# THE THEORY OF ACIDS AND BASES

By F. M. HALL, M.SC.

# Wollongong University College, N.S.W., Australia

The theory of acids and bases, like many other chemical theories, has undergone numerous changes in recent times. Always the changes have been such as to make the theory more general. The three main theories in use today are:

- (1) the Water or Arrhenius Theory;
- (2) the Proton or Brønsted-Lowry Theory;
- (3) the Electronic or Lewis Theory.

### WATER OR ARRHENIUS THEORY

The Water or Arrhenius Theory was widely accepted up to the early years of this century. It defines an acid as a hydrogen compound ionizing in water to give hydrogen ions, and a base as a hydroxyl compound which gives hydroxide ions in water. The neutralization reaction between an acid and a base produces a salt and water only:

 $HA(acid) + BOH(base) \rightleftharpoons BA(salt) +$ 

H<sub>o</sub>O(water)

and the salts so formed may be classified into four main groups, *viz*.:

- (i) those derived from strong acids and strong bases;
- (ii) those derived from weak acids and strong bases;
- (iii) those derived from strong acids and weak bases;
- (iv) those derived from weak acids and weak bases.

When dissolved in water these various salts do not necessarily give neutral solutions. Interaction between the salt and water (hydrolysis) accounts for the acidity, alkalinity or neutrality of the solution. For example, a salt BA derived from a weak acid HA and a strong base BOH gives an alkaline solution in water because the acid derived by hydrolysis gives few hydrogen ions and the base derived by hydrolysis gives many hydroxide ions. This may be shown as

 $B^+ + A^- + H_2O \rightleftharpoons HA + B^+ + OH^-$ 

and the term hydrolysis relates to the interaction of the ions of the salt with water to give (a) a weak acid or a weak base, or (b) a weak acid and a weak base.

Applying the Law of Mass Action to such a system, the hydrolysis constant, at equilibrium, may be written as

$$K_{\rm h} = \frac{[\text{Base}] [\text{Acid}]}{[\text{Unhydrolysed salt}]} = \frac{[\text{OH}^{-}] [\text{HA}]}{[\text{A}^{-}]}$$

and if x is the extent to which hydrolysis occurs and c is the molar concentration of salt in solution

$$K_{
m h}=rac{xc imes xc}{(1-x)c}=rac{x^2c}{(1-x)}$$

The equilibria involved for the salt of a weak acid and strong base in water are

(a) 
$$H_2O \rightleftharpoons H^+ + OH^-; K = \frac{[H^+] [OH^-]}{[H_2O]}$$

(b) 
$$\operatorname{HA} \Rightarrow \operatorname{H}^+ + \operatorname{A}^-$$
;  $K_a = \frac{[\operatorname{H}^+][\operatorname{A}^-]}{[\operatorname{HA}]}$ 

(c) 
$$A^- + H_2O \Rightarrow HA + OH^-$$
;  
[HA] [OH<sup>-</sup>]

$$K_{h} = \overline{[A^{-}][H_{2}O]}$$

Since  $[H_2O]$  is effectively constant in dilute solutions we may replace K and  $K_h'$  by two new constants,  $K_w$  and  $K_h$  respectively, defined by

$$K_{
m w} = [{
m H}^+] \; [{
m OH}^-]$$
  
and  $K_{
m h} = rac{[{
m HA}] \; [{
m OH}^-]}{[{
m A}^-]}$ 

 $K_{\rm w}$  is called the ionic product of water and has a value of  $\sim 10^{-14}$  mole<sup>2</sup> litre<sup>-2</sup> at 25°C. It follows that

$$\frac{K_{\rm w}}{K_{\rm a}} = \frac{[{\rm H}^+] \; [{\rm O}{\rm H}^-] \; [{\rm H}{\rm A}]}{[{\rm H}^+] \; [{\rm A}^-]} = \frac{[{\rm O}{\rm H}^-] \; [{\rm H}{\rm A}]}{[{\rm A}^-]} = K_{\rm h}$$

If two assumptions are now made:

 (i) that there is only a pure aqueous solution of the salt of the acid HA (no added hydrogen or hydroxide ions); and

