Chemistry

For the IB Diploma

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Chapter 19

Proton transfer reactions

Brønsted–Lowry

Acids and bases

An acid is a proton (H^+) donor

A base/alkali is a proton (H^+) acceptor

Johannes Nicolaus Brønsted (1879-1947)

Thomas Martin Lowry (1874-1936)

Figure 19.1: Photographs of Brønsted and Lowry.

Conjugate acid–base pairs

Conjugate acid–base pair: two species that differ by one proton (H^+); when an acid donates a proton, it forms the conjugate base (CH_3COO^- is the conjugate base of CH_3COOH); when a base gains a proton, it forms the conjugate acid (H_3O^+ is the conjugate acid of H_2O).

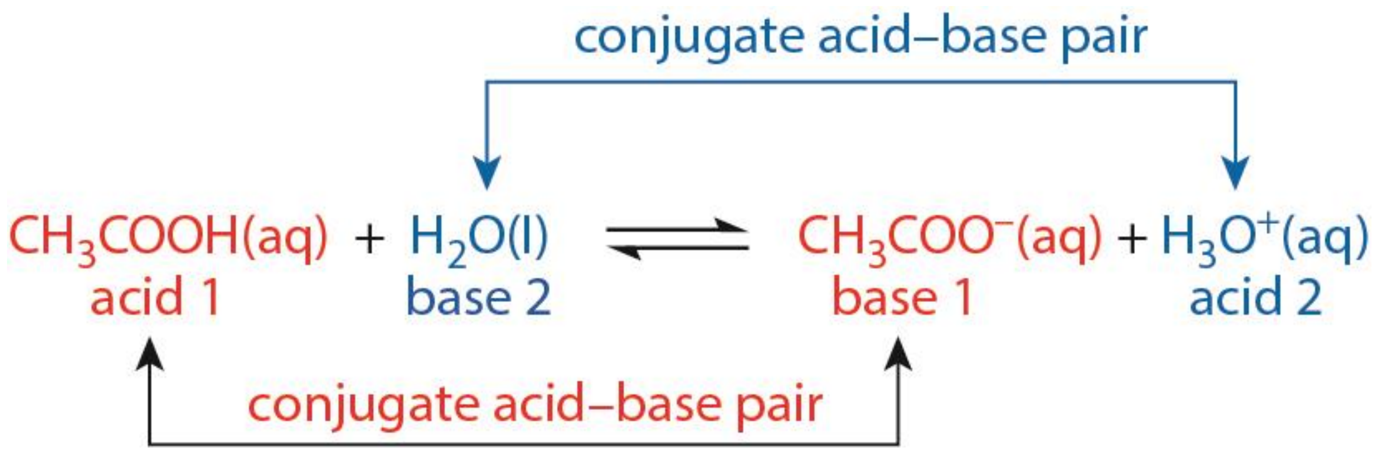


Figure 19.2: Conjugate acid–base pairs.

