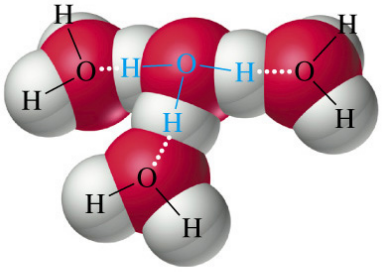
Unit 1 - Inorganic & Physical Chemistry

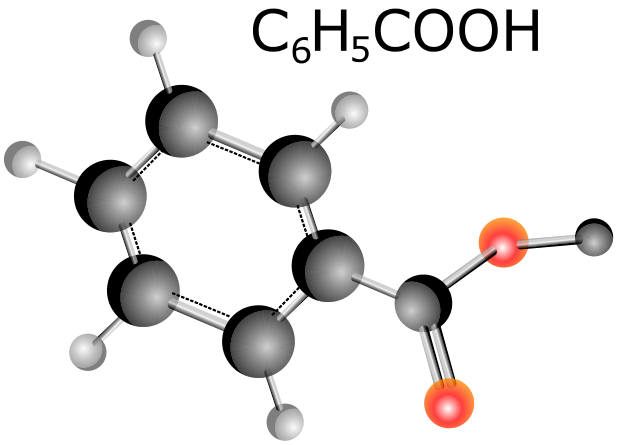
1.4 Chemical Equilibria Part 2

Acid / Base Equilibria
Indicators
pH Curves
Buffer Solutions

Hydronium ion
H_3O^+



A hydrated proton
$H_9O_4^+$



A carboxylic acid molecule.
Benzoic Acid.

Pupil Notes
Learning Outcomes
Questions & Answers

1.4 CHEMICAL EQUILIBRIUM- part 2

Equilibria involving ions

1 *The **Bronsted-Lowry** definitions of acid and base state that an acid is a proton donor and a base is a proton acceptor*

2 *For every acid there is a **conjugate base**, formed by loss of a proton.*

3 *For every base there is a **conjugate acid**, formed by gain of a proton.*

4 *The ionisation of water can be represented by:*

$$H_2O_{(l)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + OH^-_{(aq)}$$

5 *Water is **amphoteric**.*

6 *pH is a measure of $[H_3O^+]$ where **$pH = -\log [H_3O^+]$** or simpler, **$pH = -\log [H^+]$***

7 *The equilibrium constant for the ionisation of water is known as the **ionic product** and is represented by:*

$$K_w = [H_3O^+][OH^-]$$

8 *The value of the ionic product varies with temperature.*

9 *At 25°C the value of K_w is approximately 1×10^{-14} $mol^2\ l^{-2}$*

10 *A shorthand representation of H_3O^+ is H^+. **Stoichiometric equations and equilibrium expressions can be written using H^+ instead of H_3O^+ where meaning is clear.***

11 *The dissociation in aqueous solution of an acid of general formula HA can be represented as:*

$$HA_{(aq} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

12 *The acid dissociation constant of acid HA is given by:*

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

13 *The conjugate base of an acid of general formula HA is A^-.*

14 *The pH of a weak acid can be calculated from the dissociation constant.*

15 *The dissociation constant of an acid can be represented by pKa where*

$$pK_a = -\log K_a$$

Indicators

16 *Indicators are weak acids for which the dissociation can be represented as*

$$HIn_{(aq} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + In^-_{(aq)}$$

17 *The acid dissociation constant is represented as K_{In} and is given by the following expression*

$$K_{In} = \frac{[H_3O^+]\,[In^-]}{[HIn]}$$

18 *In aqueous solution the colour of the acid (HIn) is distinctly different from that of its conjugate base (In^-).*

19 *The colour of the indicator is determined by the ratio of [Hln] to [In^-].*

20 *The theoretical mid-point at which colour changes occurs when*

$$[H^+] = K_{ln} \quad or \quad pH = pK_{In}$$

21 *The colour change is assumed to be distinguishable when [Hln] and [In^-] differ by a factor of 10.*

22 *The pH range over which a colour change occurs can be estimated by the expression*

$$pH = pK_{ln} \pm 1$$

Buffer solutions

23 *A buffer solution is one in which the pH remains approximately constant when small amounts of acid or base are added.*

