b = 4.2 \times 10^{-4}$ .



$$K_b = \frac{[\text{CH}_3\text{NH}_3^+][\text{OH}^-]}{[\text{CH}_3\text{NH}_2]} = \frac{x \cdot x}{0.00250 - x} = 4.2 \times 10^{-4}$$

Now let's assume that  $x$  is very much less than 0.00250 and that  $0.00250 - x \approx 0.00250$ .

$$\frac{x^2}{0.00250} = 4.2 \times 10^{-4} \quad x^2 = 1.1 \times 10^{-6} \quad [\text{OH}^-] = x = 1.0 \times 10^{-3} \text{ M}$$

The value of  $x$  is nearly half as large as 0.00250—too large to ignore. This means using the *quadratic* formula.

$$\begin{aligned} \frac{x^2}{0.00250 - x} &= 4.2 \times 10^{-4} \\ x^2 + (4.2 \times 10^{-4}x) - (1.1 \times 10^{-6}) &= 0 \\ x &= \frac{(-4.2 \times 10^{-4}) \pm \sqrt{(4.2 \times 10^{-4})^2 + 4 \times 1.1 \times 10^{-6}}}{2} \\ x = [\text{OH}^-] &= \frac{(-4.2 \times 10^{-4}) \pm (2.1 \times 10^{-3})}{2} = 8.4 \times 10^{-4} \text{ M} \\ \text{pOH} &= -\log[\text{OH}^-] = -\log(8.4 \times 10^{-4}) = 3.08 \\ \text{pH} &= 14.00 - \text{pOH} = 14.00 - 3.08 = 10.92 \end{aligned}$$

# Significance of $K_a$ & $K_b$

- The value of  $K_a$  tells how strong an acid is and how vigorously it will take part in the reactions which are typical of acids.
  - It enables to calculate the pH of a solution of the acid.
  - It is a measure of the effectiveness of an acid in acid catalyzed reactions.
- Therefore, all these aspects of acid behavior are covered by one physical constant.
- From the values of  $K_a$  , it can be said that chloroethanoic acid is 80 times stronger than ethanoic acid.
  - The value of  $K_b$  is equally important, from the value of  $K_b$ , it can be easily said that methylamine is 23 times as strong a base as ammonia.

The quantitative measure of the strengths of acids and bases provided by the  $K_a$  and  $K_b$  values is a splendid feature of the Bronsted-Lowry treatment of acids and bases.

pK values of acids & bases can also be considered-

The higher the value of  $K_a$  or  $K_b$  , lower the value of  $pK_a$  or  $pK_b$  , and the stronger is the acid or base.

# Percent Ionization

The extent of ionization of a weak acid or weak base can be described in terms of degree of ionization or percent ionization. Consider a weak acid, HA, and  $A^-$  as the conjugate base of the acid HA.

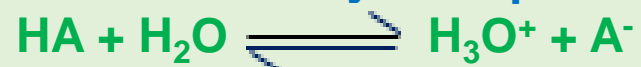
For ionization,  $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

The degree of ionization is the fraction of acid molecules that ionize. Thus, if in 1.00 M HA, ionization produces  $[H_3O^+] = [A^-] = 0.05$  M, the degree of ionization =  $0.05 \text{ M}/1.00 \text{ M} = 0.05$

Percent ionization gives the proportion of ionized molecules on a percentage basis

$$\text{Percent ionization} = \frac{\text{Molarity of } H_3O^+ \text{ derived from HA}}{\text{Initial molarity of HA}} \times 100 \%$$

If, for example, the degree of ionization is 0.05, then the percent of ionization is 5%. **Figure (following slide) compares percent ionization and solution molarity for a weak acid and a strong acid. The percent ionization of a weak acid or a weak base increases as the solution becomes more dilute, a fact that we can also demonstrate by a simple analysis of the ionization reaction,**



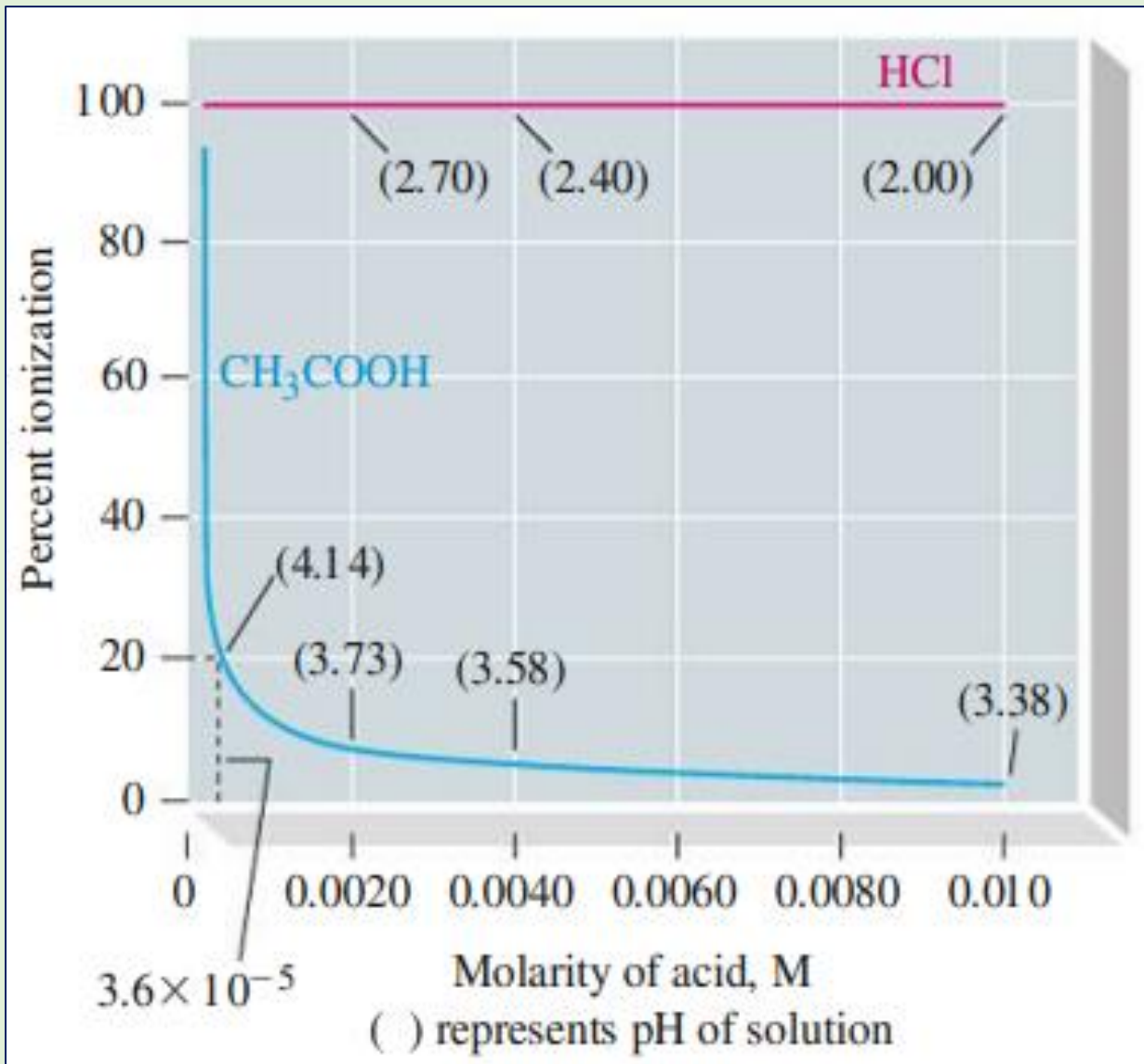
At equilibrium,  $n_{HA}$  moles of the acid HA,  $n_{H_3O^+}$  moles of  $H_3O^+$  and  $n_{A^-}$  moles of  $A^-$  are present in a volume of  $V$  liters. The expression  $K_a$  is,

$$K_a = \frac{[H_3O^+][A^-]}{[HA]} = \frac{(n_{H_3O^+}/V)(n_{A^-}/V)}{n_{HA}/V} = \frac{(n_{H_3O^+})(n_{A^-})}{n_{HA}} \times \frac{1}{V}$$

When we dilute the solution,  $V$  increases,  $1/V$  decreases, and the ratio  $(n_{H_3O^+})(n_{A^-})/n_{HA}$  must increase to maintain the constant value of  $K_a$ . In turn,  $n_{H_3O^+}$  and  $n_{A^-}$  must increase and  $n_{HA}$  must decrease, signifying an increase in the percent ionization.



# Percent Ionization



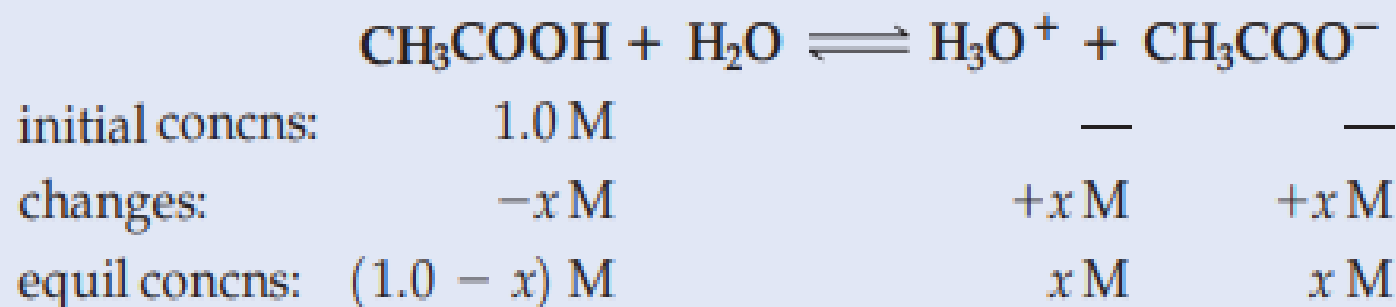
## Percent ionization of an acid as a function of concentration

Over the concentration range shown, HCl, a strong acid, is essentially 100% ionized. The percent ionization of CH<sub>3</sub>COOH, a weak acid, increases from about 4% in 0.010 M to 20% in  $3.6 \times 10^{-5}$  M. For solutions of acetic acid more dilute than  $3.6 \times 10^{-5}$  M, the percent ionization rises sharply with increasing dilution. The pH of  $1.0 \times 10^{-7}$  M CH<sub>3</sub>COOH is about 6.79, the same as for  $1.0 \times 10^{-7}$  M HCl.