Measuring pH

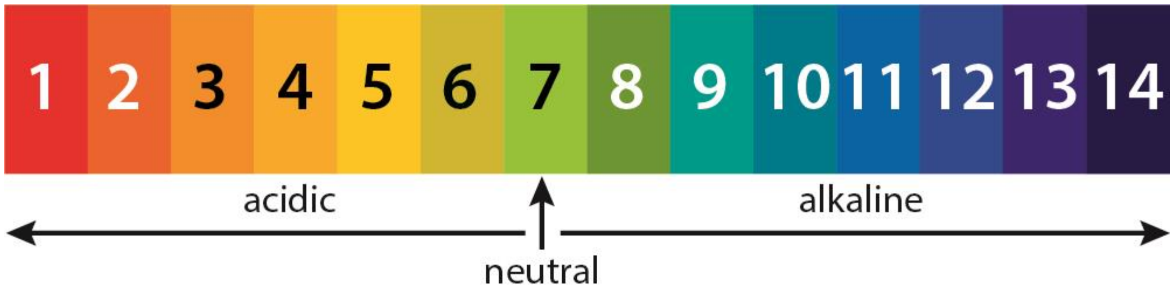


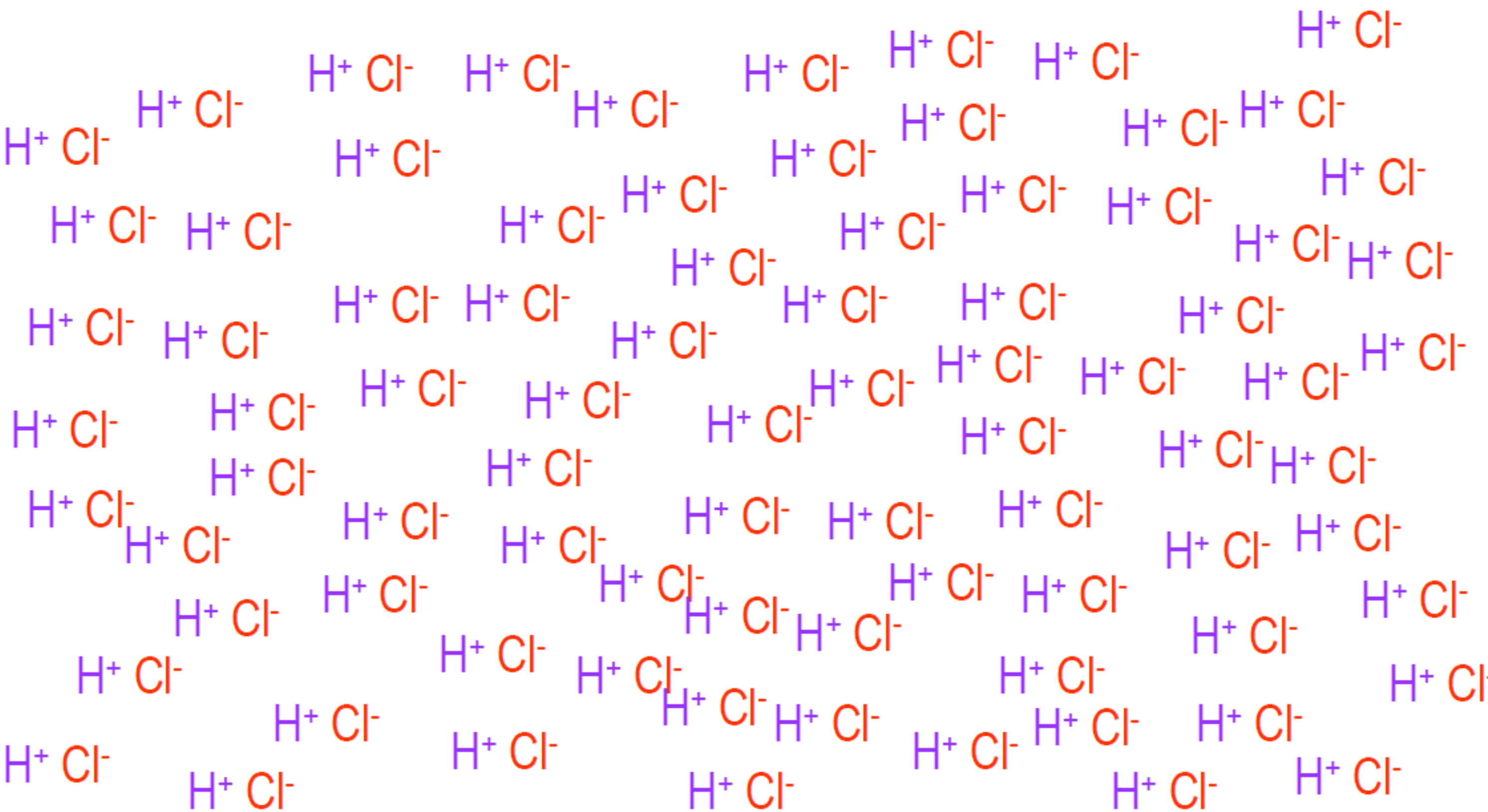
Figure 19.3: The pH scale showing the colours of universal indicator.