91

 (ii) that the concentration of hydroxide ion obtained from the ionization of water is negligible compared with that resulting from the hydrolysis of the salt,

then  $[OH^-] = [HA]$  during hydrolysis of the salt,

and  $\frac{[OH^-]^2}{[A^-]} = K_h = \frac{K_w}{K_a}$ and  $[OH^-] = \sqrt{\frac{[A^-] \cdot K_w}{K_a}}$ but  $[H^+] = \frac{K_w}{[OH^-]}$ hence  $[H^+] = \sqrt{\frac{\overline{K_w \cdot K_a}}{[A^-]}}$ 

or  $pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a + \frac{1}{2} \log c$ 

where  $c = [A^-]$ , the stoichiometric molar concentration of the salt.\* This is only justified if the hydrolysis of the salt is very small.

This equation then allows calculation of the pH of an aqueous solution of a salt or the pH at the equivalence point of a weak acid-strong base titration.

Similarly for a strong acid-weak base system the pH is given by

 $pH = \frac{1}{2} pK_w - \frac{1}{2} pK_b - \frac{1}{2} \log c$ 

where  $K_{\rm b}$  is the ionization constant of the base and c is the molar concentration of the salt.

It should be noted that  $K_w$ , the ionic product of water, like any other equilibrium constant, varies with temperature. Table I illustrates this point.

TABLE I

$\frac{\text{Temp. °C}}{0} \frac{K_{\text{w}} \times 10^{14}}{0 \cdot 1139}$		pH of neutral solution $[H^+] = [OH^-]$	
		7.47	
10	0.2920	7.27	
20	0.6809	7.085	
25	1.008	6.998	
30	1.469	6.915	
40	2.919	6.77	
50	5.474	6.63	
60 9.614		6.51	

\* pH is here defined as  $pH = -\log[H^+]$ , *i.e.* in terms of concentration rather than activity of the hydrogen ion. This is done for the sake of simplicity in this and in all subsequent calculations in this article.

A solution then is not necessarily neutral at pH 7 but rather when the hydrogen ion concentration is equal to the hydroxide ion concentration. However, at  $25^{\circ}$ C a neutral solution has a pH of 7 and all subsequent calculations refer to this temperature.

PROTON OR BRØNSTED-LOWRY THEORY

The Arrhenius Theory makes use of hydroxide ions, which may not exist in nonaqueous solvents, and does not cover weak bases. In 1923 Brønsted and Lowry put forward a more general theory of acids and bases which incorporates all protonic solvents, and not just water. They defined an acid as a substance which yields a proton and a base as a substance which can combine with a proton.

Thus an acid HB dissociates to give a proton and its conjugate base. Alternately a base B can combine with a proton to yield the conjugate acid BH<sup>+</sup> of the base. In general terms, this may be written as

 $Acid_1 + Base_2 \rightleftharpoons Acid_2 + Base_1$ 

in which the proton is partitioned between two bases and the equilibrium constant is determined by the relative affinities for the proton.

A Brønsted acid may be an electrically neutral molecule, *e.g.* HCl, a cation, *e.g.*  $C_6H_5NH_3^+$ , or an anion, *e.g.* HSO<sub>4</sub><sup>-</sup>, whilst a Brønsted base may be a neutral molecule, *e.g.* aniline  $C_6H_5NH_2$ , or an anion, *e.g.* Cl<sup>-</sup>.

One important result of this definition of an acid is that the strength of an acid depends upon its environment. The acidic strength of a weak acid is enhanced by its solution in a strongly basic solvent and the basic strength of a weak base is enhanced by its solution in a strongly acidic solvent. In fact, all acids tend to become indistinguishable in strength in strongly basic solvents. This is known as the levelling effect of the solvent.

Solvents may be protophilic, protogenic or aprotic. If a solvent exhibits both protophilic and protogenic properties it is termed amphiprotic. Examples of each form are

- protophilic solvents—ethers, ammines (basic substances);
- protogenic solvents—sulphuric acid (acidic substances):

- amphiprotic solvents—water, acetic acid, alcohols;
- aprotic solvents—benzene, chloroform ('inert' substances).