24 *An acid buffer consists of a solution a weak acid and one of its salts.*

25 *In an acid buffer solution the weak acid can supply hydrogen ions when these are removed by the addition of a small amount of base. The salt of the weak acid provides the conjugate base, which can absorb excess hydrogen ions produced by the addition of a small amount of acid.*

26 *A basic buffer consists of a solution of a weak base and one of its salts.*

27 *In a basic buffer solution the weak base removes excess hydrogen ions and the conjugate acid provided by the salt supplies hydrogen ions when these are removed.*

28 *The pH of an acid buffer solution can be calculated from its composition and from the acid dissociation constant.*

29 *The required compositions of an acid buffer solution can be calculated from the desired pH and from the acid dissociation constant.*

1.4 Chemical Equilibria - Part 2

1.4.1 Acid/base equilibria

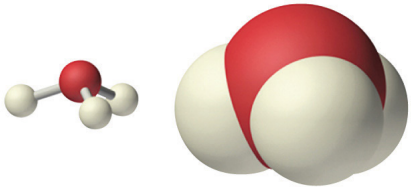
Historically ***acids*** were defined as *producing hydrogen ions* in solution and ***bases*** as *producing hydroxide ions* in solution. These two ions combine in the neutralisation equation:

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)}$$

As research continued throughout the nineteenth and early twentieth centuries, the definitions had to be refined.

For example, pure hydrogen chloride is a gas that contains no H^+ ions and ammonia has no OH^- ions but can neutralise an acid. It was also discovered that the H^+ ion could not exist in aqueous solution. The H^+ ion is so small (10^{-3} pm compared to other cations at 10^2 pm) that the electric field it creates is huge and in water it attracts a lone pair of electrons to form H_3O^+, which is called the ***hydronium ion*** (or the *oxonium ion* or the *hydroxonium ion*):

$$H^+_{(aq)} + H_2O_{(l)} \rightarrow H_3O^+_{(aq)}$$



Hydronium ion, H_3O^+

The shorthand $H^+_{(aq)}$ is always used in stoichiometric and equilibrium equations, although this is not strictly accurate.

In 1923 the new discoveries led two chemists, Brønsted and Lowry, to define acids and bases in a different way:

An acid is any substance capable of donating a proton.

A base is any substance capable of accepting a proton.

When an ***acid donates a proton*** the species left is called the *conjugate base* of that acid. When a ***base accepts a proton*** the species formed is called the *conjugate acid* of that base.

The list below gives examples of these relationships.

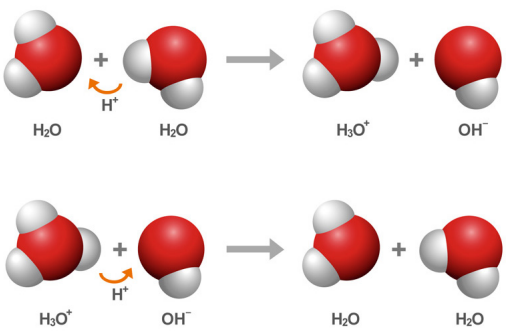
acid	+	***base***	⇋	***conjugate base***	+	***conjugate acid***
HCl	+	H_2O	⇋	Cl^-	+	H_3O^+
CH_3COOH	+	H_2O	⇋	CH_3COO^-	+	H_3O^+
H_2O	+	NH_3	⇋	OH^-	+	NH_4^+
H_2O	+	CH_3COO^-	⇋	OH^-	+	CH_3COOH

They also illustrates the ***amphoteric*** nature of water since it can act ***both*** as a *proton acceptor* and a *proton donor.*

1.4.2 The Dissociation of Water

In Brønsted–Lowry terms the ionisation of water is represented by:

$$\underset{\textit{acid}}{H_2O_{(l)}} + \underset{\textit{base}}{H_2O_{(l)}} \rightleftharpoons \underset{\textit{conjugate acid}}{H_3O^+_{(aq)}} + \underset{\textit{conjugate base}}{OH^-_{(aq)}}$$



The equilibrium constant is

$$K = \frac{[H_3O^+]\,[OH^-]}{[H_2O]}$$

Since water is a liquid, $[H_2O] = 1$, giving: $K = [H_3O^+][OH^-]$

This particular equilibrium constant is known as the ***ionic product (K_w)*** for water and has the value of 1.0×10^{-14} at 25°C. The water equilibrium is more usually written as:

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \qquad K_w = [H^+][OH^-]$$

In pure water, for every molecule which ionises, one H^+ and one OH^- ion are produced, hence the $[H^+]$ in mol l^{-1} must equal the $[OH^-]$ in mol l^{-1}, i.e. the number of H^+ and OH^- ions in water are equal.