# Determining Percent Ionization as a Function of Weak Acid Concentration

What is percent ionization of acetic acid in 1 M, 0.1 M, and 0.01 M acetic acid?

Use the ICE format to describe 1.0 M CH<sub>3</sub>COOH:



We need to calculate  $x = [\text{H}_3\text{O}^+] = [\text{CH}_3\text{COO}^-]$ . In doing so, let's make the usual assumption:  $1.0 - x \approx 1.0$ .

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = \frac{x \cdot x}{1.0 - x} = \frac{x^2}{1.0} = 1.8 \times 10^{-5}$$
$$x = [\text{H}_3\text{O}^+] = [\text{C}_2\text{H}_3\text{O}_2^-] = \sqrt{1.8 \times 10^{-5}} = 4.2 \times 10^{-3} \text{ M}$$

The percent ionization of 1.0 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> is

$$\% \text{ ionization} = \frac{[\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} \times 100\% = \frac{4.2 \times 10^{-3} \text{ M}}{1.0 \text{ M}} \times 100\% = 0.42\%$$

The assumption that  $x$  is small compared to 1.0 is clearly valid:  $x$  is only 0.42% of 1.0 M. The calculations for 0.10 M CH<sub>3</sub>COOH and 0.010 M CH<sub>3</sub>COOH are very similar. In 0.10 M CH<sub>3</sub>COOH, 1.3% of the acetic acid mol-

# Effects of Substituents on the Strength of Acids & Bases

If X is more electronegative than carbon, the acid  $\text{XCH}_2\text{CO}_2\text{H}$  is a stronger acid than  $\text{CH}_3\text{CO}_2\text{H}$ . An example is chloroethanoic acid,  $\text{ClCH}_2\text{CO}_2\text{H}$ , which is 80 times stronger than ethanoic acid. The chlorine nucleus in the anion,  $\text{ClCH}_2\text{CO}_2^-$  attracts the electron in the C-Cl bond, enabling the charge to be spread through the anion more than it is in  $\text{CH}_3\text{CO}_2^-$ .

The reduction of the charge located on the oxygen atoms makes  $\text{ClCH}_2\text{CO}_2^-$  a weaker proton acceptor (a weaker base than  $\text{CH}_3\text{CO}_2^-$ ), and therefore makes  $\text{ClCH}_2\text{CO}_2\text{H}$  a stronger acid than  $\text{CH}_3\text{CO}_2\text{H}$ . Dichloroethanoic acid is stronger still, and trichloroethanoic acid is as strong as some mineral acids.

$\text{CH}_3\text{CO}_2\text{H}$	$1.8 \times 10^{-5} \text{mol dm}^{-3}$	$\text{Cl}_3\text{CCO}_2\text{H}$	$2.2 \times 10^{-1} \text{mol dm}^{-3}$
----------------------------------	-----------------------------------------	-----------------------------------	-----------------------------------------

$\text{ClCH}_2\text{CO}_2\text{H}$	$1.4 \times 10^{-3} \text{mol dm}^{-3}$	$\text{HCO}_2\text{H}$	$1.7 \times 10^{-4} \text{mol dm}^{-3}$
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Thus, electron withdrawing substituents make acids stronger, bases weaker.

Electron donating substituents make acids weaker, bases stronger. Methanoic acid  $\text{HCO}_2\text{H}$ , is a stronger acid than ethanoic acid.  $-\text{CH}_3$  is less electronegative than hydrogen:

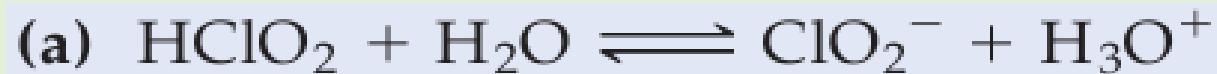
By donating electrons to the  $-\text{CO}_2^-$  group,  $-\text{CH}_3$  makes it a stronger base (a better proton acceptor) and makes  $\text{CH}_3\text{CO}_2\text{H}$  is a weaker acid than  $\text{HCO}_2\text{H}$ .

Bases are proton acceptors. If a group X is substituted for hydrogen in methylamine, then  $\text{XCH}_2\text{NH}_2$  will have a different value of  $K_b$  from  $\text{CH}_3\text{NH}_2$ . Groups such as  $-\text{CH}_3$ , which increase the availability of electrons at the nitrogen atom, increase its power to attract protons, i.e., its basicity. Thus dimethylamine,  $(\text{CH}_3)_2\text{NH}$  is a stronger base than methylamine. Values of base dissociation constants are

$\text{CH}_3\text{NH}_2$	$4.4 \times 10^{-4} \text{mol dm}^{-3}$
$(\text{CH}_3)_2\text{NH}$	$5.9 \times 10^{-4} \text{mol dm}^{-3}$

# Check List

1. Identify the acids and bases in both the following forward and reverse reactions-



2. Of the following species, one is acidic, one is basic, and one is amphoteric in their reactions with water:  $\text{HNO}_2$ ,  $\text{PO}_4^{3-}$ ,  $\text{HCO}_3^-$ . Write the four equations needed to represent these facts.

3. Is it appropriate to describe each of the following as a conjugate acid-base pair? Explain. (a)  $\text{HCO}_3^-$ - $\text{CO}_3^{2-}$ ; (b)  $\text{HSO}_3^-$ - $\text{SO}_4^{2-}$ ; (c)  $\text{H}_2\text{CO}_3$  -  $\text{H}_2\text{C}_2\text{O}_4$ ; (d)  $\text{HClO}$ -  $\text{ClO}^-$ ; (e)  $\text{H}_2\text{S}$ -  $\text{S}^{2-}$ .

3. In a laboratory experiment, students measured the pH of samples of rain water and household ammonia. Determine (a)  $[\text{H}_3\text{O}^+]$  in the rainwater, with pH measured at 4.35; (b)  $[\text{OH}^-]$  in the ammonia, with pH measured at 11.28.

4. Students found that a yogurt sample had a pH of 2.85. What are the  $[\text{H}_3\text{O}^+]$  and  $[\text{OH}^-]$  of the yogurt?

5. The pH of a solution of HCl in water is found to be 2.50. What volume of water would you add to 1.00 L of this solution to raise the pH to 3.10.

6. Calculate  $[\text{H}_3\text{O}^+]$ ,  $[\text{Cl}^-]$ , and  $[\text{OH}^-]$  in 0.015 M  $\text{HCl(aq.)}$ .

## Check List

7. Calcium hydroxide (slaked lime),  $\text{Ca}(\text{OH})_2$  is the cheapest strong base available. It is generally used for industrial operations in which a high concentration of  $\text{OH}^-$  is not required.  $\text{Ca}(\text{OH})_2$  is soluble in water only to the extent of 0.16 g  $\text{Ca}(\text{OH})_2$  /100 mL solution at 25 °C. What is the pH of saturated  $\text{Ca}(\text{OH})_2$  at 25 °C?
8. Milk of magnesia is a saturated solution of  $\text{Mg}(\text{OH})_2$  Its solubility is 9.63 mg  $\text{Mg}(\text{OH})_2$ /100 mL solution at 20 °C. What is the pH of saturated  $\text{Mg}(\text{OH})_2$  at 20 °C?
9. Calculate the pH of an aqueous solution that is 3.00% KOH, by mass, and has a density of 1.0242 g/mL.
10. Butyric acid,  $\text{CH}_3(\text{CH}_2)_2\text{CO}_2\text{H}$ , is used to make compounds employed in artificial flavorings and syrups. A 0.250 M aqueous solution of butyric acid is found to have a pH of 2.72. Determine  $K_a$  for butyric acid.
11. Calculate the pH of 0.100 M  $\text{CH}_3\text{COOH}$  having  $K_a$  for  $\text{CH}_3\text{COOH}$  as  $1.8 \times 10^{-5}$ .

# Indicators

The indicators used in acid-base titrations are weak acids or weak bases. The ions are of a different color from the undissociated molecules. Litmus is a weak acid, which can be represented by the formula HL. In solution



The molecules HL are red, and the anions L<sup>-</sup> are blue. The dissociation constant of the indicator is

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{L}^-]}{[\text{HL}]}$$

In acid solution, [H<sub>3</sub>O<sup>+</sup>] is high, and H<sub>3</sub>O<sup>+</sup> ions combine with L<sup>-</sup> ions to form HL molecules, which are red. In alkaline solution, H<sub>3</sub>O<sup>+</sup> ions are removed to form molecules of water, and HL molecules react with OH<sup>-</sup> ions to form L<sup>-</sup> ions, which are blue:



If [HL] = [L<sup>-</sup>], the indicator appears purple. Since

$$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HL}]}{[\text{L}^-]}$$

This happens when [H<sub>3</sub>O<sup>+</sup>] = K<sub>a</sub>, and pH = pK<sub>a</sub>. If the ratio [HL]/[L<sup>-</sup>] > 10/1, the solution appears red. If the ratio [HL]/[L<sup>-</sup>] < 1/10, the solution appears blue. Thus, litmus changes from red to blue over a range of 2 pH units.

