In practice, an ideal primary standard is difficult to obtain, and a compromise between the above ideal requirements is usually necessary. The substances commonly employed as primary standards are indicated below:

(a) **Acid-base reactions** — sodium carbonate Na_2CO_3, sodium tetraborate $Na_2B_4O_7$, potassium hydrogenphthalate $KH(C_8H_4O_4)$, constant boiling point hydrochloric acid, potassium hydrogeniodate $KH(IO_3)_2$, benzoic acid (C_6H_5COOH).

(b) **Complex formation reactions** — silver, silver nitrate, sodium chloride, various metals (e.g. spectroscopically pure zinc, magnesium, copper, and manganese) and salts, depending upon the reaction used.

(c) **Precipitation reactions** — silver, silver nitrate, sodium chloride, potassium chloride, and potassium bromide (prepared from potassium bromate).

(d) **Oxidation–reduction reactions** — potassium dichromate $K_2Cr_2O_7$, potassium bromate $KBrO_3$, potassium iodate KIO_3, potassium hydrogeniodate $KH(IO_3)_2$, sodium oxalate $Na_2C_2O_4$, arsenic(III) oxide As_2O_3, and pure iron.

Hydrated salts, as a rule, do not make good standards because of the difficulty of efficient drying. However, those salts which do not effloresce, such as sodium tetraborate $Na_2B_4O_7$, $10H_2O$, and copper sulphate $CuSO_4,5H_2O$, are found by experiment to be satisfactory secondary standards.[2]

A secondary standard is a substance which may be used for standardisations, and whose content of the active substance has been found by comparison against a primary standard. It follows that a secondary standard solution is a solution in which the concentration of dissolved solute has not been determined from the weight of the compound dissolved but by reaction (titration) of a volume of the solution against a measured volume of a primary standard solution.

NEUTRALISATION TITRATIONS

10.7 NEUTRALISATION INDICATORS

The object of titrating, say, an alkaline solution with a standard solution of an acid is the determination of the amount of acid which is exactly equivalent chemically to the amount of base present. The point at which this is reached is the **equivalence point, stoichiometric point**, or **theoretical end point**; the resulting aqueous solution contains the corresponding salt. If both the acid and base are strong electrolytes, the solution at the end-point will be neutral and have a pH of 7 (Section 2.17); but if either the acid or the base is a weak electrolyte, the salt will be hydrolysed to a certain degree, and the solution at the equivalence point will be either slightly alkaline or slightly acid. The exact pH of the solution at the equivalence point can readily be calculated from the ionisation constant of the weak acid or the weak base and the concentration of the solution (see Section 2.19). For any actual titration the correct end-point will be characterised by a definite value of the hydrogen-ion concentration of the solution, the value depending upon the nature of the acid and the base and the concentration of the solution.

A large number of substances, called **neutralisation** or **acid–base indicators**, change colour according to the hydrogen-ion concentration of 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 and abrupt, but takes place within a small interval of pH (usually about two pH units) termed the **colour-change interval** of the indicator. The position of the colour-change interval in the pH scale varies widely with different indicators. For most acid–base titrations it is possible to select an indicator which exhibits a distinct colour change at a pH close to that corresponding to the equivalence point.

The first useful theory of indicator action was suggested by W. Ostwald[3] based upon the concept that indicators in general use are very weak organic acids or bases.

The simple Ostwald theory of the colour change of indicators has been revised, and the colour changes are believed to be due to structural changes, including the production of quinonoid and resonance forms; these may be illustrated by reference to phenolphthalein, the changes of which are characteristic of all phthalein indicators: see the formulae I–IV given below. In the presence of dilute alkali the lactone ring in I opens to yield II, and the triphenylcarbinol structure (II) undergoes loss of water to produce the resonating ion III which is red. If phenolphthalein is treated with excess of concentrated alcoholic alkali the red colour first produced disappears owing to the formation of IV.
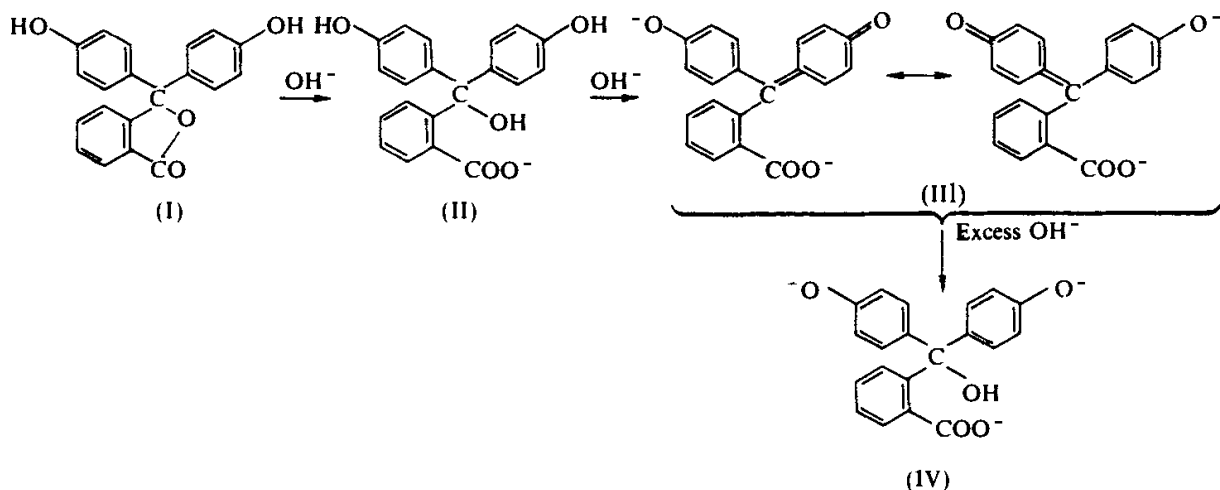
The Brønsted–Lowry concept of acids and bases[4] makes it unnecessary to distinguish between acid and base indicators: emphasis is placed upon the charge types of the acid and alkaline forms of the indicator. The equilibrium between the acidic form In_A and the basic form In_B may be expressed as:

$$In_A \rightleftharpoons H^+ + In_B \qquad (1)$$

and the equilibrium constant as:

$$\frac{a_{H^+} \times a_{In_B}}{a_{In_A}} = K_{In} \qquad (2)$$

The observed colour of an indicator in solution is determined by the ratio of the concentrations of the acidic and basic forms. This is given by:

$$\frac{[In_A]}{[In_B]} = \frac{a_{H^+} \times y_{In_B}}{K_{In} \times y_{In_A}} \qquad (3)$$

where y_{In_A} and y_{In_B} are the activity coefficients of the acidic and basic forms of the indicator. Equation (3) may be written in the logarithmic form:

$$pH = -\log a_{H^+} = pK_{In} + \log\frac{[In_B]}{[In_A]} + \log\frac{y_{In_B}}{y_{In_A}} \tag{4}$$

The pH will depend upon the ionic strength of the solution (which is, of course, related to the activity coefficient — see Section 2.5). Hence, when making a colour comparison for the determination of the pH of a solution, not only must the indicator concentration be the same in the two solutions but the ionic strength must also be equal or approximately equal. The equation incidentally provides an explanation of the so-called salt and solvent effects which are observed with indicators. The colour-change equilibrium at any particular ionic strength (constant activity-coefficient term) can be expressed by a condensed form of equation (4):

$$pH = pK'_{In} + \log\frac{[In_B]}{[In_A]} \tag{5}$$

where pK'_{In} is termed the **apparent indicator constant**.

The value of the ratio $[In_B]/[In_A]$ (i.e. [Basic form]/[Acidic form]) can be determined by a visual colour comparison or, more accurately, by a spectrophotometric method. Both forms of the indicator are present at any hydrogen-ion concentration. It must be realised, however, that the human eye has a limited ability to detect either of two colours when one of them predominates. Experience shows that the solution will appear to have the 'acid' colour, i.e. of In_A, when the ratio of $[In_A]$ to $[In_B]$ is above approximately 10, and the 'alkaline' colour, i.e. of In_B, when the ratio of $[In_B]$ to $[In_A]$ is above approximately 10. Thus only the 'acid' colour will be visible when $[In_A]/[In_B] > 10$; the corresponding limit of pH given by equation (5) is:

$$pH = pK'_{In} - 1$$

Only the alkaline colour will be visible when $[In_B]/[In_A] > 10$, and the corresponding limit of pH is:

$$pH = pK'_{In} + 1$$

The colour-change interval is accordingly $pH = pK'_{In} \pm 1$, i.e. over approximately two pH units. Within this range the indicator will appear to change from one colour to the other. The change will be gradual, since it depends upon the ratio of the concentrations of the two coloured forms (acidic form and basic form). When the pH of the solution is equal to the apparent dissociation constant of the indicator pK'_{In}, the ratio $[In_A]$ to $[In_B]$ becomes equal to 1, and the indicator will have a colour due to an equal mixture of the 'acid' and 'alkaline' forms. This is sometimes known as the 'middle tint' of the indicator. This applies strictly only if the two colours are of equal intensity. If one form is more intensely coloured than the other or if the eye is more sensitive to one colour than the other, then the middle tint will be slightly displaced along the pH range of the indicator.