Substitution of $[OH^-]$ by $[H^+]$ in the above equilibrium expression gives:

	$[H^+]^2$	=	10^{-14} mol^2 l^{-2}
taking square roots	[H+]	=	10^{-7} mol l^{-1}
also	$[OH^-]$	=	10^{-7} mol l^{-1}

Note also that $[H_2O]$ in pure water = 1000/18 mol l^{-1} (neglecting the slight ionisation) = 55.5 mol l^{-1}, therefore the ratio of hydrogen ions to water molecules, in water is:

$$[H^+] / [H_2O] = 10^{-7}\text{ mol} / 55.5\text{ mol} = (10^{-7} \times 6.02 \times 10^{23}) / (55.5 \times 6.02 \times 10^{23}) = 1 : 555\,000\,000$$

On average there is one H^+ ion and one OH^- ion for every 555 million H_2O molecules!

K_w is always quoted as 1.0×10^{-14} at 25°C since the value ***varies with temperature***:

$$H_2O_{(l)} \rightleftharpoons H^+_{(aq)} + OH^-_{(aq)} \qquad \Delta H \text{ +ve}$$

As the reaction is *endothermic*, an increase in temperature moves the equilibrium to the right and a decrease moves it to the left.

The table oposite shows the values of K_w at different temperatures.

Temperature (°C)	***K_w (× 10^{-14})***
18	0.6
25	1.0
40	2.9
75	16.9

1.4.3 The pH Scale

From previous courses it will be remembered that the pH of an aqueous solution is a ***measure of the concentration of hydrogen ions*** in the solution.

In fact the pH of any aqueous solution can be calculated using the expression:

$$pH = -\log[H_3O+] \quad \text{or} \quad pH = -\log[H^+]$$

The following examples illustrate its use:

pure water	$[H^+] = 10^{-7}$	pH = 7
1.0 mol l^{-1} HCl	$[H^+] = 1.0\ (10^0)$	pH = 0
0.2 mol l^{-1} HCl	$[H+] = 0.2\ (2 \times 10^{-1})$	pH = –log 2 – log (10^{-1}) = –0.3 + 1.0 = 0.7
0.01 mol l^{-1} NaOH	$[OH^-] = 10^{-2}$, $[H+] = 10^{-12}$	pH = 12
0.5 mol l^{-1} NaOH	$[H^+] = 2 \times 10^{-14}$	pH = –log 2 – log(10^{-14}) = –0.3 + 14 = 13.7

For calculations involving strong acids and alkalis it can be assumed that they are 100% dissociated and that the small number of hydrogen ions supplied by the water can be ignored.

Question

Calculate the pH of the following solutions:

a) 0.35 mol l^{-1} HNO_3
b) 0.14 mol l^{-1} H_2SO_4 (assume fully ionised)
c) 0.78 mol l^{-1} NaOH

1.4.4 The Dissociation of Acids

The dissociation of any acid, HA, in aqueous solution can be represented by the equation:

$$HA_{(aq)} + H_2O_{(l)} \leftrightharpoons H_3O^+_{(aq)} + A^-_{(aq)}$$

acid base conjugate acid conjugate base

The dissociation constant of acid HA from the above equation is:

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]}$$

and is a measure of the strength of the acid. The $[H_2O]$ has been omitted as it is the solvent and taken to be 1.

In strong acids the above equilibrium lies to the right with effectively complete dissociation so that K_a has no meaning. However, some acids do not dissociate well (less than 5%) in aqueous solution and these are called weak acids.

Conveniently, nearly all acids fall into one of these two categories. Within the weak acids, the value of K_a gives a measure of how weak (or how dissociated) the acid is: the smaller the value of K_a, the weaker the acid.