The indicator methyl orange is a weak base, which can be represented as B, B + H<sub>3</sub>O<sup>+</sup> → BH<sup>+</sup> + H<sub>2</sub>O. The molecules B are yellow, and the cations BH<sup>+</sup> are red. If the ratio [B] / [BH<sup>+</sup>] > 10 / 1, the indicator appears yellow, if the ratio < 1 / 10, the indicator appears red. The indicator changes from yellow to red over 2 pH units. At a pH equal to pK<sub>b</sub>, the ratio [B]/[BH<sup>+</sup>] = 1, and the indicator is orange.

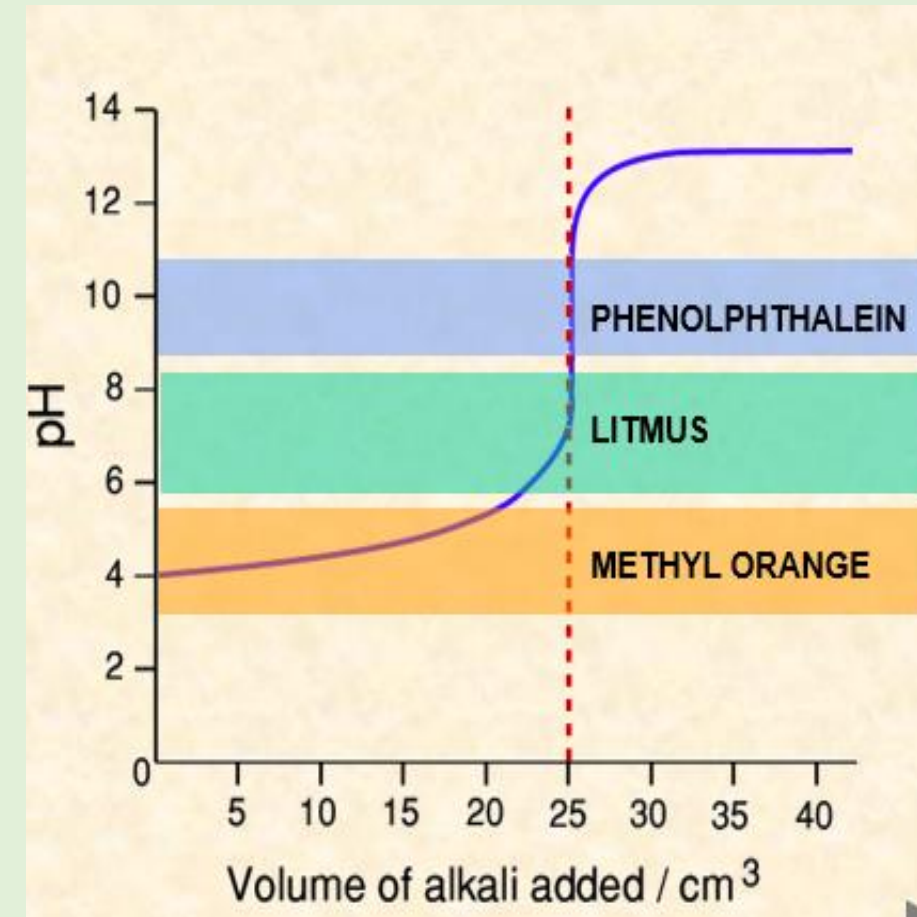
# Acid-base Indicators

Must have an easily observed colour change. Must change immediately in the required pH range over the addition of 'half' a drop of reagent.

COLOUR CHANGES OF SOME COMMON INDICATORS

pH	1	2	3	4	5	6	7	8	9	10	11	12	13	14
METHYL ORANGE	Yellow	Yellow	Yellow	CHANGE	Pink	Pink	Pink	Pink	Pink	Pink	Pink	Pink	Pink	Pink
LITMUS	Red	Red	Red	Red	Red	Red	CHANGE	Blue	Blue	Blue	Blue	Blue	Blue	Blue
PHENOLPHTHALEIN	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	Colourless	CHANGE	Pink	Pink	Pink	Pink	Pink	Pink

- To be useful, an indicator must change over the “vertical” section of the curve where there is a large change in pH for the addition of a very small volume of alkali.
- The indicator used depends on the pH changes around the end point - the indicator must change during the ‘vertical’ portion of the curve.
- In the example, the only suitable indicator is phenolphthalein.





# Acid-base Titration (Important Terminologies)

**Titrant:** Solution of a known concentration, which is added to another solution whose concentration has to be determined.

**Titrand or analyte:** The solution whose concentration has to be determined.

**Equivalence point:** Point in titration at which the amount of titrant added is just enough to completely neutralize the analyte solution. At the equivalence point in an acid-base titration, moles of base = moles of acid, and the solution only contains salt and water.

Acid-base titrations are monitored by the change of pH as titration progresses.

**Types:** There are four types of acid-base titration; each has a characteristic curve.

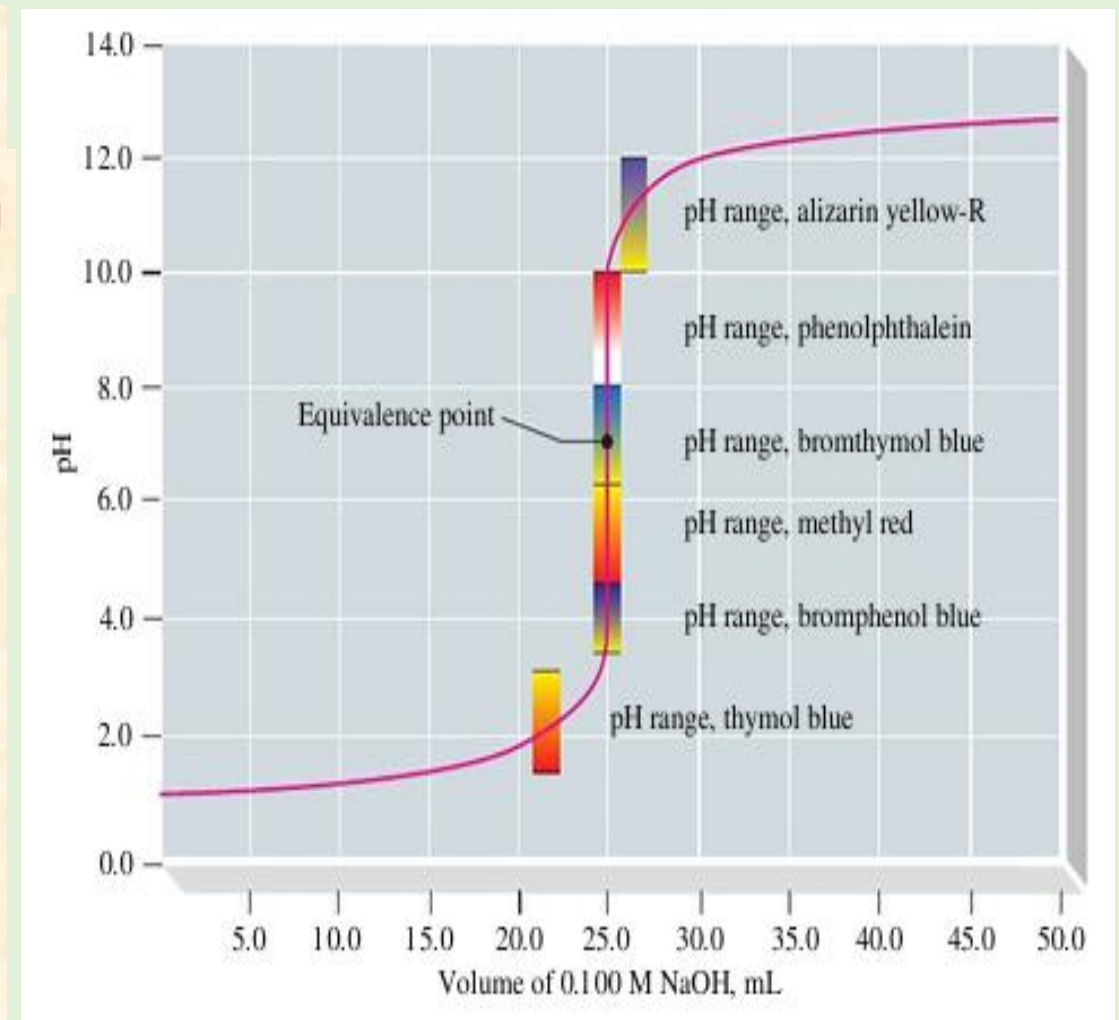
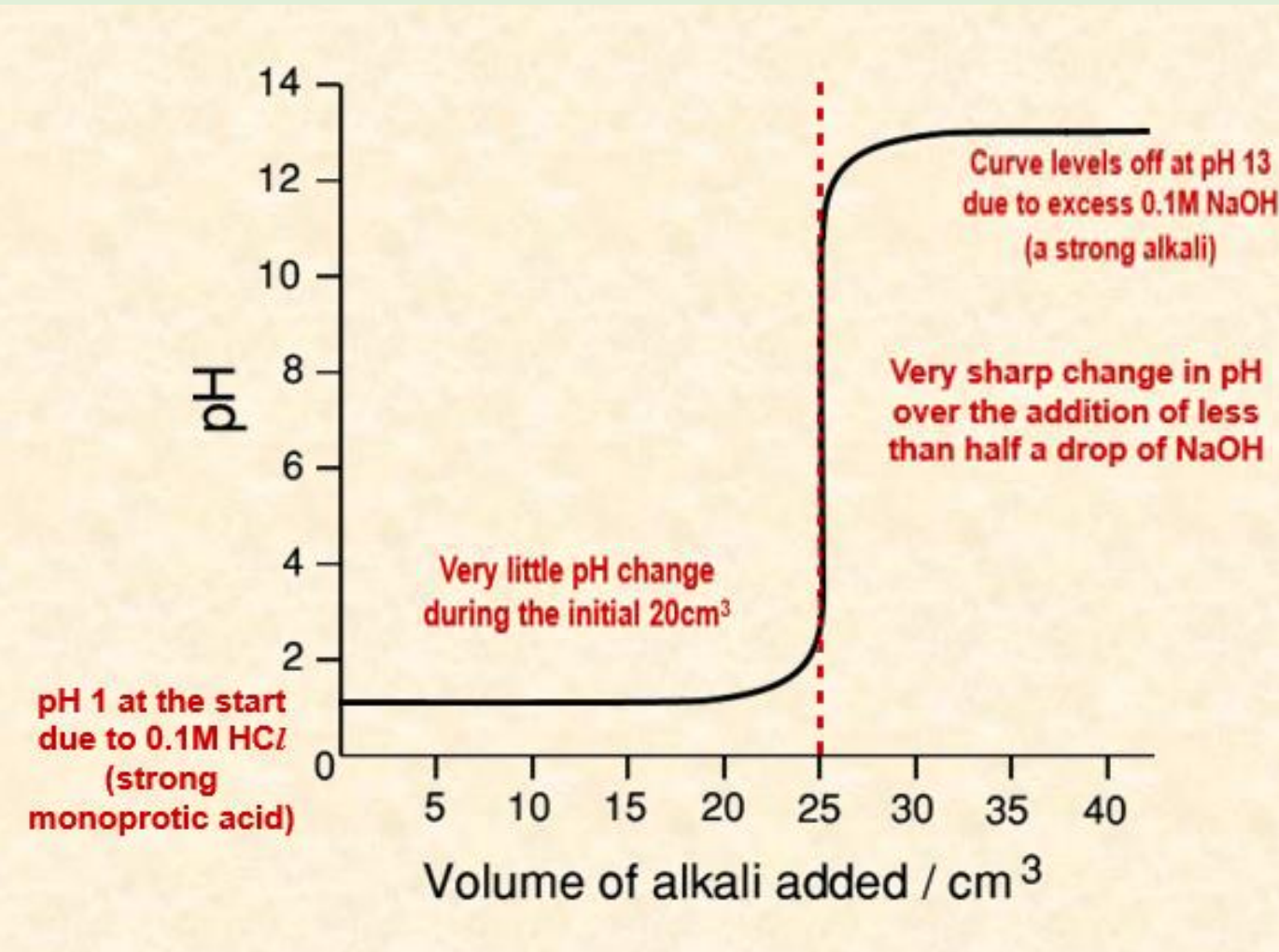
- Strong acid ( $\text{HCl}$ ) v. strong base ( $\text{NaOH}$ )
- Weak acid ( $\text{CH}_3\text{COOH}$ ) v. strong alkali ( $\text{NaOH}$ )
- Strong acid ( $\text{HCl}$ ) v. weak base ( $\text{NH}_3$ )
- Weak acid ( $\text{CH}_3\text{COOH}$ ) v. weak base ( $\text{NH}_3$ )