Table 10.1 contains a list of indicators suitable for titrimetric analysis and for the colorimetric determination of pH. The colour-change intervals of most of the various indicators listed in the table are represented graphically in Fig. 10.1.

Table 10.1 Colour changes and pH range of certain indicators

Indicator	Chemical name	pH range	Colour in acid solution	Colour in alkaline solution	pK'$_{In}$
Brilliant cresyl blue (acid)	Aminodiethylaminomethyldiphenazonium chloride	0.0–1.0	Red–orange	Blue	—
Cresol red (acid)	1-Cresolsulphonphthalein	0.2–1.8	Red	Yellow	—
m-Cresol purple	m-Cresolsulphonphthalein	0.5–2.5	Red	Yellow	—
Quinaldine red	1-(p-Dimethylaminophenylethylene)quinoline ethiodide	1.4–3.2	Colourless	Red	—
Thymol blue (acid)	Thymolsulphonphthalein	1.2–2.8	Red	Yellow	1.7
Tropaeolin OO	p-Anilinophenylazobenzenesulphonic acid sodium salt	1.3–2.8	Red	Yellow	—
Bromophenol blue	Tetrabromophenolsulphonphthalein	2.8–4.6	Yellow	Blue	4.1
Ethyl orange	Dimethylaminophenylazobenzenesulphonic acid sodium salt	3.0–4.5	Red	Orange	—
Methyl orange	Diphenyldiazobis-1-naphthylaminesulphonic acid disodium salt	2.9–4.6	Red	Orange	3.7
Congo red		3.0–5.0	Blue	Red	—
Bromocresol green	Tetrabromo-m-cresolsulphonphthalein	3.6–5.2	Yellow	Blue	4.7
Methyl red	1-Carboxybenzeneazodimethylaniline	4.2–6.3	Red	Yellow	5.0
Ethyl red		4.5–6.5	Red	Orange	—
Chlorophenol red	Dichlorophenolsulphonphthalein	4.6–7.0	Yellow	Red	6.1
4-Nitrophenol	4-Nitrophenol	5.0–7.0	Colourless	Yellow	7.1
Bromocresol purple	Dibromo-o-cresolsulphonphthalein	5.2–6.8	Yellow	Purple	6.1
Bromophenol red	Dibromophenolsulphonphthalein	5.2–7.0	Yellow	Red	—
Azolitmin (litmus)	—	5.0–8.0	Red	Blue	—
Bromothymol blue	Dibromothymolsulphonphthalein	6.0–7.6	Yellow	Blue	7.1
Neutral red	Aminodimethylaminotoluphenazonium chloride	6.8–8.0	Red	Orange	—
Phenol red	Phenolsulphonphthalein	6.8–8.4	Yellow	Red	7.8
Cresol red (base)	1-Cresolsulphonphthalein	7.2–8.8	Yellow	Red	8.2
1-Naphtholphthalein	1-Naphtholphthalein	7.3–8.7	Yellow	Blue	8.4
m-Cresol purple	m-Cresolsulphonphthalein	7.6–9.2	Yellow	Purple	—
Thymol blue (base)	Thymolsulphonphthalein	8.0–9.6	Yellow	Blue	8.9
o-Cresolphthalein	Di-o-cresolphthalide	8.2–9.8	Colourless	Red	—
Phenolphthalein	Phenolphthalein	8.3–10.0	Colourless	Red	9.6
Thymolphthalein	Thymolphthalein	9.3–10.5	Colourless	Blue	9.3
Alizarin yellow R	p-Nitrobenzeneazosalicylic acid	10.1–12.1	Yellow	Orange–red	—
Brilliant cresyl blue (base)	Aminodiethylaminomethyldiphenazonium chloride	10.8–12.0	Blue	Yellow	—
Tropaeolin O	p-Sulphobenzeneazoresorcinol	11.1–12.7	Yellow	Orange	—
Nitramine	2,4,6-Trinitrophenylmethylnitroamine	10.8–13.0	Colourless	Orange–brown	—

Indicator	pH transition colours
Brilliant cresyl blue RO	RO → B (≈0–1); B → Y (≈10–12)
Cresol red	R → Y (≈0–2); Y → R (≈7–8)
m-cresol purple	R → Y (≈0–2)
Thymol blue	R → Y (≈1–3); Y → B (≈8–9)
Tropaeolin OO	R → Y (≈1–3)
Quinaldine red	C → R (≈1–3)
Bromophenol blue	Y → B (≈3–5)
Methyl orange	R → Y (≈3–4)
Congo red	B → R (≈3–5)
Bromocresol green	Y → B (≈4–5)
Methyl red	R → Y (≈5–6)
Chlorophenol red	Y → R (≈5–6)
4-Nitrophenol	C → Y (≈5–7)
Bromocresol purple	Y → P (≈5–7)
Bromothymol blue	Y → B (≈6–8)
Neutral red	R → O (≈7–8)
Phenol red	Y → R (≈7–8)
1-Naphtholphthalein	Y → B (≈8–9)
Phenolphthalein	C → R (≈8–10)
Thymolphthalein	C → B (≈9–10)
Alizarin yellow R	Y → RO (≈10–12)
Tropaeolin O	Y → O (≈11–13)
Nitramine	C → OB (≈11–13)

P = Purple
R = Red
RO = Red – orange
Y = Yellow

B = Blue
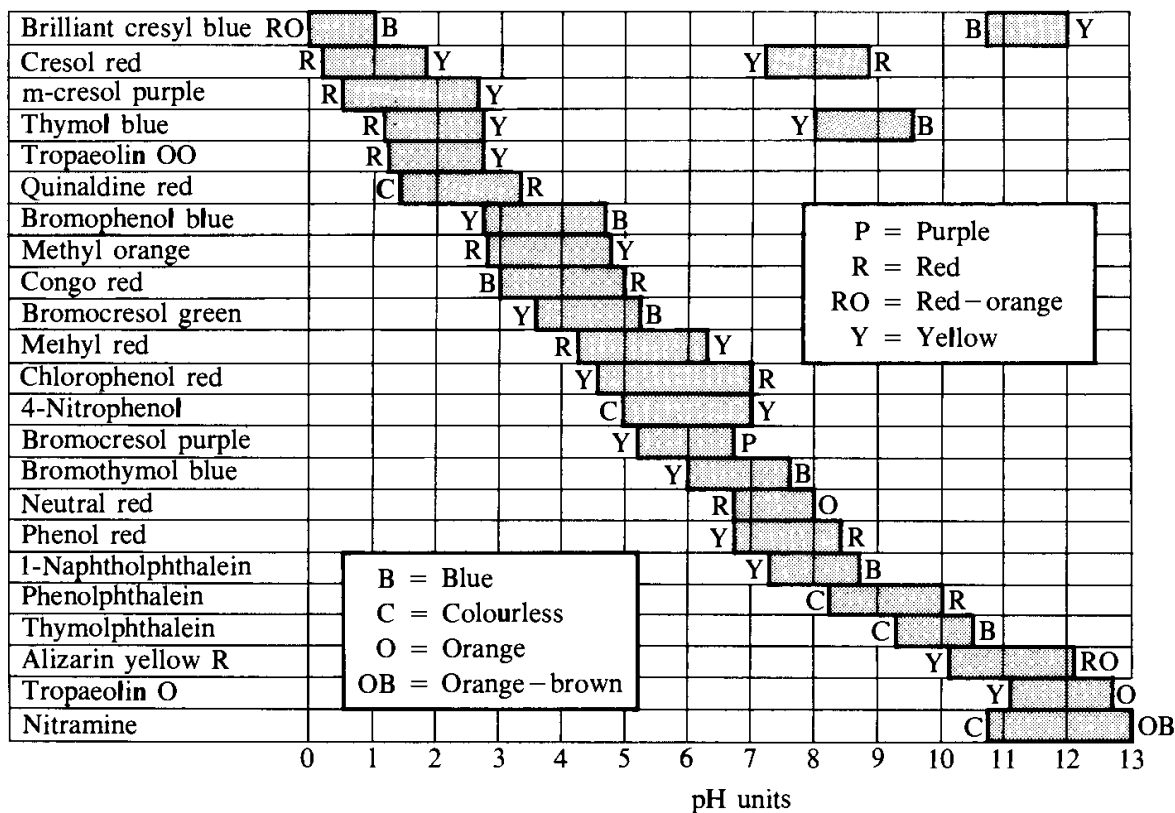C = Colourless
O = Orange
OB = Orange – brown