Actually, these definitions involve a modern extension of the Brønsted-Lowry theory, which might be termed the 'auto-protolysis theory,' *viz.* that in a solvent S in which the equilibrium

$$2S \rightleftharpoons A^+ + B^-$$

occurs, an acid is any substance whose dissolution increases the concentration of  $A^+$  and a base is any substance which increases the concentration of  $B^-$ .

Thus when water ionizes, the equation may be written as

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

where one molecule of water is behaving as an acid and another as a base (amphiprotic).

Similarly for acetic acid

$$\label{eq:CH3COOH} \begin{array}{l} \operatorname{CH_3COOH} + \operatorname{CH_3COOH} \rightleftharpoons \operatorname{CH_3COOH}_2^+ + \\ \operatorname{CH_3COO^-} \end{array}$$

one acetic acid is acting as a proton donor (acid) and the other as a proton acceptor (base).

Again, ammonia ionizes as follows:

$$\mathrm{NH}_3 + \mathrm{NH}_3 \rightleftharpoons \mathrm{NH}_4^+ + \mathrm{NH}_2^-$$

and acids are those substances which, in liquid ammonia, increase the concentration of  $NH_4^+$ .

It follows then that a substance which functions as an acid in one solvent does not necessarily react in this way in another solvent. Urea, for example, is a weak base in water, a stronger base in acetic acid and yet is an acid in liquid ammonia.

$$\begin{split} & H_2O + H_2N \cdot CO \cdot NH_2 \rightleftharpoons H_2N \cdot CO \cdot NH_3^+ + OH^- \\ & acid_1 + base_2 & acid_2 + base_1 \\ & CH_3COOH + H_2N \cdot CO \cdot NH_2 \rightleftharpoons \\ & acid_1 + base_2 \end{split}$$

 $H_2N \cdot CO \cdot NH_3^+ + CH_3COO^$ acid<sub>2</sub> + base<sub>1</sub>

 $\begin{array}{ll} \mathrm{NH}_3 + \mathrm{H}_2 \mathrm{N} \cdot \mathrm{CO} \cdot \mathrm{NH}_2 \\ \approx \mathrm{NH}_4^+ + \mathrm{H}_2 \mathrm{N} \cdot \mathrm{CO} \cdot \mathrm{NH}^- \\ \mathrm{base}_1 + \mathrm{acid}_2 & \mathrm{acid}_1 + \mathrm{base}_2 \end{array}$ 

Strictly the pH unit is limited to dilute aqueous solutions. The useful range of the pH scale is 0 to 14 and is fixed by the autoprotolysis constant for water. If the relative strengths of what, in water, are normally termed strong acids are to be determined, then solvents other than water have to be used. This necessitates the use of other acidity scales, the most familiar of which is probably the Hammett acidity scale.

For example, the acids perchloric, hydrochloric and nitric appear equally strong in water where the strongest acid that can exist is the hydroxonium ion,  $H_3O^+$ , but in other solvents their strengths differ because of variation in the ease of formation of the solvated proton in that particular solvent. The basicity and dielectric constant<sup>\*</sup> appear to be the principal factors in the manifestation of acidity.

Since the extent of acidic and basic dissociation is influenced by the ability of the solvent to accept or donate protons, the same solute may be dissociated to widely different degrees in different solvents. For example, ammonia is not highly protonated in water, but glacial acetic acid, a solvent more protogenic than water, induces extensive protolysis.

 $\rm NH_3 + CH_3COOH \Rightarrow NH_4^+ + CH_3COO^-$ 

Again, sulphuric acid is over four hundred times as acidic in acetic acid as in water at the same concentration. Such systems are often referred to as 'super-acid systems.'