Consider the titration of  $25.0 \text{ cm}^3$  of  $0.1 \text{ mol dm}^{-3}$  hydrochloric acid with  $0.1 \text{ mol dm}^{-3}$  sodium hydroxide solution. At the beginning of the titration,  $[\text{H}_3\text{O}^+] = 1.0 \times 10^{-1} \text{ mol dm}^{-3}$ ;  $\text{pH} = 1$ , When  $24.0 \text{ cm}^3$  of sodium hydroxide have been added,  $[\text{H}_3\text{O}^+] = (1.0 \text{ cm}^3 \text{ of } 1.0 \times 10^{-1} \text{ mol dm}^{-3} \text{ acid}) / (49.0 \text{ cm}^3 \text{ of solution})$

$[\text{H}_3\text{O}^+] = (1.0 \times 10^{-3} \times 1.0 \times 10^{-1}) / (49.0 \times 10^{-3}) = 2.04 \times 10^{-3} \text{ mol dm}^{-3}$ ,  $\text{pH} = 2.69$

Similar calculations have been employed to give all the pH values plotted in Figure. The figure show how the pH varies during the course of the titration. The equivalence point of the titration occurs when  $25.0 \text{ cm}^3$  of alkali have been added. The pH changes rapidly from 3.5 at  $24.9 \text{ cm}^3$  of alkali to 10.5 at  $25.1 \text{ cm}^3$  of alkali. Any indicator which changes color over the range of pH 3.5 to 10.5 can be used to show the equivalence point of the titration.

# Acid-base Titration (Titration curves for Strong acid v Strong base)



# Acid-base Titration (Titration curves for Weak acid vs Strong base)

The weak acid ethanoic acid can be titrated with sodium hydroxide solution. At the beginning of the titration, 25.0 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> ethanoic acid have a pH given by  $[H_3O^+]^2 = K_a[CH_3CO_2H]$ ; pH = 2.88.

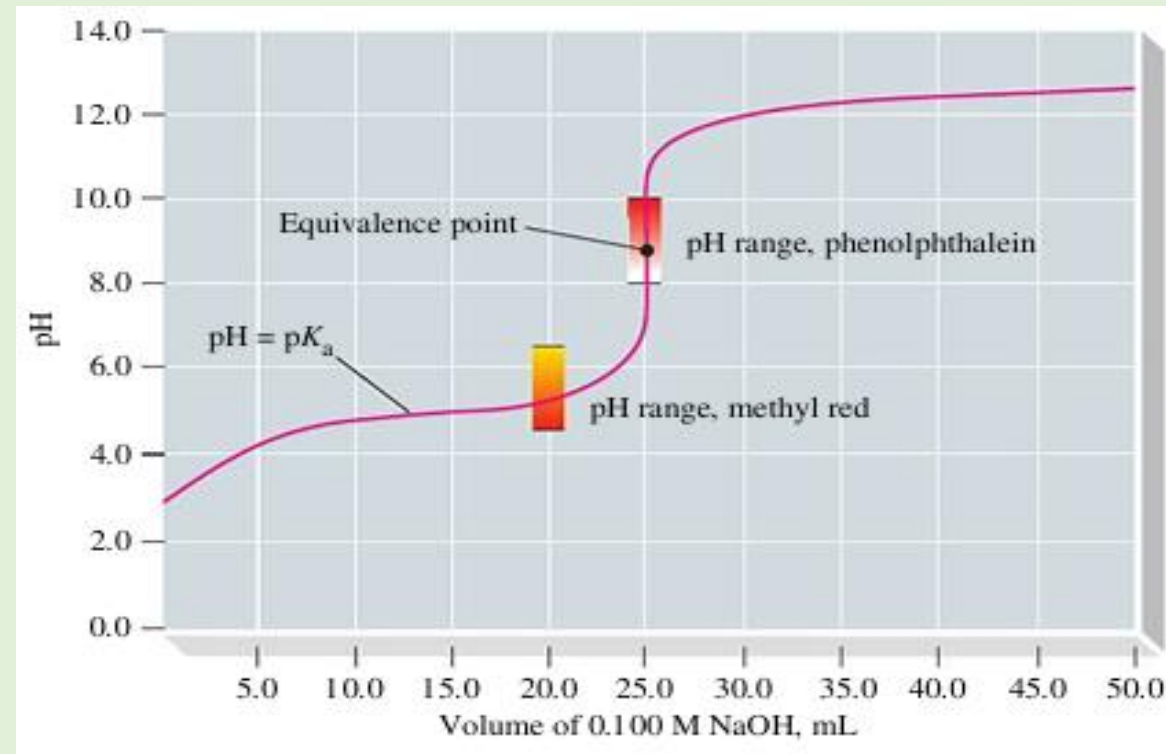
When 20.0 cm<sup>3</sup> of alkali have been added,  $[CH_3CO_2H] = 5.0 \text{ cm}^3 \times 0.1 \text{ mol dm}^{-3} / 45 \text{ cm}^3$

$[CH_3CO_2^-] = 20.0 \text{ cm}^3 \times 0.1 \text{ mol dm}^{-3} / 45 \text{ cm}^3$