Calculating pH using pH = $-\log_{10}$ [H^+(aq)]

1 A solution containing 0.01 mol dm^{-3} H^+ (aq)	
2 A solution containing 1×10^{-13} mol dm^{-3} H^+(aq)	
3 A solution of 1 mol dm^{-3} HCl (aq)	
4 A solution of 0.0002 mol dm^{-3} HNO_3(aq)	

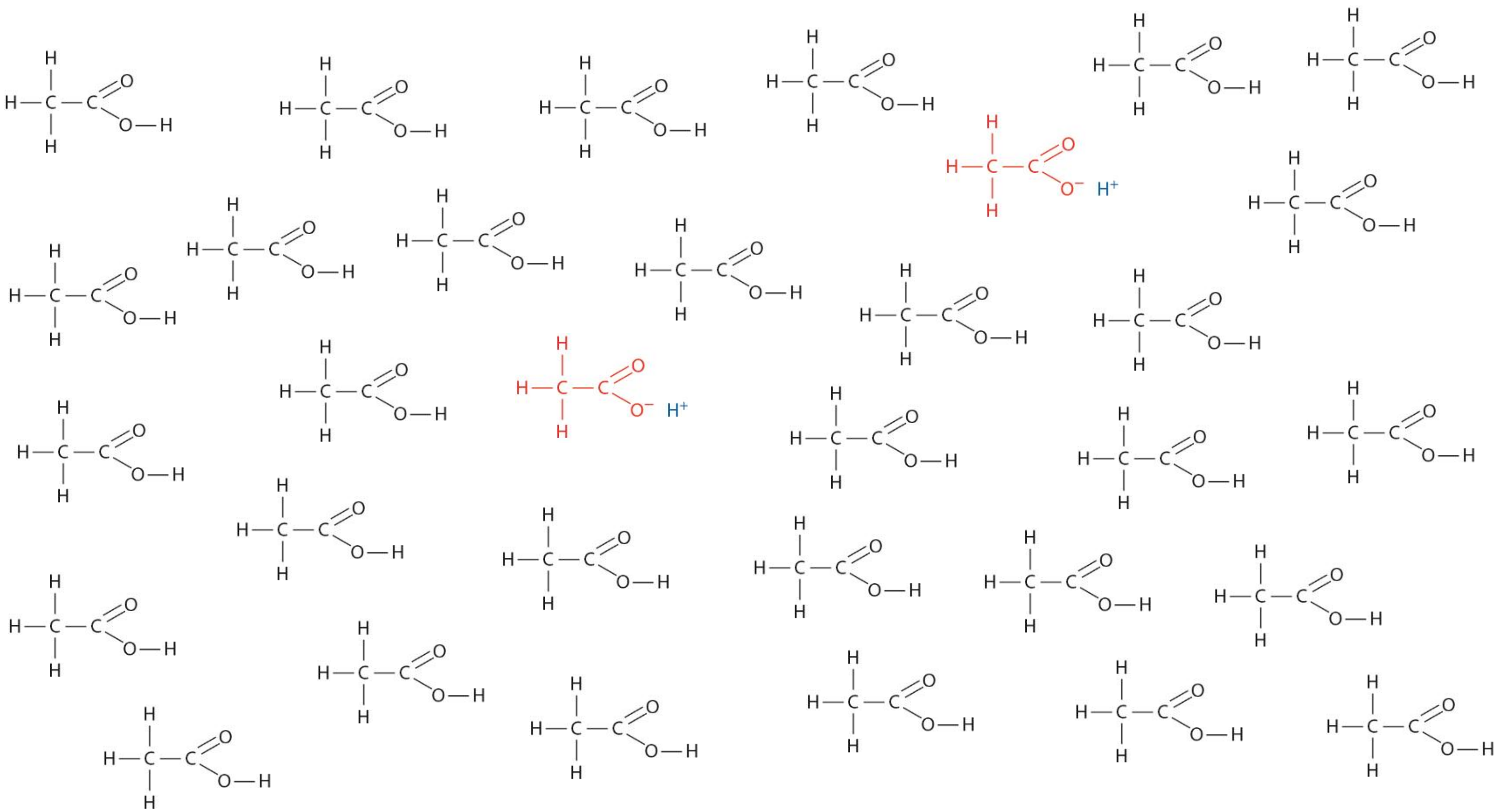
Strong acid

an acid, such as HCl, HNO_3, that dissociates completely in aqueous solution.



Weak acid

an acid, such as a carboxylic acid (ethanoic acid, propanoic acid, etc.) or carbonic acid (H_2CO_3), that dissociates only partially in aqueous solution.



The dissociation of acids in aqueous solution

$HA(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + A^-(aq)$

It can be simplified to $HA(aq) \rightleftharpoons H^+(aq) + A^-(aq)$

Ionisation

Strong base: a base that ionises completely in aqueous solution; strong bases are the Group 1 hydroxides (LiOH, NaOH, etc.) and $Ba(OH)_2$.