Perchloric acid may be dissolved in acetic acid to give a solution containing  $CH_3COOH_2^+$ ions, and, as this ion can readily give up a proton to react with a base, the solution is strongly acidic. On the other hand acetic acid may itself donate protons to a suitable base. This acidic property will exert a levelling effect on a weak base, which will thus have its basic properties enhanced. Thus the titration of perchloric acid with pyridine in water fails to give a satisfactory end-point, but the same titration in glacial acetic acid is quite successful. The reactions involved are

$$\begin{split} & \text{HClO}_4 + \text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_3\text{COOH}_2^+ + \text{ClO}_4^- \\ & \text{C}_5\text{H}_5\text{N} + \text{CH}_3\text{COOH} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+ + \text{CH}_3\text{COO}^- \\ & \text{CH}_3\text{COOH}_2^+ + \text{CH}_3\text{COO}^- \rightleftharpoons 2\text{CH}_3\text{COOH} \\ & \text{Adding, } \text{HClO}_4 + \text{C}_5\text{H}_5\text{N} \rightleftharpoons \text{C}_5\text{H}_5\text{NH}^+ + \text{ClO}_4^- \end{split}$$

<sup>\*</sup> The Debye-Hűckel equation allows the effect of changes of dielectric constant on the functional relationship between the activity coefficient of the ionic species and the ionic strength to be taken into account.

The intrinsic strength of an acid HA in a particular solvent, then, is formally expressed by its acidity constant in that solvent, and the relationship between a base and its conjugate acid makes it unnecessary to deal with basic dissociation constants when the solvent is amphiprotic.

The Brønsted theory evidently differs from the Arrhenius theory in the following ways:

- (i) proton transfer processes only need be considered (protonation and leprotonation);
- (ii) the term hydrolysis is no longer necessary;
- (iii) the value  $K_{\rm b}$  can be neglected and the strengths of all acids and bases can be given by the  $K_{\rm a}$  value alone by considering the conjugate acid of the base and the value of the solvent ionization constant (e.g.  $K_{\rm w}$ ).

To illustrate (iii) more clearly, a calculation involving the same system referred to under the Arrhenius Theory (p. 91) is more simply derived from the Brønsted approach.

In the reaction

$$\begin{array}{rcl} \mathrm{HA} + \mathrm{OH}^{-} \rightleftharpoons & \mathrm{A}^{-} + \mathrm{H}_{2}\mathrm{O} \\ \mathrm{acid}_{1} + \mathrm{base}_{2} & \mathrm{base}_{1} + \mathrm{acid}_{2} \end{array}$$

[HA] = [OH-] at the equivalence point for there is only the salt of HA in the solvent.

$$K_{\rm b} = \frac{[{\rm HA}] \; [{\rm OH}^-]}{[{\rm A}^-]} = \frac{K_{\rm w}}{K_{\rm a}}$$

since  $[H_2O]$  is effectively constant as before.

$$\therefore \quad \frac{[\text{OH}^{-}]^2}{[\text{A}^{-}]} = \frac{K_w}{K_a}$$
  
and  $[\text{OH}^{-}] = \sqrt{\frac{K_w \cdot [\text{A}^{-}]}{K_a}}$ 

∴  $pOH = \frac{1}{2} pK_w - \frac{1}{2} pK_a - \frac{1}{2} \log [A^-]$ But  $pOH = pK_w - pH (pH + pOH = pK_w = 14 \text{ at } 25^{\circ}\text{C}).$ 

Hence

 $pK_{w} - pH = \frac{1}{2}pK_{w} - \frac{1}{2}pK_{a} - \frac{1}{2}\log [A^{-}]$ or  $pH = \frac{1}{2}pK_{w} + \frac{1}{2}pK_{a} + \frac{1}{2}\log c$ 

where c is the molar stoichiometric concentration of the salt.

To explain further point (iii), consider a weak acid, *e.g.* acetic acid, and a weak base, *e.g.* ammonia.

According to the Arrhenius theory

$K_{\mathrm{a}}$	(acetic acid)	-	$\frac{\rm [H^+] \ [CH_3COO^-]}{\rm CH_3COOH}$
or	$\mathrm{p}K_{\mathrm{a}}$	=	4.76
$K_{\mathfrak{b}}$	(ammonia)	-	$\frac{\rm [NH_4^+] [OH^-]}{\rm NH_4OH}$
or	$pK_{b}$	=	4.75

However, in the Brønsted sense there is no need to invoke the presence of molecular  $NH_4OH$  (which probably does not exist) to give  $pK_b$ . Rather, using the conjugate acid of the base, *i.e.*  $NH_4^+ \rightleftharpoons H^+ + NH_3$ , a  $pK_a$ value of 9.25 can be obtained for the ammonium ion, since  $pK_a + pK_b = pK_w = 14$ .