Calculation of pH of a weak monobasic acid

Using the dissociation constant from the previous page, the pH of a weak monobasic acid can be calculated.

$$K_a = \frac{[H_3O^+]\,[A^-]}{[HA]} \qquad \text{however, } [H_3O^+] = [A^-] \qquad \text{so} \qquad K_a = \frac{[H_3O^+]^2}{[HA]}$$

Taking logs of both sides:

$$\log K_a = \log[H_3O^+]^2 - \log[HA] \quad = 2\log[H_3O^+] - \log[HA]$$

but $-\log[H_3O^+] = pH$, and $-\log Ka = pKa$ so we get:

$$-pKa = -2pH - \log[HA]$$

$$pKa = 2pH + log[HA]$$

most often it is the pH that we want to calculate, so

$$\boldsymbol{pH = \tfrac{1}{2}pKa - \tfrac{1}{2}log[HA]}$$

For a weak acid HA of concentration c mol l^{-1}, [HA] at equilibrium will be approximately equal to the original concentration c mol l^{-1}, so, in practice:

$$\boldsymbol{pH = \tfrac{1}{2}pKa - \tfrac{1}{2}log\ c}$$

This equation is only valid for weak acids in which the concentration of HA at equilibrium is almost the same as the original concentration. ***The weaker the acid is, the more closely the calculated pH will approach the actual pH of the solution.*** *The stronger the acid, the more inaccurate the calculated pH will be.*

Questions

1. Calculate the pH of a 0.2 mol l^{-1} solution of ethanoic acid if $K_a = 1.7 \times 10^{-5}$.

2. 0.02 mol l^{-1} benzoic acid C_6H_5COOH, a monobasic acid, was found to have a pH of 2.94. Calculate the K_a of this weak acid.

Indicators

Indicators are used to determine the end-point in an acid–alkali titration. A suitable indicator must be chosen for any given reaction. Indicators are dyes whose colours are sensitive to pH. An indicator is usually a weak acid that dissociates as shown:

$$HIn_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + In^-_{(aq)}$$

The unionised form of the indicator (HIn) has a different colour from its conjugate base (In–). The equilibrium constant (KIn) for the above equation is:

$$K_{In} = \frac{[H_3O^+]\,[In^-]}{[HIn]}$$

The colour observed depends on the ratio of the two coloured species [In—] / [HIn] and, rearranging the previous equation:

$$\frac{[In^-]}{[HIn]} = \frac{K_{In}}{[H_3O^+]}$$

confirms that the colour depends on the $[H_3O^+]$ (pH)

The theoretical point at which the colour change occurs is when [HIn] = [In⁻] and therefore $K_{In} = [H_3O^+]$. In other words, the colour change occurs when $\boldsymbol{pK_{In} = pH}$.

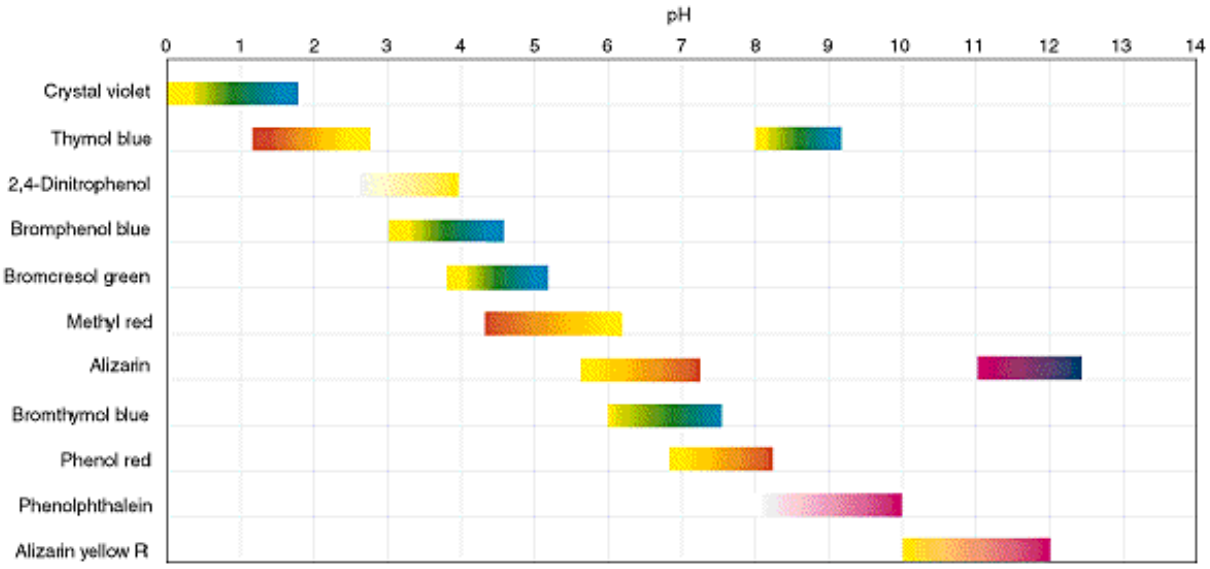
In practice the colour change cannot be seen when [HIn] = [In⁻] (***both*** colours still *too strong*) and it is only distinguishable when [HIn] and [In⁻] differ by a factor of 10.