LiOH

NaOH

$Ba(OH)_2$

KOH

RbOH

$$Ba(OH)_2\,(aq) \rightarrow Ba^{2+}(aq) + 2OH^-(aq)$$

CsOH

Weak base: a base that ionises only partially in aqueous solution, e.g., ammonia and amines.

ammonia (NH_3)

ethylamine($CH_3CH_2NH_2$)

$$NH_3(aq) + H_2O\,(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$

The dissociation (ionisation) of water

$H_2O\,(l) \rightleftharpoons H^+\,(aq) + OH^-\,(aq)$

$K_w = [H^+(aq)]\,[OH^-(aq)] = 1.0 \times 10^{-14}$ at 25°C

Complete the table to interconvert $[H^+]$, $[OH^-]$ and pH:

$[H^+(aq)]$ / mol dm^{-3}	$[OH^-(aq)]$ / mol dm^{-3}	pH	Acidic, neutral or alkaline?
1.00×10^{-10}			
	1.00×10^{-8}		
		3.00	
1.32		–0.121	Acidic
	5.03×10^{-3}		
		2.18	

Neutrality

Because the value of K_w varies with temperature, the definition of neutrality must now be taken as

$[H^+(aq)] = [OH^-(aq)]$

and not pH = 7 for this is only true at 25 °C.

Recognition of acidic and basic solutions by the relative concentrations of H^+ and OH^-

- If $[H^+(aq)] > [OH^-(aq)]$, the solution is **acidic**
- If $[OH^-(aq)] > [H^+(aq)]$, the solution is **alkaline**

Strong acid

strong alkali titration curve

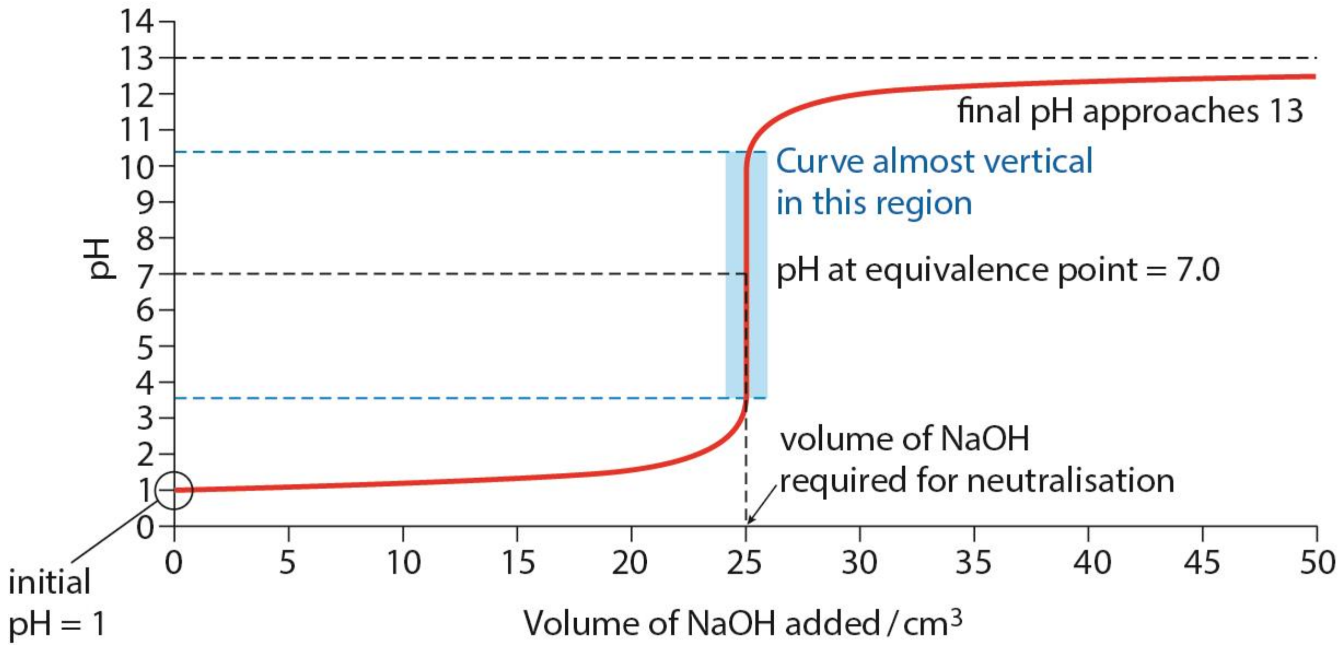


Figure 19.4: Strong acid–strong alkali titration curve.