The major weakness of the Brønsted– Lowry Theory is that it makes the definition of an acid and a base as rigidly dependent upon the solvent as does the Arrhenius Theory. However, it does take into account that there are solvents other than water which exhibit typical basic properties, even though it does not recognize the complementary data with regard to acids.

#### ELECTRONIC OR LEWIS THEORY

The Lewis Theory first introduced in 1923 is a more embracing theory still than those of Arrhenius and Brønsted.

It is an electronic theory and the definitions of acids and bases do not depend upon the presence of any particular solvent.

An acid is defined as an electron-deficient species or one that seeks a molecular species containing available pairs of electrons. For example,  $H^+$ ,  $NO_2^+$ ,  $BF_3$  and  $AlCl_3$  are acids.

Bases are species which contain a pair of electrons capable of being donated to another species. For example,  $Cl^-$ ,  $H_2O$ ,  $OH^-$ ,  $NH_3$ , ethers, esters and ketones are bases.

Searching for a property common to all acids, or that common to all bases, Lewis concluded that acids and bases correspond respectively to what Sidgwick later called 'acceptor' and 'donor' molecules. Neutralization is the formation of a co-ordinate covalent bond between the acid and the base. For example.

$$\begin{array}{ccc} \mathrm{H^{+}} + : \ddot{\mathrm{O}} : \mathrm{H^{-}} \rightarrow \mathrm{H} : \ddot{\mathrm{O}} : \mathrm{H} \\ \mathrm{acid} & \ddot{\mathrm{base}} \\ & \mathrm{Cl} & \mathrm{H} & \mathrm{Cl} & \mathrm{H} \\ & & & & \\ \mathrm{Cl^{-}B} + : \mathrm{N^{-}H} \rightarrow \mathrm{Cl^{-}B} : \mathrm{N^{-}H} \\ & & & & \\ \mathrm{Cl^{-}B} & \mathrm{H} & & \mathrm{Cl^{+}H} \end{array}$$

The base donates a share in a lone pair of electrons to the acid to form the co-ordinate covalent bond between the two. Formation of this bond is always to be considered the first step, even though ionization may subsequently take place. In the above case of boron trichloride and ammonia, ionization does not occur after neutralization. In other cases, however, the electrical 'strain' produced by the formation of the co-ordinate covalent bond is sufficient to result in ionization of the neutralization product, as when aluminium bromide reacts with pyridine.



Lewis was concerned with broadening the basis of the acid-base definition from both the experimental and theoretical standpoints. He chose four familiar experimental criteria, viz. neutralization, titration with indicators, displacement and catalysis, and defined as acids and bases all substances which exhibit the ability to take part in these 'typical' functions. On the theoretical side he related these properties to the acceptance and donation of electron pairs irrespective of whether the transfer of protons was involved.

The scope of the electronic theory is sufficiently broad to include the proton-transfer definition of an acid, and, since electrondonor molecules are able to combine with protons, the Lewis concept of a base embraces the Brønsted-Lowry definition. On the other hand the Lewis definition of an acid embraces many substances which do not contain a hydrogen atom, and consequently radically increases the number of acids over those as defined by the Brønsted concept.

For example, it is evident that precisely the same principles are involved in the reaction of aluminium chloride with pyridine as in the more usual neutralization of pyridine by a proton-donating acid:





Again solutions of boron trifluoride or sulphur trioxide in inert solvents bring about colour changes in indicators very similar to those produced by protonic acids. These changes can be reversed by adding bases so that a titration is possible; yet no proton is involved.

The major disadvantage of the Lewis system appears when its quantitative aspect is considered. The protonic acids make up a group which show greater uniformity than do



the non-protonic acids of the Lewis definition, when related to any simple system of acidbase strengths.