pH units

Fig. 10.1

It is necessary to draw attention to the variable pH of water which may be encountered in quantitative analysis. Water in equilibrium with the normal atmosphere which contains 0.03 per cent by volume of carbon dioxide has a pH of about 5.7; very carefully prepared conductivity water has a pH close to 7; water saturated with carbon dioxide under a pressure of one atmosphere has a pH of about 3.7 at 25 °C. The analyst may therefore be dealing, according to the conditions that prevail in the laboratory, with water having a pH between the two extremes pH 3.7 and pH 7. Hence for indicators which show their alkaline colours at pH values above 4.5, the effect of carbon dioxide introduced during a titration, either from the atmosphere or from the titrating solutions, must be seriously considered. This subject is discussed again later (Section 10.12).

10.8 PREPARATION OF INDICATOR SOLUTIONS

As a rule laboratory solutions of the indicators contain 0.5–1 g of indicator per litre of solvent. If the substance is soluble in water, e.g. a sodium salt, water is the solvent; in most other cases 70–90 per cent ethanol is employed.

Methyl orange. This indicator is available either as the free acid or as the sodium salt.

Dissolve 0.5 g of the free acid in 1 litre of water. Filter the cold solution to remove any precipitate which separates.

Dissolve 0.5 g of the sodium salt in 1 litre of water, add 15.2 mL of 0.1 M hydrochloric acid, and filter, if necessary, when cold.

Methyl red. Dissolve 1 g of the free acid in 1 litre of hot water, or dissolve in 600 mL of ethanol and dilute with 400 mL of water.

1-Naphtholphthalein. Dissolve 1 g of the indicator in 500 mL of ethanol and dilute with 500 mL of water.

Phenolphthalein. Dissolve 5 g of the reagent in 500 mL of ethanol and add 500 mL of water with constant stirring. Filter, if a precipitate forms.

Alternatively, dissolve 1 g of the dry indicator in 60 mL of 2-ethoxyethanol (Cellosolve), b.p. 135 °C, and dilute to 100 mL with distilled water: the loss by evaporation is less with this preparation.

Thymolphthalein. Dissolve 0.4 g of the reagent in 600 mL of ethanol and add 400 mL of water with stirring.

Sulphonphthaleins. These indicators are usually supplied in the acid form. They are rendered water-soluble by adding sufficient sodium hydroxide to neutralise the sulphonic acid group. One gram of the indicator is triturated in a clean glass mortar with the appropriate quantity of 0.1 M sodium hydroxide solution, and then diluted with water to 1 L. The following volumes of 0.1 M sodium hydroxide are required for 1 g of the indicators: bromophenol blue, 15.0 mL; bromocresol green, 14.4 mL; bromocresol purple, 18.6 mL; chlorophenol red, 23.6 mL; bromothymol blue, 16.0 mL; phenol red, 28.4 mL; thymol blue, 21.5 mL; cresol red, 26.2 mL; metacresol purple, 26.2 mL.

Quinaldine red. Dissolve 1 g in 100 mL of 80 per cent ethanol.

Methyl yellow, neutral red, and Congo red. Dissolve 1 g of the indicator in 1 L of 80 per cent ethanol. Congo red may also be dissolved in water.

4-Nitrophenol. Dissolve 2 g of the solid in 1 L of water.

Alizarin yellow R. Dissolve 0.5 g of the indicator in 1 L of 80 per cent ethanol.

Tropaeolin O and tropaeolin OO. Dissolve 1 g of the solid in 1 L of water.

Many of the indicator solutions are available from commercial suppliers already prepared for use.

10.9 MIXED INDICATORS

For some purposes it is desirable to have a sharp colour change over a narrow and selected range of pH; this is not easily seen with an ordinary acid–base indicator, since the colour change extends over two units of pH. The required result may, however, be achieved by the use of a suitable mixture of indicators; these are generally selected so that their pK'_{In} values are close together and the overlapping colours are complementary at an intermediate pH value. A few examples will be given in some detail.

(a) A mixture of equal parts of neutral red (0.1 per cent solution in ethanol) and methylene blue (0.1 per cent solution in ethanol) gives a sharp colour change from violet–blue to green in passing from acid to alkaline solution at pH 7. This indicator may be employed to titrate acetic acid (ethanoic acid) with ammonia solution or vice versa. Both acid and base are approximately of the same strength, hence the equivalence point will be at a pH $\approx$ 7 (Section 10.15); owing to the extensive hydrolysis and the flat nature of the titration curve, the titration cannot be performed except with an indicator of very narrow range.

(b) A mixture of phenolphthalein (3 parts of a 0.1 per cent solution in ethanol) and 1-naphtholphthalein (1 part of a 0.1 per cent solution in ethanol) passes from pale rose to violet at pH = 8.9. The mixed indicator is suitable for the titration of phosphoric acid to the diprotic stage ($K_2 = 6.3 \times 10^{-8}$; the equivalence point at pH $\approx$ 8.7).

(c) A mixture of thymol blue (3 parts of a 0.1 per cent aqueous solution of the sodium salt) and cresol red (1 part of a 0.1 per cent aqueous solution of the sodium salt) changes from yellow to violet at pH = 8.3. It has been recommended for the titration of carbonate to the hydrogencarbonate stage.

Other examples are included in Table 10.2.

Table 10.2 Some mixed indicators

Indicator mixture	pH	Colour change	Composition*
Bromocresol green; methyl orange	4.3	Orange → blue–green	1 p 0.1% (Na) in w; 1 p 0.2% in w
Bromocresol green; chlorophenol red	6.1	Pale green → blue violet	1 p 0.1% (Na) in w; 1 p 0.1% (Na) in w
Bromothymol blue; neutral red	7.2	Rose pink → green	1 p 0.1% in e; 1 p 0.1% in e
Bromothymol blue; phenol red	7.5	Yellow → violet	1 p 0.1% (Na) in w; 1 p 0.1% (Na) in w
Thymol blue; cresol red	8.3	Yellow → violet	3 p 0.1% (Na) in w; 1 p 0.1% (Na) in w
Thymol blue; phenolphthalein	9.0	Yellow → violet	1 p 0.1% in 50% e; 3 p 0.1% in 50% e
Thymolphthalein; phenolphthalein	9.9	Colourless → violet	1 p 0.1% in e; 1 p 0.1% in w

*Abbreviations: p = part, w = water, e = ethanol, Na = Na salt

The colour change of a single indicator may also be improved by the addition of a pH-sensitive dyestuff to produce the complement of one of the indicator colours. A typical example is the addition of xylene cyanol FF to methyl orange (1.0 g of methyl orange and 1.4 g of xylene cyanol FF in 500 mL of 50 per cent ethanol): here the colour change from the alkaline to the acid side is green → grey → magenta, the middle (grey) stage being at pH = 3.8. The above is an example of a **screened indicator**, and the mixed indicator solution is sometimes known as 'screened' methyl orange. Another example is the addition of methyl green (2 parts of a 0.1 per cent solution in ethanol) to phenolphthalein (1 part of a 0.1 per cent solution in ethanol); the former complements the red–violet basic colour of the latter, and at a pH of 8.4–8.8 the colour change is from grey to pale blue.

10.10 UNIVERSAL OR MULTIPLE-RANGE INDICATORS

By mixing suitable indicators together changes in colour may be obtained over a considerable portion of the pH range. Such mixtures are usually called 'universal indicators'. They are not suitable for quantitative titrations, but may be employed for the determination of the approximate pH of a solution by the colorimetric method. One such universal indicator is prepared by dissolving 0.1 g of phenolphthalein, 0.2 g of methyl red, 0.3 g of methyl yellow, 0.4 g of

bromothymol blue, and 0.5 g of thymol blue in 500 mL of absolute ethanol, and adding sodium hydroxide solution until the colour is yellow. The colour changes are: pH 2, red; pH 4, orange; pH 6, yellow; pH 8, green; pH 10, blue.