Equivalence point, in a titration, is the point at which equivalent numbers of moles of acid and alkali have been added.

Acid dissociation constant

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

Calculate the acid dissociation constant for the following acids, assuming $[HA]_{initial} = [HA]_{equilibrium}$:

Acid	**Concentration / mol dm^{-3}**	**$[H^+]_{eqm}$ / mol dm^{-3}**	**K_a**
CH_3COOH	0.100	1.32×10^{-3}	
HCN	1.00	2.21×10^{-5}	
HCO_2H	0.0100	1.33×10^{-3}	
HF	0.200	9.97×10^{-3}	
$HClO_2$	0.0200	1.41×10^{-2}	

Base ionisation constant

$B(aq) + H_2O(l) \rightleftharpoons BH^+(aq) + OH^-(aq)$

$$K_b = \frac{[BH^+(aq)][OH^-(aq)]}{[B(aq)]}$$

Calculate the base ionisation constant for the following bases, assuming $[B]_{\text{initial}} = [B]_{\text{equilibrium}}$

Base	Concentration / mol dm^{-3}	$[OH^-]$ / mol dm^{-3}	K_b
CH_3NH_2	0.0100	0.0021	
NH_3	1.00	4.24×10^{-3}	
$C_2H_5NH_2$	0.0500	5.18×10^{-3}	
$(CH_3)_2NH$	0.0100	2.29×10^{-3}	

The larger the value of K_b, the stronger the base.

The relationship between K_a, K_b and K_w

$HA\,(aq) \rightleftharpoons A^-(aq) + H^+(aq)$

$A^-(aq) + H_2O\,(l) \rightleftharpoons AH\,(aq) + OH^-(aq)$

1 What is the relationship between HA and A^-?

2 Write expressions for K_a for the first equilibrium and K_b for the second equilibrium.

3 Find the product K_aK_b.

The stronger the acid, the weaker its conjugate base

$K_a \times K_b = K_w$ $\quad$ $pK_a + pK_b = pK_w$

Complete the following table:

Acid	K_a / $mol dm^{-3}$	pK_a	Conjugate base	pK_b
C_6H_5COOH		4.20		
	1.35×10^{-5}		$CH_3CH_2COO^-$	
			CN^-	4.69
			CH_3NH_2	3.34

Predict whether the pH of the following solutions will be =7, <7, >7

1. 0.1 mol dm^{-3} $CH_3COO^- Na^+$
2. 0.1 mol dm^{-3} Na_2CO_3
3. 0.1 mol dm^{-3} $CH_3CH_2NH_3^+Cl^-$ (ethylammonium chloride)
4. 0.1 mol dm^{-3} KNO_3

Acid–base titration curves

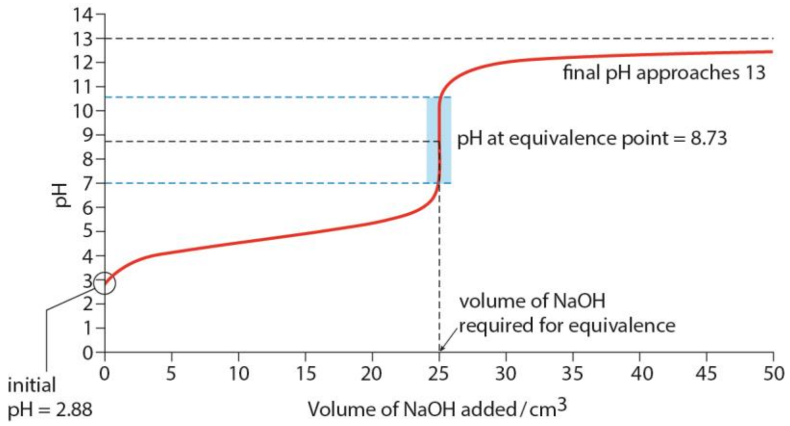


Figure 19.5: Weak acid–strong alkali titration curve.