$$\frac{[In^-]}{[HIn]} = 10 \quad \textit{or} \quad \frac{[In^-]}{[HIn]} = 0.1$$

The pH range over which a colour change can be seen is therefore established using the expression:

$$\boldsymbol{pH = pK_{In} \pm 1} \quad (\log 10 = 1,\ \log 0.1 = -1)$$

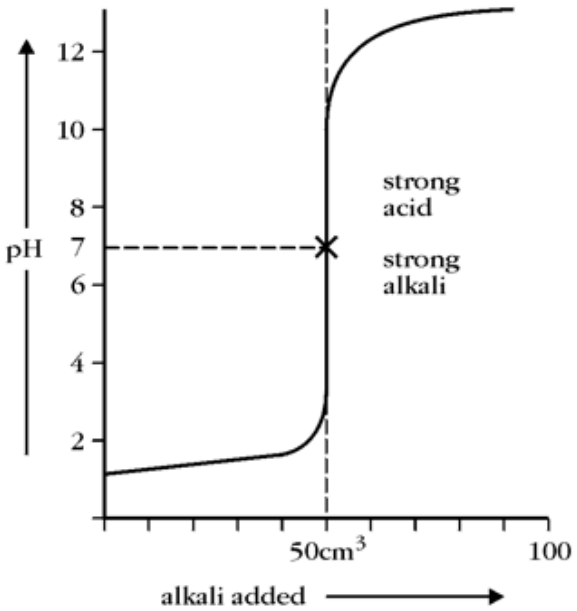
The significance of the above expression is that an *indicator will change colour* over a ***pH range = 2 units***



The appropriate indicator for any titration must be chosen such that the colour change occurs over the pH range when the pH is changing very rapidly. This means that the indicator must change colour during the addition of, say, half a drop of reagent. The indicator for a reaction can therefore be chosen by reference to titration curves, which are drawn from data obtained by measuring the pH of an acid continuously against the volume of alkali added during and after neutralisation

pH Curves

Consider the titration of a strong acid with a strong alkali e.g. the addition of 0.01 mol l^{-1} NaOH solution to 50 cm^3 of 0.01 mol l^{-1} HCl. The pH of the original acid solution will be 2 ($[H^+] = 10^{-2}$ mol l^{-1}).



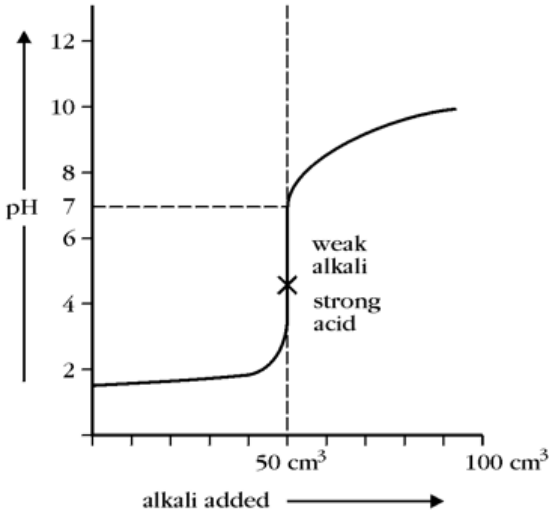
When 49 cm^3 of NaOH solution has been added there will be only 1 cm^3 of the original 0.01 mol l^{-1} HCl left un-neutralised. This amount is now in an overall volume of 50 + 49 cm^3 ~ 100 cm^3, i.e. the solution is now 10^{-4} mol l^{-1} with respect to $H^+_{(aq)}$, thus $[H^+] = 10^{-4}$ mol l^{-1} and pH = 4.