Another recipe for a universal indicator is as follows: 0.05 g of methyl orange, 0.15 g of methyl red, 0.3 g of bromothymol blue, and 0.35 g of phenolphthalein in 1 L of 66 per cent ethanol. The colour changes are: pH up to 3, red; pH 4, orange–red; pH 5, orange; pH 6, yellow; pH 7, yellowish–green; pH 8, greenish–blue; pH 9, blue; pH 10, violet; pH 11, reddish–violet. Several 'universal indicators' are available commercially as solutions and as test papers.

10.11 NEUTRALISATION CURVES

The mechanism of neutralisation processes can be understood by studying the changes in the hydrogen ion concentration during the course of the appropriate titration. The change in pH in the neighbourhood of the equivalence point is of the greatest importance, as it enables an indicator to be selected which will give the smallest titration error. The curve obtained by plotting pH as the ordinate against the percentage of acid neutralised (or the number of mL of alkali added) as abscissa is known as the neutralisation (or, more generally, the titration) curve. This may be evaluated experimentally by determination of the pH at various stages during the titration by a potentiometric method (Sections 15.15 and 15.20), or it may be calculated from theoretical principles.

10.12 NEUTRALISATION OF A STRONG ACID WITH A STRONG BASE

For this calculation it is assumed that both the acid and the base are completely dissociated and the activity coefficients of the ions are unity in order to obtain the pH values during the course of the neutralisation of the strong acid and the strong base, or vice versa, at the laboratory temperature. For simplicity of calculation consider the titration of 100 mL of $1M$ hydrochloric acid with $1M$ sodium hydroxide solution. The pH of $1M$ hydrochloric acid is 0. When 50 mL of the $1M$ base have been added, 50 mL of unneutralised $1M$ acid will be present in a total volume of 150 mL.

$[H^+]$ will therefore be $50 \times 1/150 = 3.33 \times 10^{-1}$, or pH $= 0.48$
For 75 mL of base, $[H^+] = 25 \times 1/175 = 1.43 \times 10^{-1}$, pH $= 0.84$
For 90 mL of base, $[H^+] = 10 \times 1/190 = 5.26 \times 10^{-2}$, pH $= 1.3$
For 98 mL of base, $[H^+] = 2 \times 1/198 = 1.01 \times 10^{-2}$, pH $= 2.0$
For 99 mL of base, $[H^+] = 1 \times 1/199 = 5.03 \times 10^{-3}$, pH $= 2.3$
For 99.9 mL of base, $[H^+] = 0.1 \times 1/199.9 = 5.00 \times 10^{-4}$, pH $= 3.3$

Upon the addition of 100 mL of base, the pH will change sharply to 7, i.e. the theoretical equivalence point. The resulting solution is simply one of sodium chloride. Any sodium hydroxide added beyond this will be in excess of that needed for neutralisation.

With 100.1 mL of base, $[OH^-] = 0.1/200.1 = 5.00 \times 10^{-4}$, pOH $= 3.3$ and pH $= 10.7$
With 101 mL of base, $[OH^-] = 1/201 = 5.00 \times 10^{-3}$, pOH $= 2.3$, and pH $= 11.7$

These results show that as the titration proceeds, initially the pH rises slowly, but between the addition of 99.9 and 100.1 mL of alkali, the pH of the solution

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rises from 3.3 to 10.7, i.e. in the vicinity of the equivalence point the rate of change of pH of the solution is very rapid.

The complete results, up to the addition of 200 mL of alkali, are collected in Table 10.3; this also includes the figures for 0.1 M and 0.01 M solutions of acid and base respectively. The additions of alkali have been extended in all three cases to 200 mL; it is evident that the range from 200 to 100 mL and beyond represents the reverse titration of 100 mL of alkali with the acid in the presence of the non-hydrolysed sodium chloride solution. The data in the table are presented graphically in Fig. 10.2.

Table 10.3 pH during titration of 100 mL of HCl with NaOH of equal concentration

NaOH added (mL)	1 M solution (pH)	0.1 M solution (pH)	0.01 M solution (pH)
0	0.0	1.0	2.0
50	0.5	1.5	2.5
75	0.8	1.8	2.8
90	1.3	2.3	3.3
98	2.0	3.0	4.0
99	2.3	3.3	4.3
99.5	2.6	3.6	4.6
99.8	3.0	4.0	5.0
99.9	3.3	4.3	5.3
100.0	7.0	7.0	7.0
100.1	10.7	9.7	8.7
100.2	11.0	10.0	9.0
100.5	11.4	10.4	9.4
101	11.7	10.7	9.7
102	12.0	11.0	10.0
110	12.7	11.7	10.7
125	13.0	12.0	11.0
150	13.3	12.3	11.3
200	13.5	12.5	11.5

In quantitative analysis it is the changes of pH near the equivalence point which are of special interest. This part of Fig. 10.2 is accordingly shown on a larger scale in Fig. 10.3, on which are also indicated the colour-change intervals of some of the common indicators.

With 1 M *solutions,* it is evident that any indicator with an effective range between pH 3 and 10.5 may be used. The colour change will be sharp and the titration error negligible.

With 0.1 M *solutions,* the ideal pH range for an indicator is limited to 4.5–9.5. Methyl orange will exist chiefly in the alkaline form when 99.8 mL of alkali have been added, and the titration error will be 0.2 per cent, which is negligibly small for most practical purposes; it is therefore advisable to add sodium hydroxide solution until the indicator is present completely in the alkaline form. The titration error is also negligibly small with phenolphthalein.

With 0.01 M solutions, the ideal pH range is still further limited to 5.5–8.5; such indicators as methyl red, bromothymol blue, or phenol red will be suitable. The titration error for methyl orange will be 1–2 per cent.

The above considerations apply to solutions which do not contain carbon dioxide. In practice, carbon dioxide is usually present (compare Section 10.7)
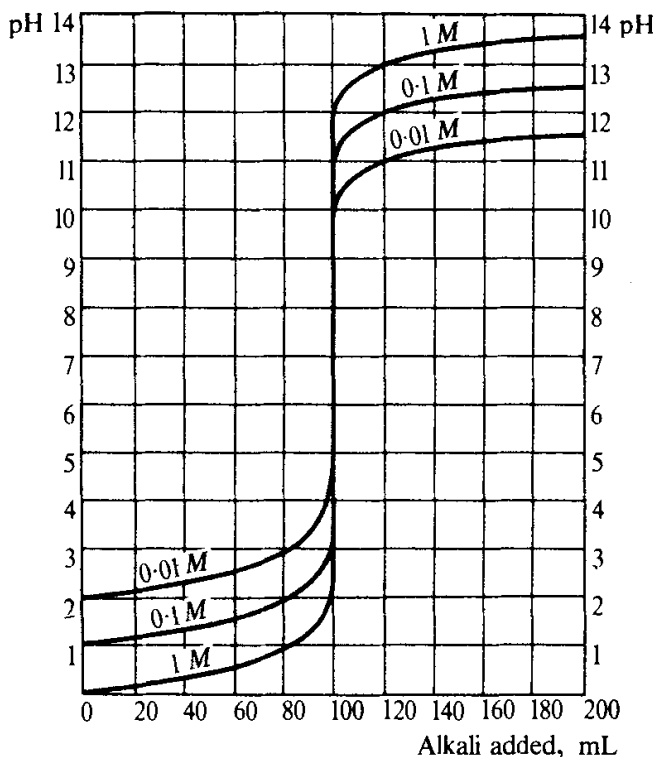
Fig. 10.2 Neutralisation curves of 100 mL of HCl with NaOH of same concentration (calculated).
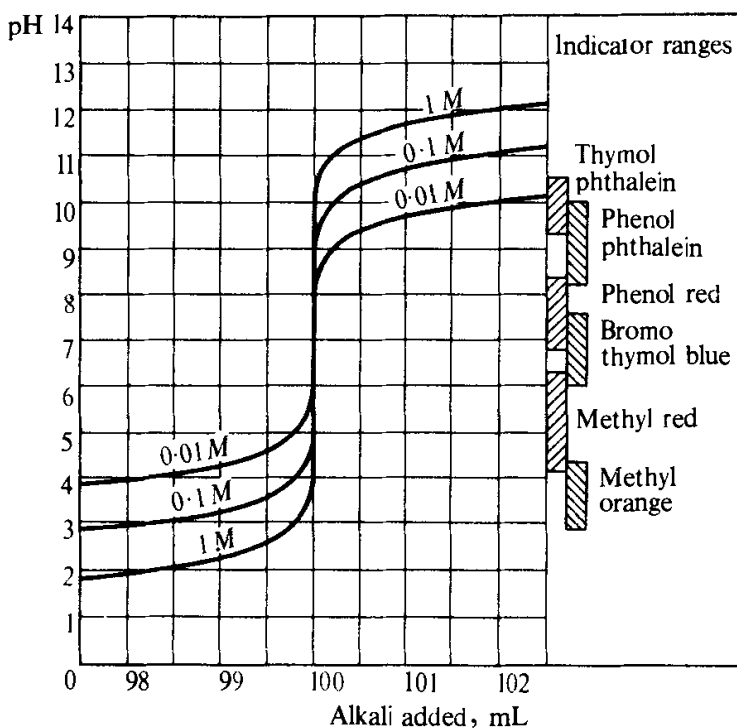