A further disadvantage is that certain substances which experimentally behave like acids, e.g. HCl and CO<sub>2</sub>, have electronic formulae which, as usually written, do not show the possibility of their acting as electronpair acceptors. Such acids and bases are called 'secondary' by Lewis as distinct from his 'primary' acids and bases which involve electron-pair sharing. This introduces a cumbrous name for common substances and raises the question of the value of the term 'acid' as commonly used.

### CALCULATIONS IN ACID-BASE TITRATIONS

Each of the above theories presents certain difficulties, and a practical point at issue is which theory is able to clearly and quantitatively assist in calculations involving acidbase systems. The Arrhenius Theory is restricted to water as the solvent. The Lewis Theory covers more completely substances that show the qualitative attributes normally associated with acids. The Brønsted-Lowry acids, on the other hand, form a more uniform group and obey the quantitative relationships confined to this group.

For this reason, and because a solvent is normally used in simple acid-base systems, the Brønsted-Lowry approach is generally used in the following calculations of acid-base titrations.

### 1. Strong Acid – Strong Base Titration

The pH change is due only to the dilution effect and the neutralization of some of the acid or base. Both acid and base are fully dissociated, and calculations involve assessing the actual acid or base concentration before and after the equivalence point. The equivalence point in water is at pH 7 at 25°C.

*Example:* If to 50 ml of 0.1 MCl, 20 ml of 0.1 NaOH are added, the total acid concentration is 30 ml of 0.1 in a volume of 70 ml.

$$[\mathrm{H^+}] = \frac{30}{70} \times 0.1 \text{ or pH} = 1.37$$

If to 50 ml of 0.1 N HCl, 51 ml of 0.1 N NaOH are added, the total hydroxide ion concentration is  $\frac{1}{101} \times 0.1$ , or pOH = 4.0, or pH = 10.0.

# 2. Weak Acid-Strong Base Titration

The pH change, up to the region of the equivalence point, is due to the dilution effect, neutralization of the acid and the protophilic character of the conjugate base. Beyond the equivalence point the pH change is due only to the dilution effect of the strong base. The equivalence point occurs at a pH greater than 7.0 at  $25^{\circ}$ C.

The pH values can be calculated from the following equations:

Before any base is added:

 $pH = \frac{1}{2} pK_{a} - \frac{1}{2} \log c \text{ (acid)}$ 

Titration up to equivalence point:

$$pH = pK_a + \log \frac{c \text{ (salt)}}{c \text{ (acid)}}$$

At the equivalence point:

 $pH = \frac{1}{2} pK_{a} + \frac{1}{2} pK_{w} + \frac{1}{2} \log c \text{ (salt)}.$ 

# 3. Strong Acid – Weak Base Titration

The pH change, up to the region of the equivalence point, is due to the dilution effect, neutralization of the base and the protogenic character of the conjugate acid of the base. Beyond the equivalence point (pH < 7) the pH change is due only to the dilution effect of the strong acid.

The pH values can be calculated from the following equations:

Before addition of any acid:

 $pH = \frac{1}{2} pK_w + \frac{1}{2} pK_a^b + \frac{1}{2} \log c \text{ (base)}$ 

Up to the equivalence point:

$$pH = pK_w - pK_b - \log \frac{c \text{ (salt)}}{c \text{ (base)}}$$
$$= pK_a^b - \log \frac{c \text{ (salt)}}{c \text{ (base)}}$$

At the equivalence point:

$$pH = \frac{1}{2} pK_{w} - \frac{1}{2} pK_{b} - \frac{1}{2} \log c \text{ (salt)}$$
$$= \frac{1}{2} pK_{a^{b}} - \frac{1}{2} \log c \text{ (salt)}$$

where  $pK_{a^{b}}$  refers to the conjugate acid of the base and is equal to  $pK_{w} - pK_{b}$ .

## 4. Weak Acid - Weak Base Titration

The pH change throughout is due to dilution, neutralization and the proton affinities of the conjugate acid and conjugate base. This type of titration is rarely used, but calculations may be made from the equations under (2) and (3) above, except that at the equivalence point itself the pH is given by

$$pH = \frac{1}{2}pK_w + \frac{1}{2}pK_a - \frac{1}{2}pK_b = \frac{1}{2}pK_a + \frac{1}{2}pK_a^b$$

where  $pK_a^b$  again refers to the conjugate acid of the base.