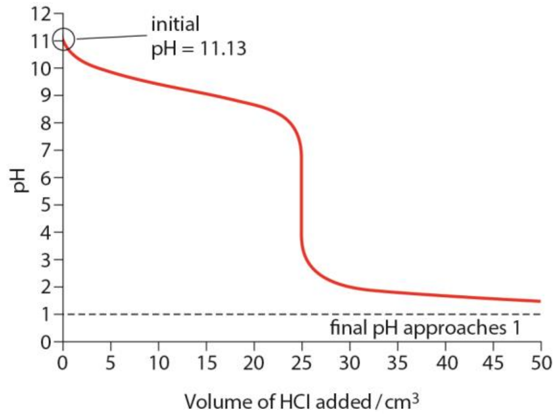


Figure 19.6: Strong acid–weak alkali titration curve.

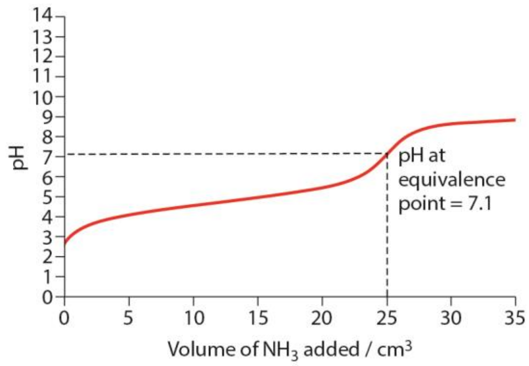


Figure 19.7: Weak acid–weak alkali titration curve.

Indicators

Indicators are usually weak acids

HIn ⇌ H^+(aq) + In^-(aq)

The ionised (In^-) and unionised (HIn) forms must have different colours.

The molecules that act as indicators are usually organic molecules with large delocalised systems, e.g., phenolphthalein.

Range of the indicator (pH range over which colour change takes place) = pK_a ± 1

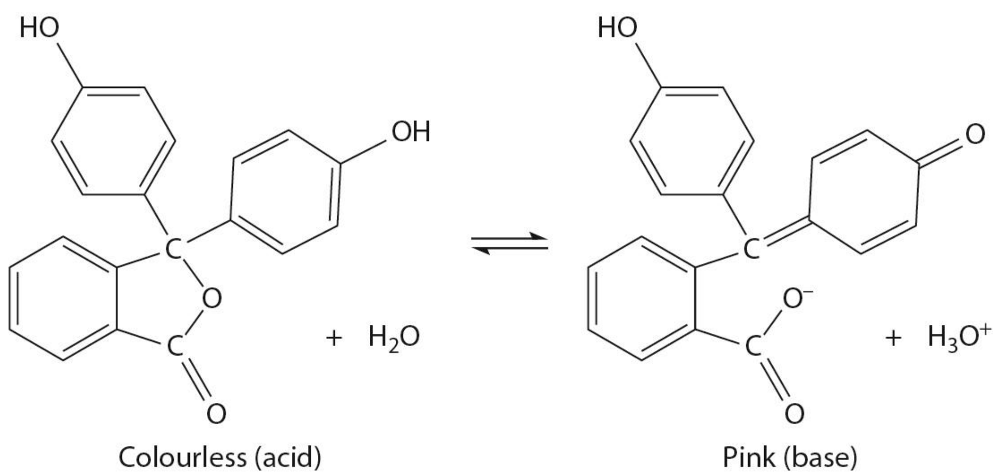


Figure 19.8: Phenolphthalein dissociating and showing different colours.

pH indicators

Titration indicators are used to determine the equivalence point not pH = 7.

Therefore, it is important to choose indicators that change colour around the equivalence point of a titration.

Indicator	Acid colour	Range	Alkali Colour
Methyl Orange	Red	3.1–4.4	Yellow
Methyl Red	Red	4.4–6.2	Yellow
Bromothymol Blue	Yellow	6.0–7.6	Blue
Phenolphthalein	Colourless	8.3–10.0	Pink

How a buffer works

$CH_3COOH(aq) \rightleftharpoons H^+(aq) \quad + \quad CH_3COO^-(aq)$

Adding H^+: $CH_3COO^-(aq) + H^+(aq) \rightarrow CH_3COOH(aq)$

Adding OH^-: $CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(l)$

The changes in the concentrations of CH_3COOH or CH_3COO^- are small compared with the amount present (little shift in the position of equilibrium); the change in pH is also very small.

Calculating the pH of a buffer

$pH = pK_a + \log_{10}$[conjugate base]/[acid] for an acidic buffer solution

$pH = pK_w - pK_b + \log_{10}$ [base]/[conjugate acid] for a basic buffer solution