Fig. 10.3 Neutralisation curves of 100 mL of HCl with NaOH of same concentration in vicinity of equivalence point (calculated).

arising from the small quantity of carbonate in the sodium hydroxide and/or from the atmosphere. The gas is in equilibrium with carbonic acid, of which both stages of ionisation are weak. This will introduce a small error when

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indicators of high pH range (above pH 5) are used, e.g. phenolphthalein or thymolphthalein. More acid indicators, such as methyl orange and methyl yellow, are unaffected by carbonic acid. The difference between the amounts of sodium hydroxide solution used with methyl orange and phenolphthalein is not greater than 0.15–0.2 mL of 0.1 M sodium hydroxide when 100 mL of 0.1 M hydrochloric acid are titrated. A method of eliminating this error, other than that of selecting an indicator with a pH range below pH 5, is to boil the solution while still acid to expel carbon dioxide and then to continue the titration with the cold solution. Boiling the solution is particularly efficacious when titrating dilute (e.g. 0.01 M) solutions.

10.13 NEUTRALISATION OF A WEAK ACID WITH A STRONG BASE

The neutralisation of 100 mL of 0.1 M acetic acid (ethanoic acid) with 0.1 M sodium hydroxide solution will be considered here; other concentrations can be treated similarly. The pH of the solution at the equivalence point is given by (Section 2.19)

$$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a - \tfrac{1}{2}pc = 7 + 2.37 - \tfrac{1}{2}(1.3) = 8.72$$

For other concentrations, we may employ the approximate Mass Action expression:

$$[H^+] \times [CH_3COO^-]/[CH_3COOH] = K_a \tag{6}$$

$$\text{or} \quad [H^+] = [CH_3COOH] \times K_a/[CH_3COO^-]$$

$$\text{or} \quad pH = \log[Salt]/[Acid] + pK_a \tag{7}$$

The concentration of the salt (and of the acid) at any point is calculated from the volume of alkali added, due allowance being made for the total volume of the solution.

The initial pH of 0.1 M acetic acid is computed from equation (6); the dissociation of the acid is relatively so small that it may be neglected in expressing the concentration of acetic acid. Hence from equation (6):

$$[H^+] \times [CH_3COO^-]/[CH_3COOH] = 1.82 \times 10^{-5}$$

$$\text{or} \quad [H^+]^2/0.1 = 1.82 \times 10^{-5}$$

$$\text{or} \quad [H^+] = \sqrt{1.82 \times 10^{-6}} = 1.35 \times 10^{-3}$$

$$\text{or} \quad pH = 2.87$$

When 50 mL of 0.1 M alkali have been added,

$$[Salt] = 50 \times 0.1/150 = 3.33 \times 10^{-2}$$

$$\text{and} \quad [Acid] = 50 \times 0.1/150 = 3.33 \times 10^{-2}$$

$$pH = \log(3.33 \times 10^{-2}/3.33 \times 10^{-2}) + 4.74 = 4.74$$

The pH values at other points on the titration curve are similarly calculated. After the equivalence point has been passed, the solution contains excess of OH⁻ ions which will repress the hydrolysis of the salt; the pH may be assumed, with sufficient accuracy for our purpose, to be that due to the excess of base present, so that in this region the titration curve will almost coincide with that

for 0.1M hydrochloric acid (Fig. 10.2 and Table 10.3). All the results are collected in Table 10.4, and are depicted graphically in Fig. 10.4. The results for the titration of 100 mL of 0.1M solution of a weaker acid ($K_a = 1 \times 10^{-7}$) with 0.1M sodium hydroxide at the laboratory temperature are also included.
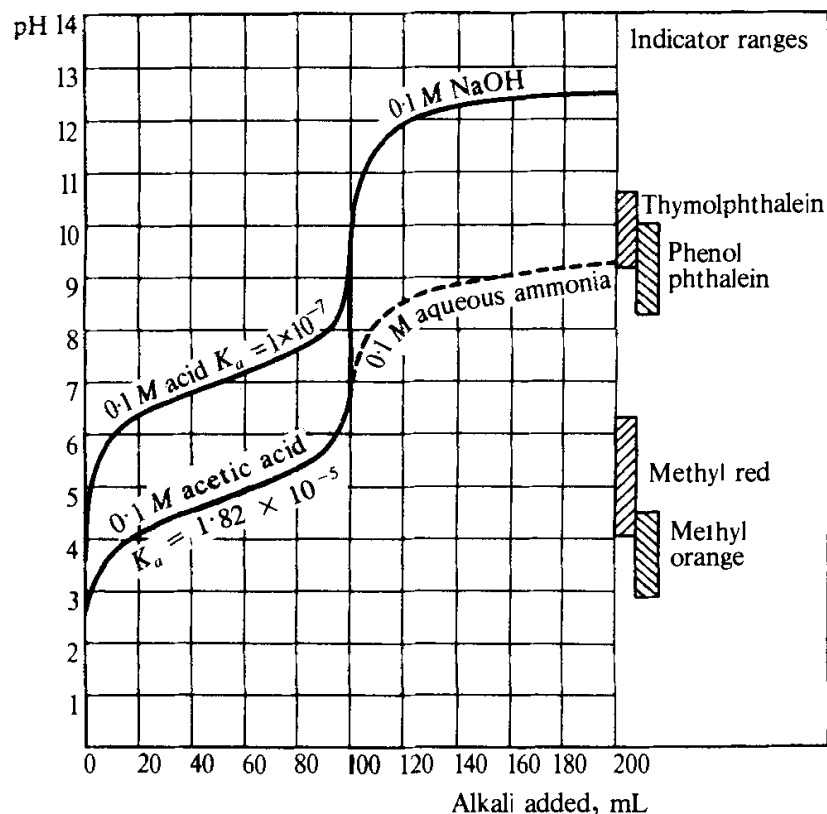
Table 10.4 Neutralisation of 100 mL of 0.1M acetic acid ($K_a = 1.82 \times 10^{-5}$) and of 100 mL of 0.1$M$ HA ($K_a = 1 \times 10^{-7}$) with 0.1M sodium hydroxide

Vol. of 0.1M NaOH used (mL)	0.1M acetic acid (pH)	0.1M HA ($K_a = 1 \times 10^{-7}$) (pH)
0	2.9	4.0
10	3.8	6.0
25	4.3	6.5
50	4.7	7.0
90	5.7	8.0
99.0	6.7	9.0
99.5	7.0	9.3
99.8	7.4	9.7
99.9	7.7	9.8
100.0	8.7	9.9
100.2	10.0	10.0
100.5	10.4	10.4
101	10.7	10.7
110	11.7	11.7
125	12.0	12.0
150	12.3	12.3
200	12.5	12.5

Fig. 10.4 Neutralisation curves of 100 mL of 0.1M acetic acid ($K_a = 1.82 \times 10^{-5}$) and of 0.1$M$ acid ($K_a = 1 \times 10^{-7}$) with 0.1M sodium hydroxide (calculated).

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For $0.1M$ acetic acid and $0.1M$ sodium hydroxide, it is evident from the titration curve that neither methyl orange nor methyl red can be used as indicators. The equivalence point is at pH 8.7, and it is necessary to use an indicator with a pH range on the slightly alkaline side, such as phenolphthalein, thymolphthalein, or thymol blue (pH range, as base, 8.0–9.6). For the acid with $K_a = 10^{-7}$, the equivalence point is at pH $= 10$, but here the rate of change of pH in the neighbourhood of the stoichiometric point is very much less pronounced, owing to considerable hydrolysis. Phenolphthalein will commence to change colour after about 92 mL of alkali have been added, and this change will occur to the equivalence point; thus the end point will not be sharp and the titration error will be appreciable. With thymolphthalein, however, the colour change covers the pH range 9.3–10.5; this indicator may be used, the end point will be sharper than for phenolphthalein, but nevertheless somewhat gradual, and the titration error will be about 0.2 per cent. Acids that have dissociation constants less than 10^{-7} cannot be satisfactorily titrated in $0.1M$ solution with a simple indicator.