$[H_3O^+] = K_a [CH_3CO_2H] / [CH_3CO_2^-] = K_a \times 5.0 / 20.0$

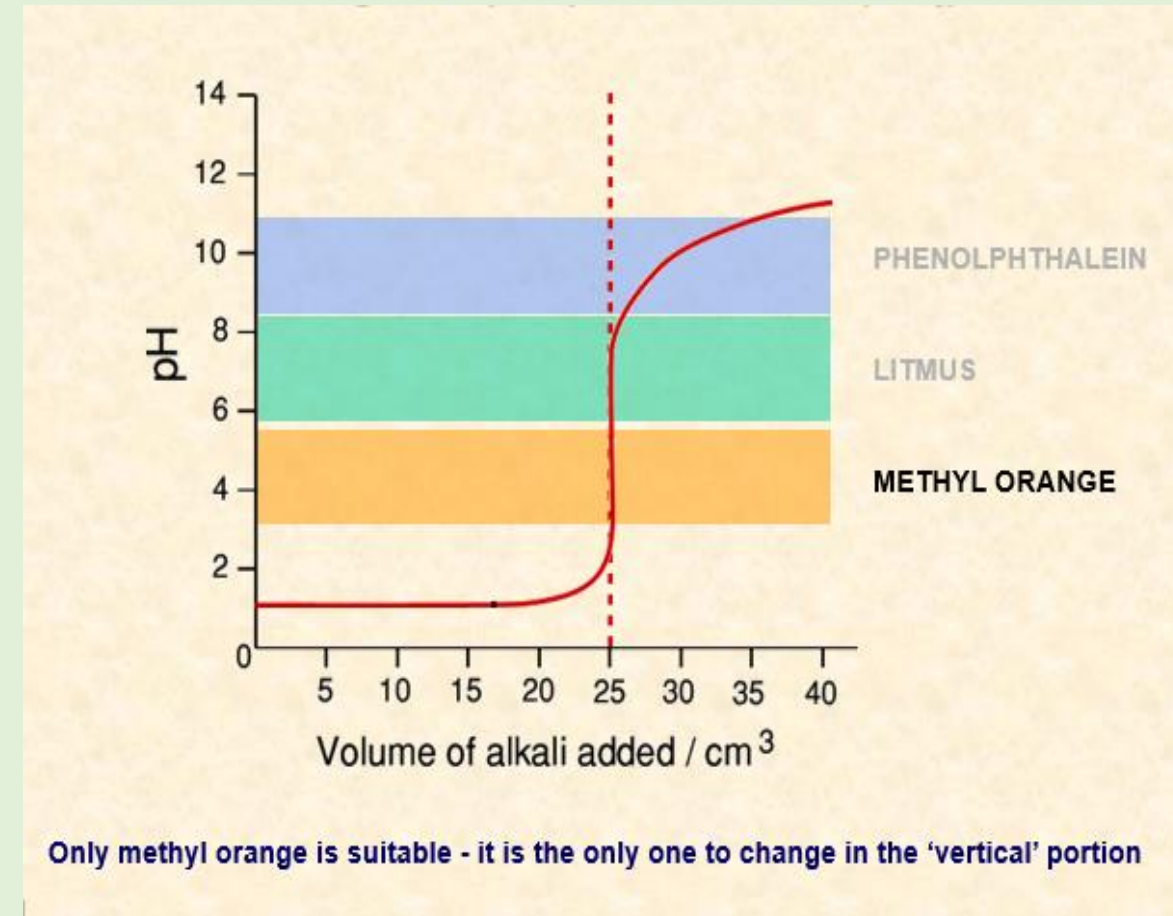
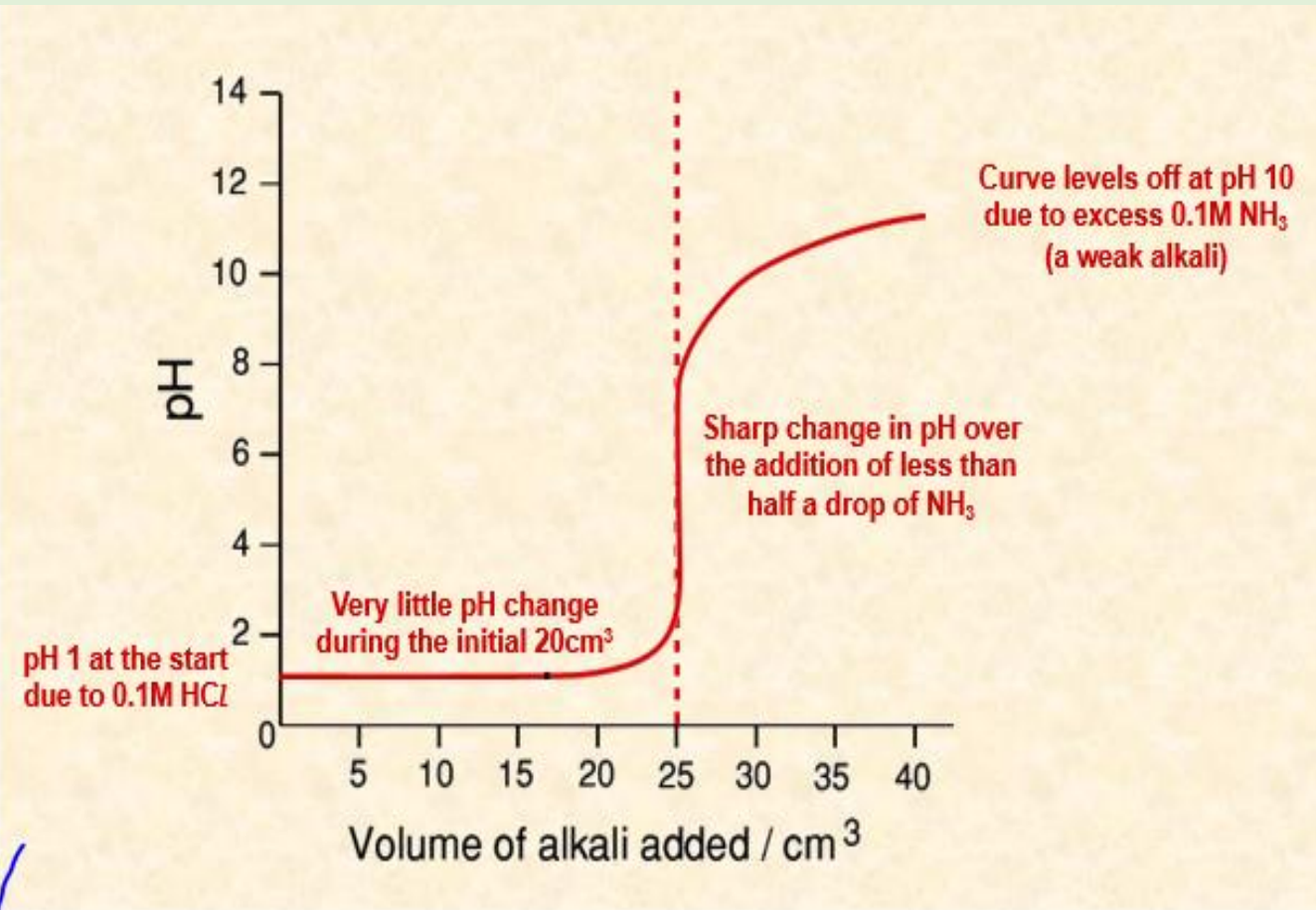
pH = pK<sub>a</sub> - lg(5.0/20.0) = 5.35

The results of calculations of pH over the range of the titration are shown in figure. In figure the pH changes from 5 to 10.5 rapidly at the end point. Indicators which change in this region are litmus and phenolphthalein.