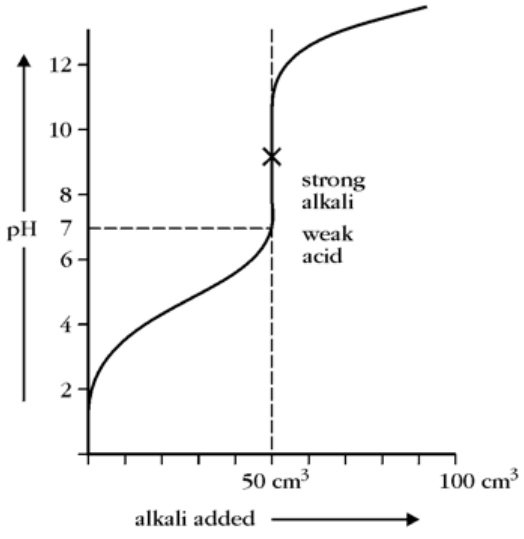
On adding 49.9 cm^3 alkali, only 0.1 cm^3 of acid will remain in ~100 cm^3 solution and therefore $[H^+] = 10^{-5}$ mol l^{-1} and pH = 5. When 49.99 cm^3 alkali has been added the pH of the solution is 6 and at 50 cm^3 the pH rises to 7 and neutralisation is complete.

Note the ***rapid rise in pH*** as the end-point of the titration is approached. Thereafter the alkali added has nothing to react with and the pH continues to rise to a final value of 12.

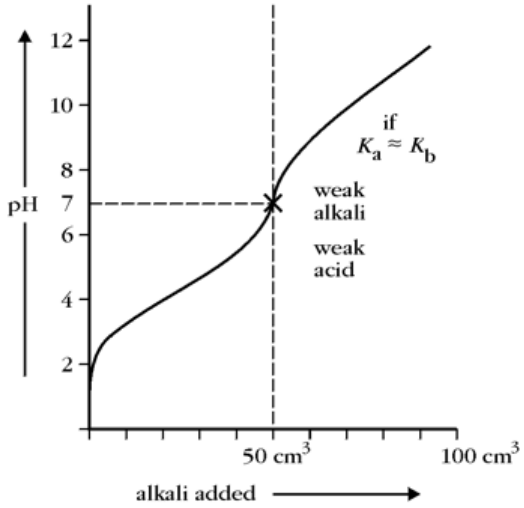
It can be seen that for a strong acid and strong alkali a suitable indicator can have a colour change within the ***pH range 3–10***. Any indicator, whose colour change is within this range would be suitable.

The titration curves below show the pH changes that occur on titrating weak and strong alkalis (50 cm^3) with equimolar solutions of strong and weak acids (50 cm^3) respectively





It can be seen from the above curves that there is a ***region of rapid pH change*** around the *end-point*. For an indicator to be suitable, its pH range must fall within this region. An indicator for a *strong acid and weak alkali* would change somewhere in the ***pH range 3–7***. Similarly, for a *weak acid and strong alkali*, a suitable indicator must change colour within the ***pH range 7–10***.



It is not possible to select any suitable indicator for a *weak acid/ weak alkali* combination, since the pH does not change rapidly enough at the end-point, i.e. the titration curve does not have an almost vertical section like the others.

Name of indicator	***pH of colour change***	***Colour (HIn)***	***Colour (In)***
Methyl orange	3.0–4.4	Orange	Yellow
Methyl red	4.2–6.3	Red	Yellow
Bromothymol blue	6.0–7.6	Yellow	Blue
Phenolphthalein	8.0–9.8	Colourless	Red

1.4.5 Buffer Solutions

A buffer solution is one in which the pH of the solution ***remains approximately constant*** when small amounts of acid or base are added or the solution is diluted with water.