In general, it may be stated that weak acids $(K_a > 5 \times 10^{-6})$ should be titrated with phenolphthalein, thymolphthalein, or thymol blue as indicators.

10.14 NEUTRALISATION OF A WEAK BASE WITH A STRONG ACID

This may be illustrated by the titration of 100 mL of $0.1M$ aqueous ammonia $(K_b = 1.85 \times 10^{-5})$ with $0.1M$ hydrochloric acid at the ordinary laboratory temperature. The pH of the solution at the equivalence point is given by the equation (Section 2.19):

$$pH = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_b + \tfrac{1}{2}pc = 7 - 2.37 + \tfrac{1}{2}(1.3) = 5.28$$

For other concentrations, the pH may be calculated with sufficient accuracy as follows (compare previous section):

$$[NH_4^+] \times [OH^-]/[NH_3] = K_b \tag{8}$$

$$\text{or} \quad [OH^-] = [NH_3] \times K_b/[NH_4^+] \tag{9}$$

$$\text{or} \quad pOH = \log[Salt]/[Base] + pK_b \tag{10}$$

$$\text{or} \quad pH = pK_w - pK_b - \log[Salt]/[Base] \tag{11}$$

After the equivalence point has been reached, the solution contains excess of H^+ ions, hydrolysis of the salt is suppressed, and the subsequent pH changes may be assumed, with sufficient accuracy, to be those due to the excess of acid present.

The results computed in the above manner are represented graphically in Fig. 10.5; the results for the titration of 100 mL of a $0.1M$ solution of a weaker base $(K_b = 1 \times 10^{-7})$ are also included.

It is clear that neither thymolphthalein nor phenolphthalein can be employed in the titration of $0.1M$ aqueous ammonia. The equivalence point is at pH 5.3, and it is necessary to use an indicator with a pH range on the slightly acid side (3–6.5), such as methyl orange, methyl red, bromophenol blue, or bromocresol green. The last-named indicators may be utilised for the titration of all weak bases $(K_b > 5 \times 10^{-6})$ with strong acids.
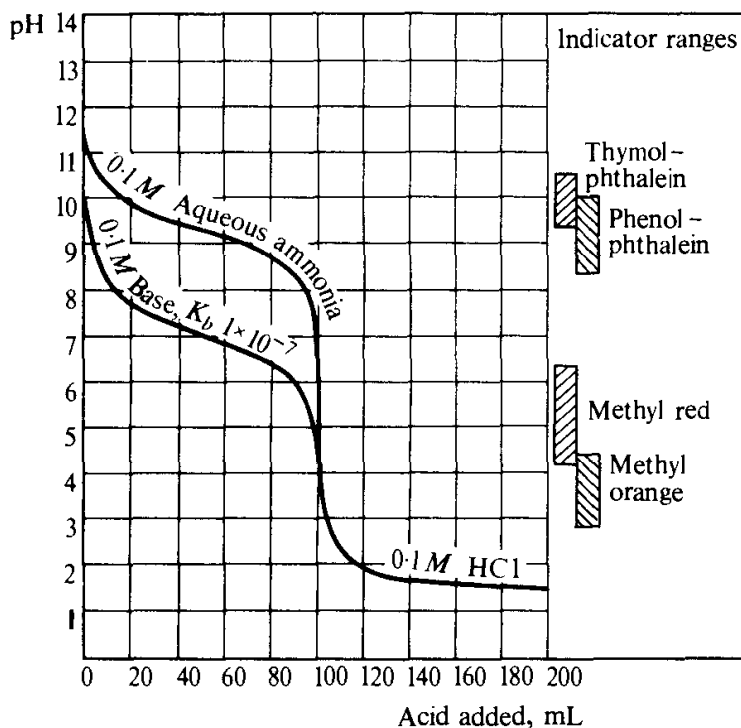
Fig. 10.5 Neutralisation curves of 100 mL 0.1M aqueous ammonia ($K_a = 1.8 \times 10^{-5}$) and of 0.1M base ($K_a = 1 \times 10^{-7}$) with 0.1M hydrochloric acid.

For the weak base ($K_b = 1 \times 10^{-7}$), bromophenol blue or methyl orange may be used; no sharp colour change will be obtained with bromocresol green or with methyl red, and the titration error will be considerable.

10.15 NEUTRALISATION OF A WEAK ACID WITH A WEAK BASE

This case is exemplified by the titration of 100 mL of 0.1M acetic acid ($K_a = 1.82 \times 10^{-5}$) with 0.1$M$ aqueous ammonia ($K_b = 1.8 \times 10^{-5}$). The pH at the equivalence point is given by (Section 2.19)

$$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a - \tfrac{1}{2}pK_b = 7.0 + 2.38 - 2.37 = 7.1$$

The neutralisation curve up to the equivalence point is almost identical with that using 0.1M sodium hydroxide as the base; beyond this point the titration is virtually the addition of 0.1M aqueous ammonia solution to 0.1M ammonium acetate solution and equation (11) (Section 10.14) is applicable to the calculation of the pH. The titration curve for the neutralisation of 100 mL of 0.1M acetic acid with 0.1M aqueous ammonia at the laboratory temperature is shown by the broken line in Fig. 10.4. The chief feature of the curve is that the change of pH near the equivalence point and, indeed, during the whole of the neutralisation curve is very gradual. There is no sudden change in pH, and hence no sharp end point can be found with any simple indicator. A mixed indicator, which exhibits a sharp colour change over a very limited pH range, may sometimes be found which is suitable. Thus for acetic acid–ammonia solution titrations, neutral red–methylene blue mixed indicator may be used (see Section 10.9), but on the whole, it is best to avoid the use of indicators in titrations involving *both* a weak acid and a weak base.

10.16 NEUTRALISATION OF A POLYPROTIC ACID WITH A STRONG BASE

The shape of the titration curve will depend upon the relative magnitudes of the various dissociation constants. It is assumed that titrations take place at the ordinary laboratory temperature in solutions of concentration of $0.1 M$ or stronger. For a diprotic acid, if the difference between the primary and secondary dissociation constants is very large ($K_1/K_2 > 10\,000$), the solution behaves like a mixture of two acids with constants K_1 and K_2 respectively; the considerations given previously may be applied. Thus for sulphurous acid, $K_1 = 1.7 \times 10^{-2}$ and $K_2 = 1.0 \times 10^{-7}$, it is evident that there will be a sharp change of pH near the first equivalence point, but for the second stage the change will be less pronounced, yet just sufficient for the use of, say, thymolphthalein as indicator (see Fig. 10.4). For carbonic acid, however, for which $K_1 = 4.3 \times 10^{-7}$ and $K_2 = 5.6 \times 10^{-11}$, only the first stage will be just discernible in the neutralisation curve (see Fig. 10.4); the second stage is far too weak to exhibit any point of inflexion and there is no suitable indicator available for direct titration. As indicator for the primary stage, thymol blue may be used (see Section 10.13), although a mixed indicator of thymol blue (3 parts) and cresol red (1 part) (see Section 10.9) is more satisfactory; with phenolphthalein the colour change will be somewhat gradual and the titration error may be several per cent.

It can be shown that the pH at the first equivalence point for a diprotic acid is given by

$$[H^+] = \sqrt{\frac{K_1 K_2 c}{K_1 + c}}$$

Provided that the first stage of the acid is weak and that K_1 can be neglected by comparison with c, the concentration of salt present, this expression reduces to

$$[H^+] = \sqrt{K_1 K_2}, \text{ or pH} = \tfrac{1}{2}pK_1 + \tfrac{1}{2}pK_2.$$

With a knowledge of the pH at the stoichiometric point and also of the course of the neutralisation curve, it should be an easy matter to select the appropriate indicator for the titration of any diprotic acid for which K_1/K_2 is at least 10^4. For many diprotic acids, however, the two dissociation constants are too close together and it is not possible to differentiate between the two stages. If K_2 is not less than about 10^{-7}, all the replaceable hydrogen may be titrated, e.g. sulphuric acid (primary stage — a strong acid), oxalic acid, malonic, succinic, and tartaric acids.