#### 5. Polyprotic Acids and Bases

In a polyprotic system, where transfer of more than one proton is involved, *e.g.* in  $H_3X$ , there are three dissociation constants:

$$\begin{split} K_1 &= \frac{[\mathrm{H}^+] \; [\mathrm{H}_2 \mathrm{X}^-]}{[\mathrm{H}_3 \mathrm{X}]} \\ K_2 &= \frac{[\mathrm{H}^+] \; [\mathrm{H} \mathrm{X}^{2-}]}{[\mathrm{H}_2 \mathrm{X}^-]} \\ K_3 &= \frac{[\mathrm{H}^+] \; [\mathrm{X}^{3-}]}{[\mathrm{H} \mathrm{X}^{2-}]} \end{split}$$

Provided  $pK_1$ ,  $pK_2$  and  $pK_3$  differ by at least four units, then each step, involving one proton transfer, proceeds virtually to completion (99.99 per cent for four units) before the next neutralization step commences. Such a titration will give two or three inflection points, and the pH at the first inflection point is given by

$$pH = \frac{1}{2} (pK_1 + pK_2)$$

which corresponds to the pH of the salt NaH<sub>2</sub>X.

The pH at the second inflection point is given by

$$pH = \frac{1}{2} (pK_2 + pK_3)$$

and corresponds to the pH of the salt Na<sub>2</sub>HX.

The appearance of a third inflection point in the titration of  $H_3X$  with alkali depends upon the pH of the solution of the salt  $Na_3X$ in relation to the pH of the solution when a slight excess of the alkali titrant has been added.

## DETECTION OF END-POINTS IN ACID-BASE TITRATIONS

In all titrations some means of detecting the end-point or end-points is necessary. In acid—base systems two distinct techniques are commonly used:

- (i) instrumental, *e.g.* pH meter, conductivity cell;
- (ii) indicators.

Indicators which cover a wide range of the pH scale are available, and it is necessary to select one whose colour change occurs at a pH attained immediately after the equivalence point is reached, that is, at the point where the rate of change of pH with change of volume of titrant is at a maximum. Naturally this does not necessarily occur at pH 7 at 25°C.

Indicators are themselves weak acids or bases, and consequently the ratio of ionized to unionized form depends on the pH. For simplicity they may be considered as acting like any other weak acid or base, that is

$$\mathrm{HIn} \rightleftharpoons \mathrm{H^{+} + In^{-}}$$

where HIn and  $In^-$  are of different colour in the solution.

The chief characteristic of these indicators is that the change from a predominantly 'acid' colour to a predominantly 'alkaline' colour is not sudden, but takes place over a pH range of about two units. This is termed the colour-change interval of the indicator and arises because the ratio in the concentrations of the two coloured forms of the indicator will vary continuously as the hydrogenion concentration is changed.

For ease in observing colour change, screened or mixed indicators may be used. A screened indicator contains an indifferent dye which allows the colour change to be more easily seen. A mixed indicator consists of a main indicator and an auxiliary indicator which indicates the approach of the change point, or two indicators with overlapping pH change. The advantage of this latter type is that a sharp colour change occurs over a more limited pH range.

For a substance or system of substances to function satisfactorily as a pH indicator, the change observed should satisfy the following conditions:

- (i) the change should be a distinct one and should occur over the shortest possible pH range;
- (ii) the indicator change should be reversible and the reaction involved should be rapid in both directions;
- (iii) the indicator should be sensitive, *i.e.* only a small quantity should be required to impart a distinct colour to the solution.

Common pH indicators, their colours and pH ranges are given in Table II.