# Acid-base Titration (Titration curves for Weak acid vs Strong base)

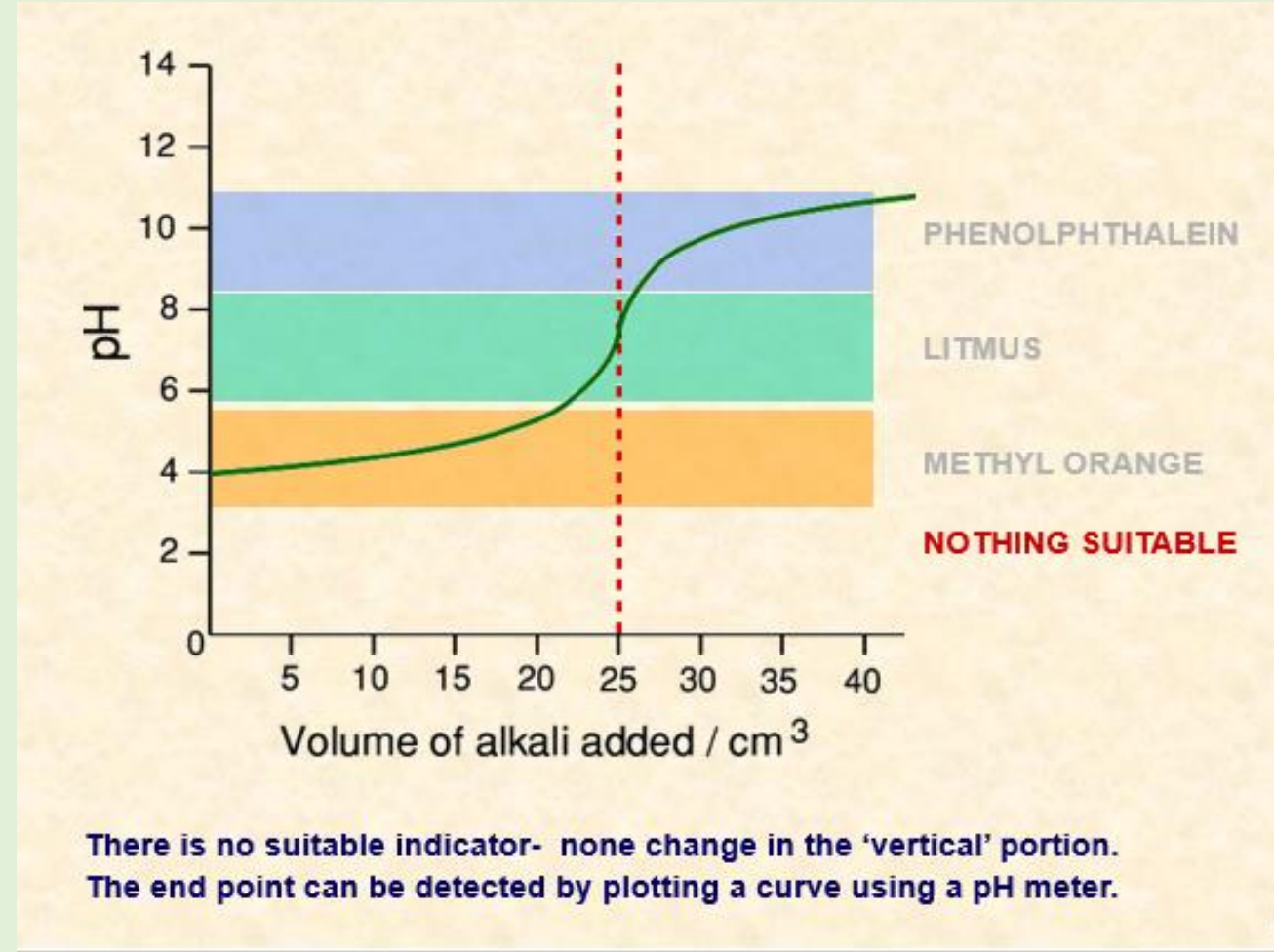
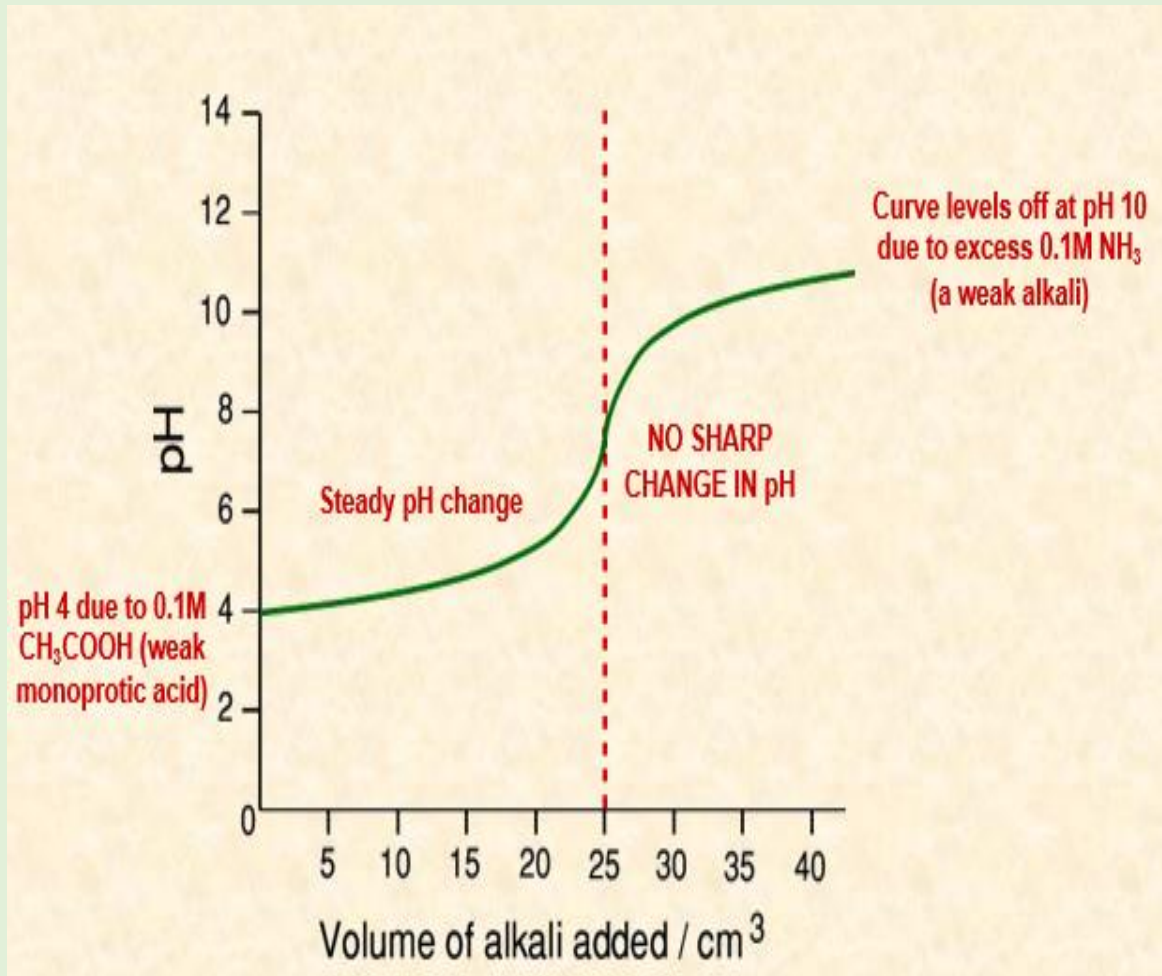
The titration of the weak base ammonia with a strong acid is shown in a figure in which pH changes rapidly from 3 to 7 at the end point. Indicators which can be used are methyl orange and litmus. Phenolphthalein can not be used in the titration of a weak base as it changes at pH 9.





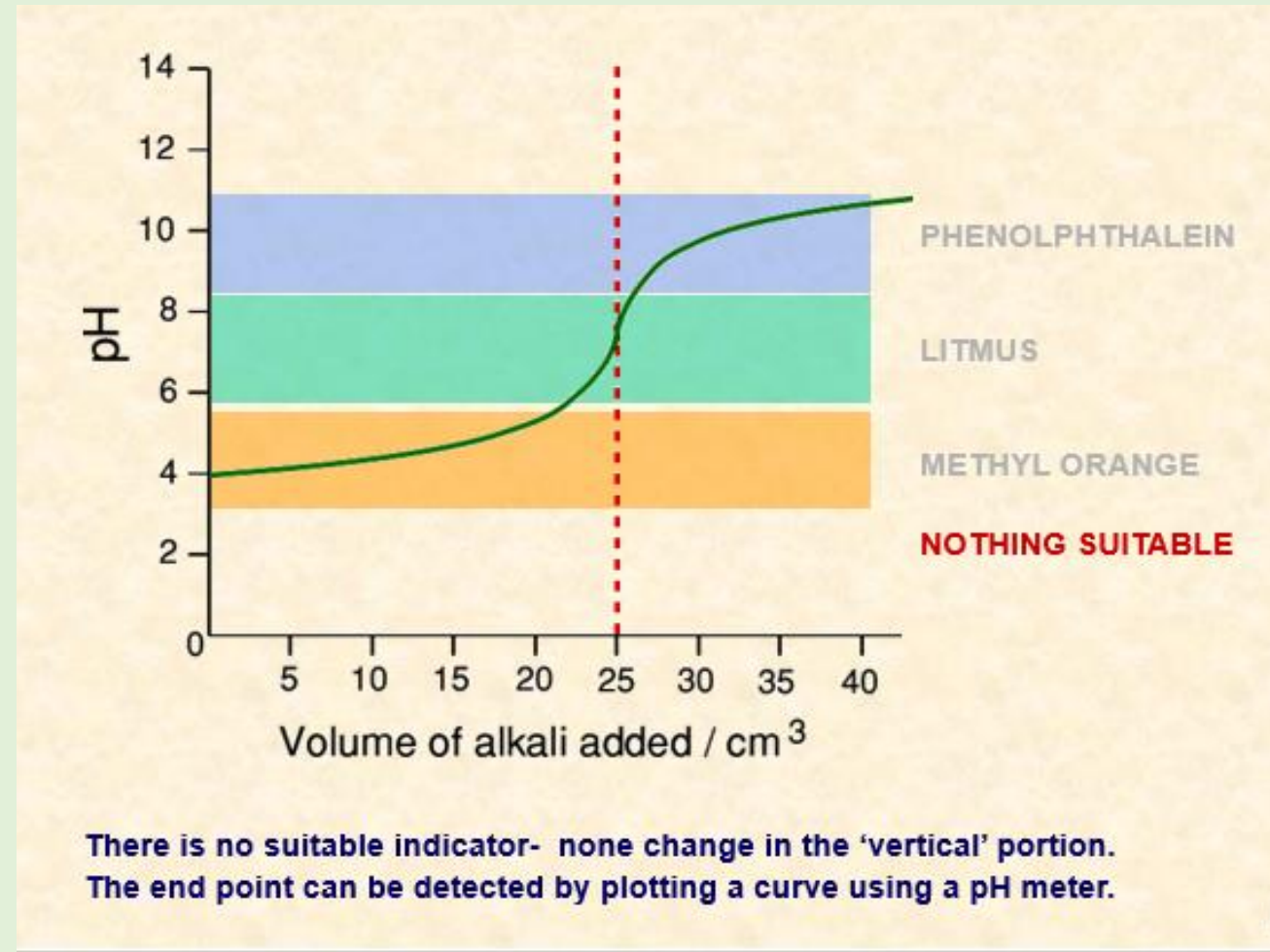
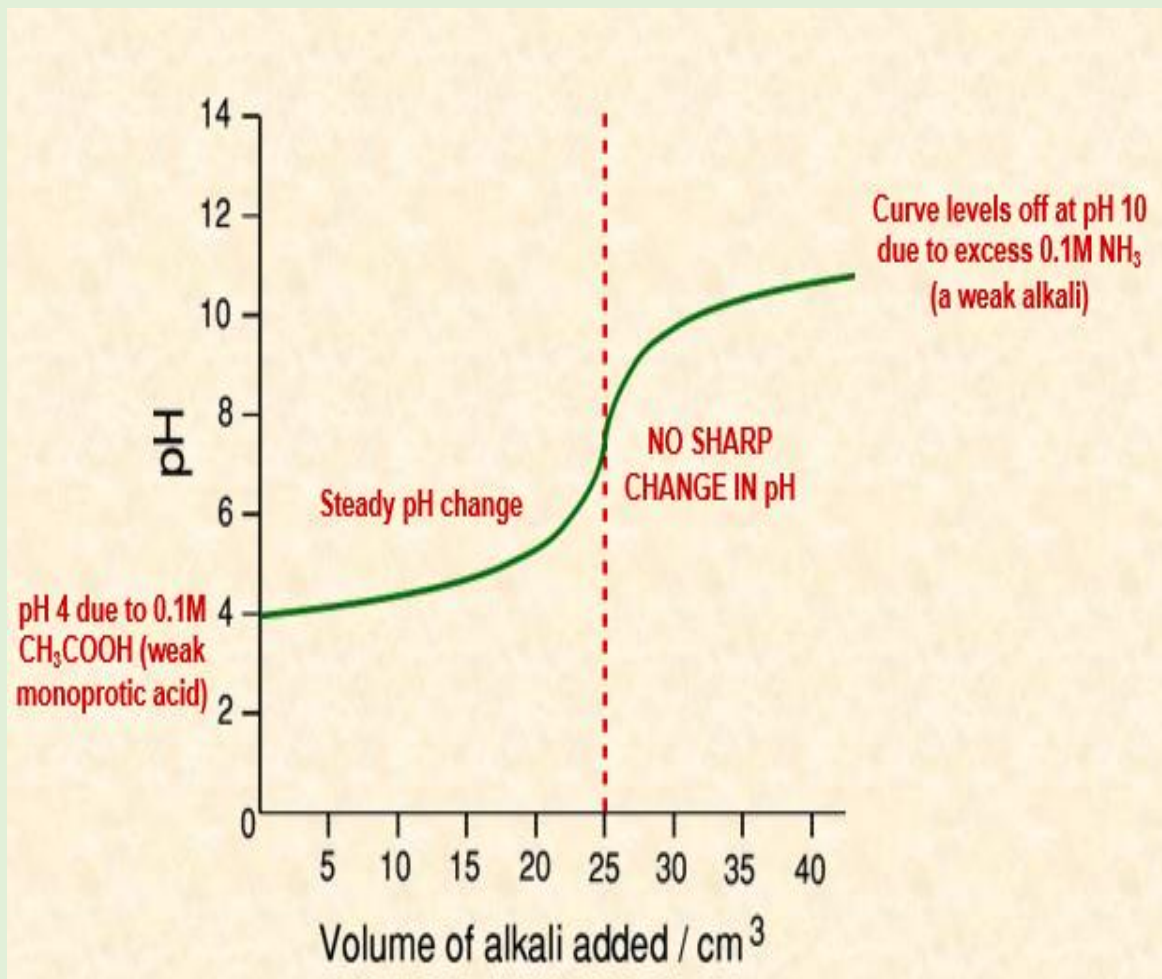
# Acid-base Titration (Titration curves for Weak acid vs Weak base)