Similar remarks apply to triprotic acids. These may be illustrated by reference to phosphoric(V) acid (orthophosphoric acid), for which $K_1 = 7.5 \times 10^{-3}$, $K_2 = 6.2 \times 10^{-8}$, and $K_3 = 5 \times 10^{-13}$. Here $K_1/K_2 = 1.2 \times 10^5$ and $K_2/K_3 = 1.2 \times 10^5$, so that the acid will behave as a mixture of three monoprotic acids with the dissociation constants given above. Neutralisation proceeds almost completely to the end of the primary stage before the secondary stage is appreciably affected, and the secondary stage proceeds almost to completion before the tertiary stage is apparent. The pH at the first equivalence point is given approximately by $(\tfrac{1}{2}pK_1 + \tfrac{1}{2}pK_2) = 4.6$, and at the second equivalence point by $(\tfrac{1}{2}pK_2 + \tfrac{1}{2}pK_3) = 9.7$; in the very weak third stage, the curve is very flat and no indicator is available for direct titration. The third equivalence point

may be calculated approximately from the equation (Section 10.13):

$$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a - \tfrac{1}{2}pc = 7.0 + 6.15 - \tfrac{1}{2}(1.6) = 12.35 \text{ for } 0.1M \text{ } H_3PO_4.$$

For the primary stage (phosphoric(V) acid as a monoprotic acid), methyl orange, bromocresol green, or Congo red may be used as indicators. The secondary stage of phosphoric(V) acid is very weak (see acid $K_a = 1 \times 10^{-7}$ in Fig. 10.4) and the only suitable simple indicator is thymolphthalein (see Section 10.14); with phenolphthalein the error may be several per cent. A mixed indicator composed of phenolphthalein (3 parts) and 1-naphtholphthalein (1 part) is very satisfactory for the determination of the end point of phosphoric(V) acid as a diprotic acid (see Section 10.9). The experimental neutralisation curve of 50 mL of $0.1M$ phosphoric(V) acid with $0.1M$ potassium hydroxide, determined by potentiometric titration, is shown in Fig. 10.6.
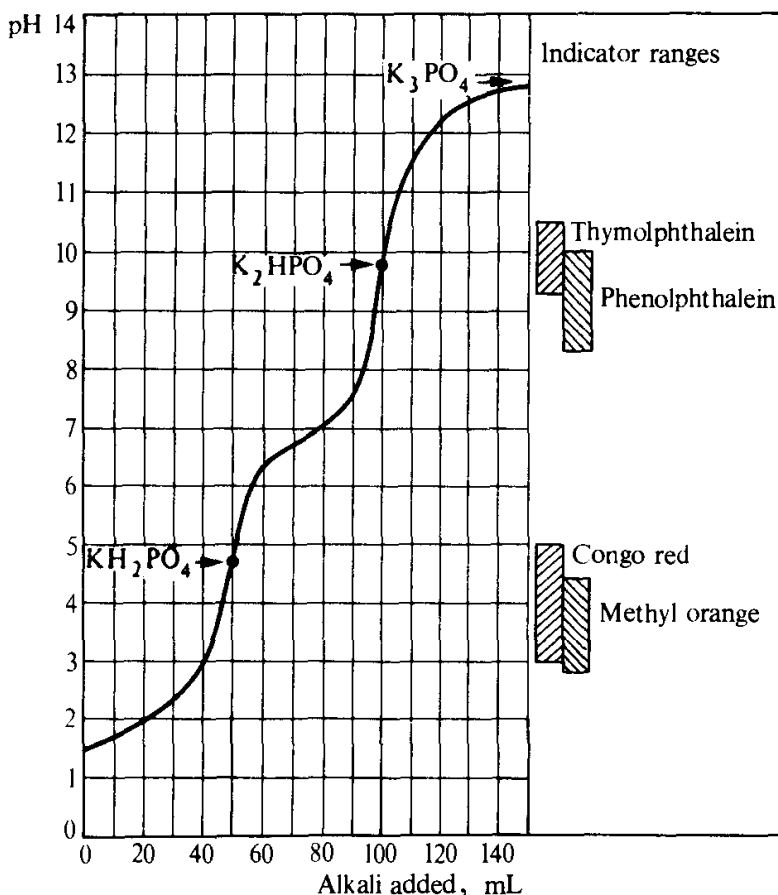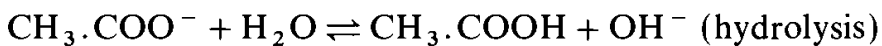

Fig. 10.6 Titration of 50 mL of $0.1M$ H_3PO_4 with $0.1M$ KOH.

There are a number of triprotic acids, e.g. citric acid with $K_1 = 9.2 \times 10^{-4}$, $K_2 = 2.7 \times 10^{-5}$, $K_3 = 1.3 \times 10^{-6}$, the three dissociation constants of which are too close together for the three stages to be differentiated easily. If $K_3 > ca$ 10^{-7}, all the replaceable hydrogen may be titrated; the indicator will be determined by the value of K_3.
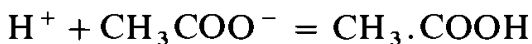
10.17 TITRATION OF ANIONS OF WEAK ACIDS WITH STRONG ACIDS: 'DISPLACEMENT TITRATIONS'

So far the titrations considered have involved a strong base, the hydroxide ion,

but titrations are also possible with weaker bases, such as the carbonate ion, the borate ion, the acetate ion, etc. Formerly titrations involving these ions were regarded as titrations of solutions of hydrolysed salts, and the net result was that the weak acid was displaced by the stronger acid. Thus in the titration of sodium acetate solution with hydrochloric acid the following equilibria were considered:

$$CH_3.COO^- + H_2O \rightleftharpoons CH_3.COOH + OH^- \text{ (hydrolysis)}$$

$H^+ + OH^- = H_2O$ (strong acid reacts with OH^- produced by hydrolysis).

The net result thus appeared to be:

$$H^+ + CH_3COO^- = CH_3.COOH$$

$$\text{or} \quad CH_3.COONa + HCl = CH_3.COOH + NaCl$$

i.e. the weak acetic acid was apparently displaced by the strong hydrochloric acid, and the process was referred to as a **displacement titration**. According to the Brønsted–Lowry theory the so-called titration of solutions of hydrolysed salts is merely the titration of a weak base with a strong (highly ionised) acid. When the anion of a weak acid is titrated with a strong acid the titration curve is identical with that observed in the reverse titration of a weak acid itself with a strong base (compare Section 10.13).

A few examples encountered in practice include the following.

Titration of borate ion with a strong acid. The titration of the tetraborate ion with hydrochloric acid is similar to that described above. The net result of the displacement titration is given by:

$$B_4O_7^{2-} + 2H^+ + 5H_2O = 4H_3BO_3$$
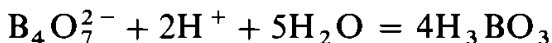
Boric acid behaves as a weak monoprotic acid with a dissociation constant of 6.4×10^{-10}. The pH at the equivalence point in the titration of $0.2M$ sodium tetraborate with $0.2M$ hydrochloric acid is that due to $0.1M$ boric acid, i.e. 5.6. Further addition of hydrochloric acid will cause a sharp decrease of pH and any indicator covering the pH range 3.7–5.1 (and slightly beyond this) may be used; suitable indicators are bromocresol green, methyl orange, bromophenol blue, and methyl red.

Titration of carbonate ion with a strong acid. A solution of sodium carbonate may be titrated to the hydrogencarbonate stage (i.e. with one mole of hydrogen ions), when the net reaction is:

$$CO_3^{2-} + H^+ = HCO_3^-$$
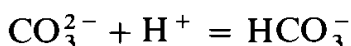
The equivalence point for the primary stage of ionisation of carbonic acid is at $pH = (\frac{1}{2}pK_1 + \frac{1}{2}pK_2) = 8.3$, and we have seen (Section 10.14) that thymol blue and, less satisfactorily, phenolphthalein, or a mixed indicator (Section 10.9) may be employed to detect the end point.