TABLE II

	Colo	- H	
Name	Acid	Alkaline	pH range
Thymol blue	red	vellow	$1 \cdot 2 - 2 \cdot 8$
Methyl orange	red	orange- vellow	$3 \cdot 1 - 4 \cdot 4$
Bromo cresol blue	yellow	blue	$3 \cdot 8 - 5 \cdot 4$
Methyl red	red	yellow	$4 \cdot 2 - 6 \cdot 2$
Bromothymol blue	yellow	blue	$6 \cdot 0 - 7 \cdot 6$
Cresol red	vellow	red	$7 \cdot 2 - 8 \cdot 8$
Phenolphthalein	colourless	red	8.2-10.0
Thymolphthalein	colourless	blue	$9 \cdot 3 - 10 \cdot 5$

#### SUMMARY

Because of the gradual fusion of ideas on acid-base theory from which our present concepts have sprung, the importance of this topic has extended far beyond the reaction of an acid and a base to give a salt and water. Indeed calculations of pH in acid-base systems, as described above, are only a part of its usefulness.

The Brønsted-Lowry definition has initiated many investigations of acid-base equilibria and kinetics in different solvents, whilst the Lewis concept has led to much valuable work on the reactions of acceptor molecules.

The following are but a few examples of studies involving acid-base theories and serve to illustrate the scope of this field:

- (a) the formation of the so-called hydroxides of iron and other metals;
- (b)determination of equilibrium and stability constants of simple and complex molecules, both organic and inorganic;
- the role of sulphuric-nitric acid in (c)nitration processes;
- (d)the use of lithium aluminium hydride in the reduction of organic compounds.

There is, of course, a temptation when dealing with rival points of view to assume that one of them is 'right' and the others

'wrong,' forgetting that they are only convenient, altogether artificial schemes for classifying systems. No one of them is either true or false and the differences are in degree, not kind. The choice between them should depend solely upon the region of chemistry in which one is operating. The water theory is applicable to aqueous solutions, the proton theory is preferable for dealing with a variety of solvents, whilst the electronic theory covers acid behaviour in the absence of protons.

#### FURTHER READING

- Bates, R. G., Electrometric pH Determinations. Chapman & Hall, London, 1954.
- Bell, R. P., The Proton in Chemistry. Methuen & Co., London, 1959.
- Bell, R. P., Quart. Rev. Chem. Soc., 1947, 1, 113.
   Becket, A. H., and Tinley, E. H., Titrations in Non-Aqueous Solvents (booklet). Third Edition. British Drug Houses Ltd., 1960.
- Bryson, A., Background to Chemistry (Editor: D. P. Mellor), pp. 54-63. The University of New South Wales, 1960.
- Gold, V., pH Measurements: Their Theory and
- Practice. Methuen & Co., London, 1956. Luder, W. F., and Zuffanti, S., Electronic Theory of Acids and Bases. John Wiley & Sons, New York, 1946.
- Vogel, A. I., Textbook of Quantitative Inorganic Analysis. Third Edition. Longmans, Green & Co., London, 1961.

# COURSES AND SYMPOSIA FOR TEACHERS

The following symposia have been arranged by Local Sections of the Royal Institute of Chemistry in collaboration with the Association for Science Education:

- University of Liverpool, 25 April, 1964-'New Techniques in Practical Chemistry for Schools
- The School of Pharmacy, University of London, 2 May, 1964-'The Teaching of Inorganic Chemistry at Pre-University Level.'
- University of Leicester, 2 May, 1964-'The Teaching of Chemistry in Schools.' (A follow-up conference arising from the symposium on the teaching of organic chemistry held on 26 October, 1963.)
- Manchester College of Science and Technology, 9 May, 1964-'CHEM Study-a new look at the teaching of chemistry.' (Guest Speaker, Professor J. Arthur

Campbell, Director, CHEM Study Project.)

The following information has been received from Local Education Authorities about courses for teachers that are being arranged during the Summer Term:

- Cambridgeshire Local Education Authority (in collaboration with the Ministry of Education), 13-17 April, 1964—'Science Teaching in the Secondary School.'
- Surrey Local Education Authority (Kingston College of Technology), July, 1964-'New approaches to teaching theoretical and practical chemistry in secondary schools.'
- Somerset Local Education Authority (in collaboration with the Ministry of Education), 27 April-1 May, 1964—'Science Teaching in the Secondary School.'