In the titration of a weak acid and a weak base, a titration curve is obtained in which the change in pH at the end point is gradual, and indicators will change color gradually. No indicator will give a sharp end-point. The way out of this difficulty is to titrate the weak acid against a strong base and the weak base against a strong acid.



# Acid-base Titration (Titration curves for Weak acid vs Weak base)

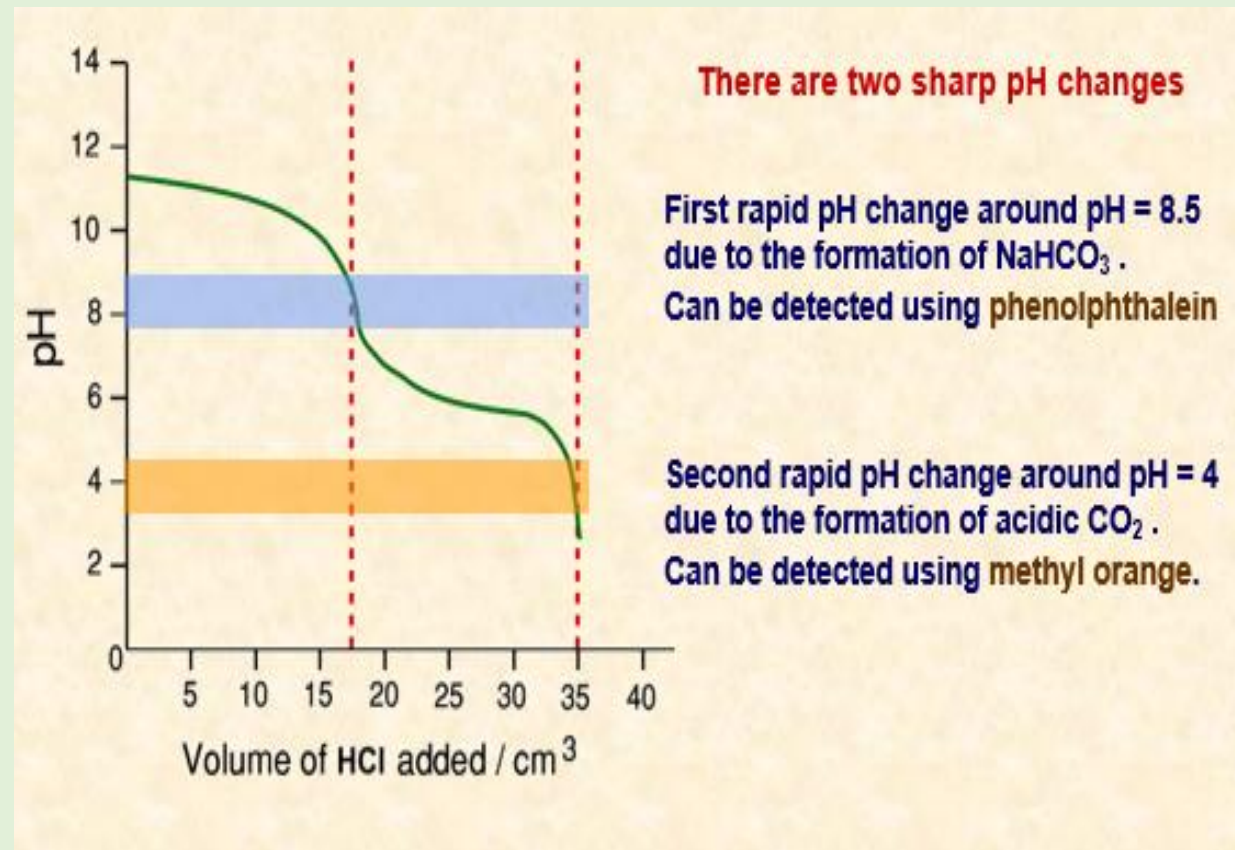
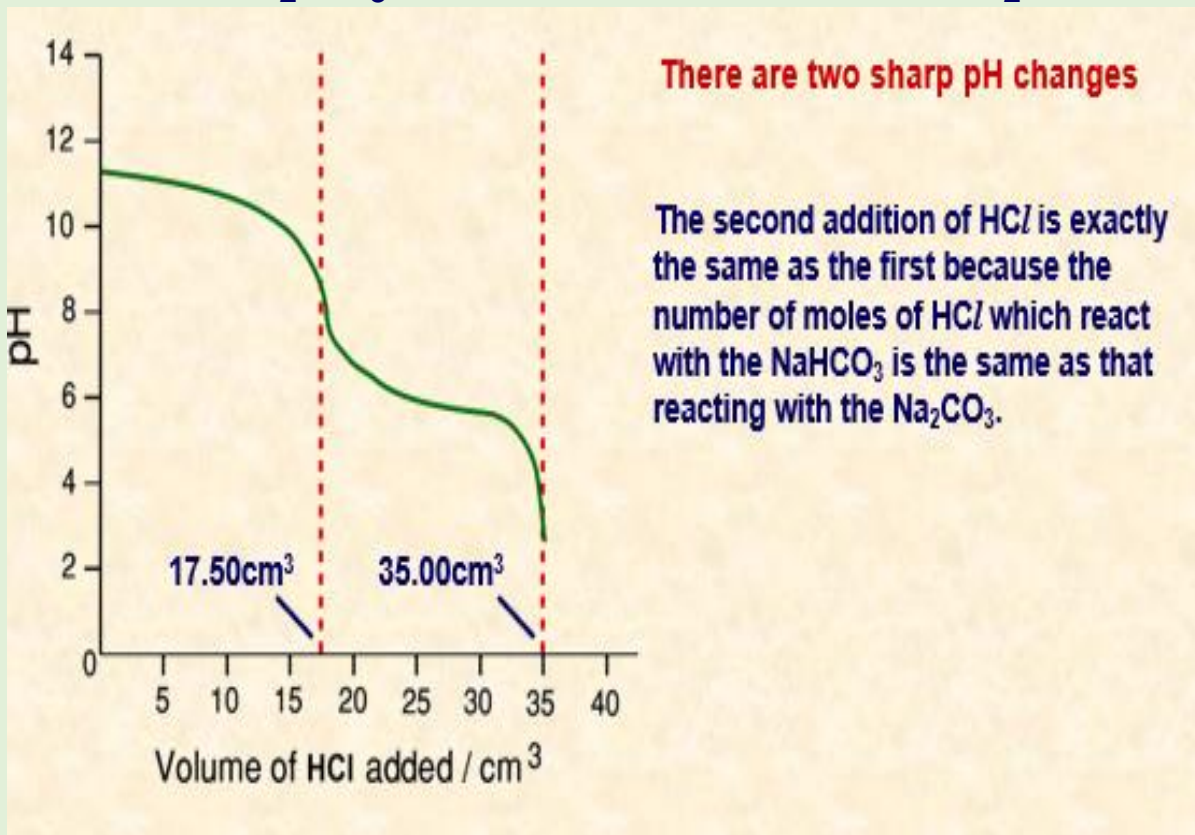
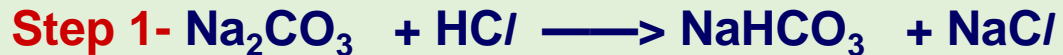
In the titration of a weak acid and a weak base, a titration curve is obtained in which the change in pH at the end point is gradual, and indicators will change color gradually. No indicator will give a sharp end-point. The way out of this difficulty is to titrate the weak acid against a strong base and the weak base against a strong acid.