Sodium carbonate solution may also be titrated until all the carbonic acid is displaced. The net reaction is then:

$$CO_3^{2-} + 2H^+ = H_2CO_3$$
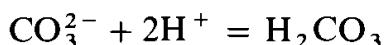
The same end point is reached by titrating sodium hydrogencarbonate solution with hydrochloric acid:

$$HCO_3^- + H^+ = H_2CO_3$$
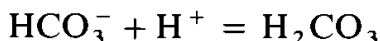
The end point with 100 mL of $0.2M$ sodium hydrogencarbonate and $0.2M$ hydrochloric acid may be deduced as follows from the known dissociation constant and concentration of the weak acid. The end point will obviously occur when 100 mL of hydrochloric acid has been added, i.e. the solution now has a total volume of 200 mL. Consequently since the carbonic acid liberated from the sodium hydrogencarbonate (0.02 moles) is now contained in a volume of 200 mL, its concentration is $0.1M$. K_1 for carbonic acid has a value of 4.3×10^{-7}, and hence we can say:

$$[H^+] \times [HCO_3^-]/[H_2CO_3] = K_1 = 4.3 \times 10^{-7} \, mol \, L^{-1}$$

and since

$$[H^+] = [HCO_3^-]$$

$$[H^+] = \sqrt{4.3 \times 10^{-7} \times 0.1} = 2.07 \times 10^{-4}$$

The pH at the equivalence point is thus approximately 3.7; the secondary ionisation and the loss of carbonic acid, due to any escape of carbon dioxide, have been neglected. Suitable indicators are therefore methyl yellow, methyl orange, Congo red, and bromophenol blue. The experimental titration curve, determined with the hydrogen electrode, for 100 mL of $0.1M$ sodium carbonate and $0.1M$ hydrochloric acid is shown in Fig. 10.7.
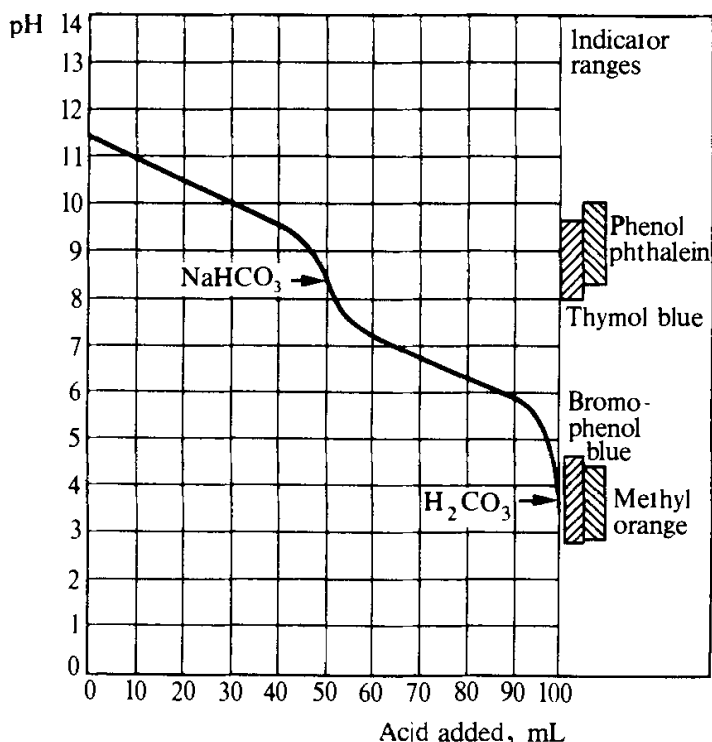

Fig. 10.7 Titration of 100 mL of $0.1M$ Na$_2$CO$_3$ with $0.1M$ HCl.

Cations of weak bases (i.e. Brønsted acids such as the phenylammonium ion $C_6H_5NH_3^+$) may be titrated with strong bases, and the treatment is similar. These were formerly regarded as salts of weak bases (e.g. aniline (phenylamine), $K_b = 4.0 \times 10^{-10}$) and strong acids: an example is aniline hydrochloride (phenylammonium chloride).

10.18   CHOICE OF INDICATORS IN NEUTRALISATION REACTIONS

As a general rule, for a titration to be feasible there should be a change of approximately two units of pH at or near the stoichiometric point produced by the addition of a small volume of the reagent. The pH at the equivalence point may be calculated by using the equations given in Section 2.19 (see also below), the pH at either side of the equivalence point (0.1–1 mL) may be calculated as described in the preceding sections, and the difference will indicate whether the change is large enough to permit a sharp end point to be observed. Alternatively, the pH change on both sides of the equivalence point may be obtained from the neutralisation curve determined by potentiometric titration (Sections 15.15 and 15.20). If the pH change is satisfactory, an indicator should be selected that changes at or near the equivalence point.

For convenience of reference, the conclusions already deduced from theoretical principles are summarised below.

Strong acid and strong base. For $0.1 M$ or more concentrated solutions, any indicator may be used which has a range between the limits pH 4.5 and pH 9.5. With $0.01 M$ solutions, the pH range is somewhat smaller (5.5–8.5). If carbon dioxide is present, either the solution should be boiled while still acid and the solution titrated when cold, or an indicator with a range below pH 5 should be employed.

Weak acid and a strong base. The pH at the equivalence point is calculated from the equation:

$$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a - \tfrac{1}{2}pc$$

The pH range for acids with $K_a > 10^{-5}$ is 7–10.5; for weaker acids ($K_a > 10^{-6}$) the range is reduced (8–10). The pH range 8–10.5 will cover most of the examples likely to be encountered; this permits the use of thymol blue, thymolphthalein, or phenolphthalein.

Weak base and strong acid. The pH at the equivalence point is computed from the equation:

$$pH = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_b + \tfrac{1}{2}pc$$

The pH range for bases with $K_b > 10^{-5}$ is 3–7, and for weaker bases ($K_b > 10^{-6}$) 3–5. Suitable indicators will be methyl red, methyl orange, methyl yellow, bromocresol green, and bromophenol blue.

Weak acid and weak base. There is no sharp rise in the neutralisation curve and, generally, no simple indicator can be used. The titration should therefore be avoided, if possible. The approximate pH at the equivalence point can be computed from the equation:

$$pH = \tfrac{1}{2}pK_w + \tfrac{1}{2}pK_a - \tfrac{1}{2}pK_b$$

It is sometimes possible to employ a mixed indicator (see Section 10.9) which exhibits a colour change over a very limited pH range, for example, neutral red–methylene blue for dilute ammonia solution and acetic (ethanoic) acid.

Polyprotic acids (or mixtures of acids, with dissociation constants K_1, K_2, and K_3) and strong bases. The first stoichiometric end point is given approximately

by:

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

The second stoichiometric end point is given approximately by:

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

Anion of a weak acid titrated with a strong acid. The pH at the equivalence point is given by:

$$pH = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_a - \tfrac{1}{2}pc$$

Cation of a weak base titrated with a strong base. The pH at the stoichiometric end point is given by:

$$pH = \tfrac{1}{2}pK_w - \tfrac{1}{2}pK_b - \tfrac{1}{2}pc$$

As a general rule, wherever an indicator does not give a sharp end point, it is advisable to prepare an equal volume of a comparison solution containing the same quantity of indicator and of the final products and other components of the titration as in the solution under test, and to titrate to the colour shade thus obtained.

In cases where it proves impossible to find a suitable indicator (and this will occur when dealing with strongly coloured solutions) then titration may be possible by an electrometric method such as conductimetric, potentiometric or amperometric titration; see Chapters 13–16. In some instances, spectrophotometric titration (Chapter 17) may be feasible. It should also be noted that if it is possible to work in a non-aqueous solution rather than in water, then acidic and basic properties may be altered according to the solvent chosen, and titrations which are difficult in aqueous solution may then become easy to perform. This procedure is widely used for the analysis of organic materials but is of very limited application with inorganic substances and is discussed in Sections 10.19–10.21.

10.19 TITRATIONS IN NON-AQUEOUS SOLVENTS

The Brønsted–Lowry theory of acids and bases referred to in Section 10.7 can be applied equally well to reactions occurring during acid–base titrations in non-aqueous solvents. This is because their approach considers an acid as any substance which will tend to donate a proton, and a base as a substance which will accept a proton. Substances which give poor end points due to being weak acids or bases in aqueous solution will frequently give far more satisfactory end points when titrations are carried out in non-aqueous media. An additional advantage is that many substances which are insoluble in water are sufficiently soluble in organic solvents to permit their titration in these non-aqueous media.

In the Brønsted–Lowry theory, any acid (HB) is considered to dissociate in solution to give a proton (H^+) and a conjugate base (B^-); whilst any base (B) will combine with a proton to produce a conjugate acid (HB^+).

$$HB \rightleftharpoons H^+ + B^- \qquad\qquad (a)$$

$$B + H^+ \rightleftharpoons HB^+ \qquad\qquad (b)$$

The ability of substances to act as acids or bases will depend very much upon