# Acid-base Titration (Titration curves for Acid vs Carbonate)

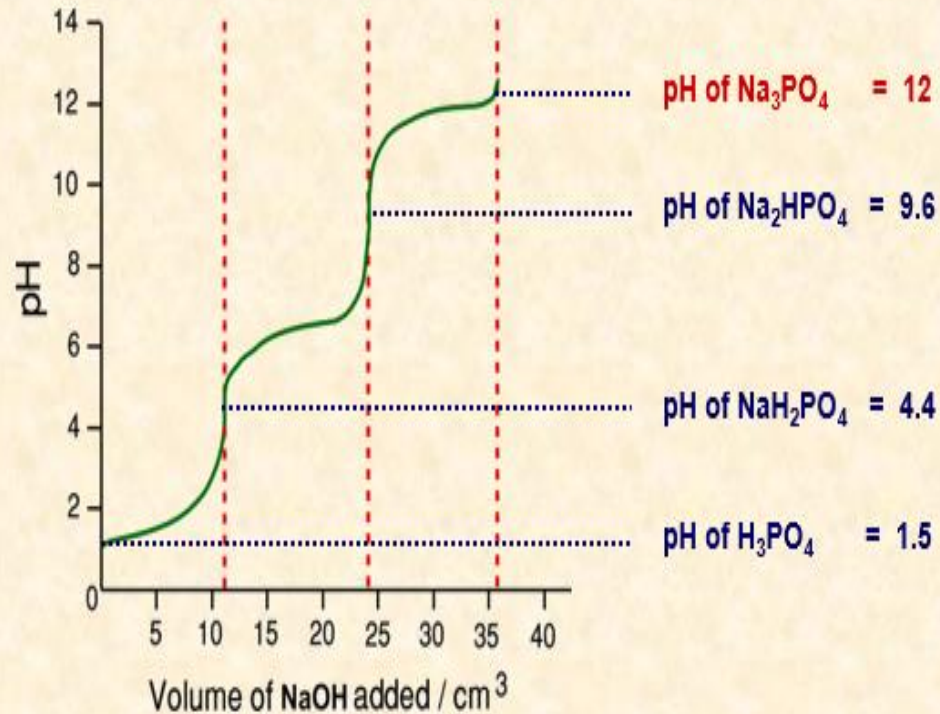
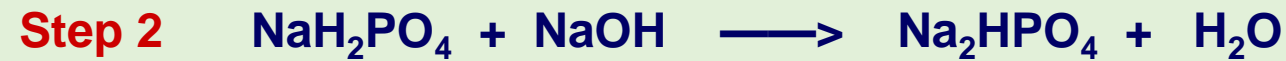
Sodium carbonate reacts with hydrochloric acid in two steps...





# Acid-base Titration (Titration curves for polyprotic acids ( $\text{H}_3\text{PO}_4$ ))

Phosphoric acid is triprotic; it reacts with sodium hydroxide in three steps-

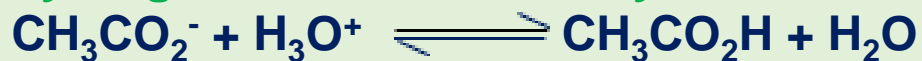


## pH Range of Indicators

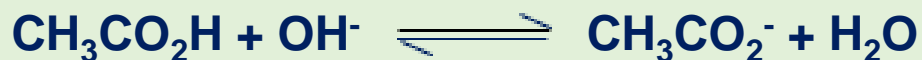
Name	Acid Color	pH Range of Color Change	Base Color
Methyl violet	Yellow	0.0 - 1.6	Blue
Thymol blue	Red	1.2 - 2.8	Yellow
Methyl orange	Red	3.2 - 4.4	Yellow
Bromocresol green	Yellow	3.8 - 5.4	Blue
Methyl red	Red	4.8 - 6.0	Yellow
Litmus	Red	5.0 - 8.0	Blue
Bromothymol blue	Yellow	6.0 - 7.6	Blue
Thymol blue	Yellow	8.0 - 9.6	Blue
Phenolphthalein	Colorless	8.2 - 10.0	Pink
Thymolphthalein	Colorless	9.4 - 10.6	Blue
Alizarin yellow R	Yellow	10.1 - 12.0	Red

# Buffer Solution

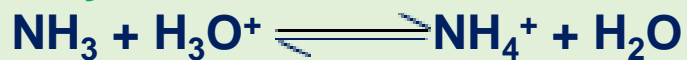
A buffer solution is one which will resist changes in pH due to the addition of small amounts of acid and alkali. An effective buffer can be made by preparing a solution containing both a weak acid, and also one of its salt with a strong base. E.g. Ethanoic acid and sodium ethanoate. This will absorb a small amounts of hydrogen ions because they react with ethanoate ions to form molecules of ethanoic acid:



Hydroxide ions are absorbed (in small amounts) by combining with ethanoic acid molecules to form ethanoate ions and water.



A solution of a weak base and one of its salt formed with a strong acid, e.g. ammonia solution and ammonium chloride, will act as a buffer. If hydrogen ions are added, they largely combine with ammonia., and if hydroxide ions are added, they largely combine with ammonium ion:



The pH of a buffer solution consisting of a weak acid HA and its salt with a strong base is calculated from the equation

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$[\text{H}_3\text{O}^+] = K_a [\text{HA}] / [\text{A}^-]; \text{ pH} = \text{p}K_a + \lg [\text{A}^-] / [\text{HA}] \quad \text{Henderson Hasselbalch Equation}$$

Since the salt is completely ionized and the acid only slightly ionized, we can assume that all the ions come from the salt.  $[\text{A}^-] = [\text{Salt}]$ ,  $[\text{HA}] = [\text{Acid}]$ ;  $\text{pH} = \text{p}K_a + \lg [\text{Salt}] / [\text{Acid}]$

An effective buffering action is obtained at pH values fairly close to  $\text{p}K_a$ .

# Buffer Solution

## Calculation of the pH of a Buffer Solution

For a buffer made from a weak base B and its salt with a strong acid  $BH^+X^-$ , a similar treatment shows that

$$pH = pK_w - pK_b + \lg[\text{Base}]/[\text{Salt}]$$

Three solutions contain ethanoic acid ( $K_a = 1.80 \times 10^{-5} \text{ mol dm}^{-3}$ ) at a concentration of  $0.1 \text{ mol dm}^{-3}$  and sodium ethanoate at a concentration (a)  $0.1 \text{ mol dm}^{-3}$  (b)  $0. \text{ mol dm}^{-3}$  (c)  $0.5 \text{ mol dm}^{-3}$ . Calculate the pH values of the three solutions.

## Biological Importance of Buffer Solutions

Protein molecules are long chain amino acid groups. Forces of attraction between the polar groups such as  $-\text{CO}_2^-$  and  $\text{NH}_3^+$  hold the protein chain in a complicated three- dimensional structure. Should the medium become too acidic,  $-\text{CO}_2^-$  groups would be converted into  $-\text{CO}_2\text{H}$  groups.

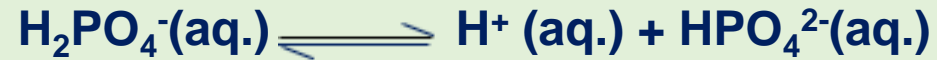


This would interfere with the attraction between  $-\text{CO}_2^-$  and  $\text{NH}_3^+$  groups.

The reactions that take place in living things are catalyzed by enzymes. Enzymes are proteins, and the ability of enzymes to act as catalysts depends on their three- dimensional structure. Outside the range of pH which maintains the structure of the protein, the enzyme cannot do its job. There is an optimum pH of each enzyme, and the enzyme will only function over a range of 2 or 3 pH units. Most cells and tissues require a pH value close to 7

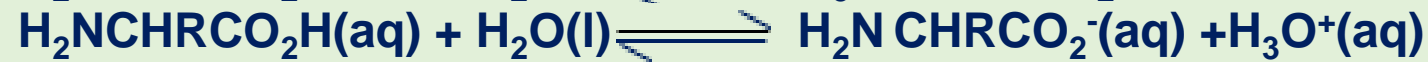
# Buffer Solution

Buffer keeps the cell pH as constant as possible. Many tissues contain hydrogen phosphate ions and since phosphoric acid is a weak acid, the equilibrium is set up:



When the hydrogen ion concentration increases, the equilibrium is displaced from right to left, thus moving hydrogen ions from solution. If the hydrogen ion concentration decreases, the  $\text{H}_2\text{PO}_4^-$  ions dissociate to release  $\text{H}^+$  ions. Thus, the buffer tends to maintain a constant hydrogen ion concentration.

Amino acids have the formula  $\text{H}_2\text{NCHRCO}_2\text{H}$ , where R can be a no. of different groups. They can ionize as weak acids and as weak bases. Both the weakly acidic carboxyl group and the weakly basic amino group can act as buffers.



Peptides and proteins are condensation polymers of amino acids and share this buffering action. Amino acids, peptides and proteins are important buffering agents in living tissues.