An acidic buffer consists of a solution of a ***weak acid*** and one of its ***salts*** with a strong alkali. A basic buffer consists of a solution of a ***weak base*** and one of its ***salts*** with a strong acid. Both types of buffer solution work in the same way.

In an acid buffer solution, the ***weak acid supplies more hydrogen ions*** when the existing ones are removed by a base being added, while the ***salt*** of the weak acid provides the ***conjugate base*** to ***react with the hydrogen ions*** when small amounts of acid are added.

In a basic buffer solution, the ***weak base reacts with the hydrogen ions*** when acid is added and the ***salt*** provides the ***conjugate acid***, which dissociates to ***replace the hydrogen ions*** when these are removed by addition of small amounts of base.

In consequence, the pH hardly changes in both cases.

This principle is illustrated by an acid buffer of weak acid HA and the sodium salt of that acid NaA. In solution the following occurs:

$$HA_{(aq)} + H_2O_{(l)} \rightleftharpoons H_3O^+_{(aq)} + A^-_{(aq)} \qquad \textit{equilibrium}$$

and

$$NaA_{(aq)} \rightarrow Na^+_{(aq)} + A^-_{(aq)} \qquad \textit{fully ionised}$$

Being a *weak acid*, [$HA_{(aq)}$] remains ***high*** and acts as a 'store' ***capable of releasing $H^+_{(aq)}$ when needed***.

As a *soluble* salt, [$A^-_{(aq)}$] will be ***high*** and is ***capable of removing $H^+_{(aq)}$ when needed***.

To show how buffers can also resist the addition of water, it is necessary to take a more mathematical approach.

Starting with $K_a = \dfrac{[H_3O^+]\,[A^-]}{[HA]}$ and rearranging, $[H_3O^+] = K_a \; x \; \dfrac{[HA]}{[A^-]}$

Adding water should ***dilute*** [HA] and [A^-] ***equally*** so the ratio [HA] / [A^-] remains ***constant***.

As a result, [H_3O^+] and hence ***pH remains constant***.

Similar reasoning can be used to show how a basic buffer solution operates.

pH Buffer Calculations

As previously shown, $[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$

Taking -logs converts $[H_3O^+]$ to pH and , $pH = pK_a - \log ([HA]/[A^-])$

Which is usually quoted as, ***$pH = pK_a$ - log (ACID / SALT)***

Questions

1. Calculate the pH of the buffer solution made from 1.0 mol l^{-1} methanoic acid and 1.78 mol l^{-1} sodium methanoate solution. The pKa of methanoic acid is 3.8.

2. Calculate the pH of the buffer solution made from 0.1 mol l^{-1} solution of ethanoic acid and potassium ethanoate. The pKa of ethanoic acid is 4.8.

The composition of an acid buffer solution can be calculated from the same equation as long as the required pH and the pKa of the acid are known, e.g. *to make an acidic buffer of pH 5.0, using propanoic acid pKa 4.9.*

$pH = pK_a$ - log (ACID / SALT)

5.0 = 4.9 - log (ACID / SALT)

0.1 = -log (ACID / SALT) so ACID / SALT = 0.794

The buffer is therefore made by mixing 0.794 moles of propanoic acid with 1.0 mole of sodium propanoate per litre of solution.

Question Calculate the concentrations of acid and salt solutions required to make:

a) a buffer of pH 6.0 from carbonic acid and sodium hydrogen carbonate (pKa of carbonic acid is 6.4)

b) a buffer of pH 3.1 from chloroethanoic acid and its potassium salt (pKa of chloroethanoic acid is 2.9).

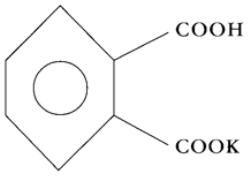
Buffer solutions are important in biological systems, especially those where enzymes work within narrow pH ranges, e.g. blood is a buffered solution of pH around 7.4 (CO_2/bicarbonate equilibrium is maintained by respiration and excretion of bicarbonate into the urine).

The sea is also a buffer because it contains significant concentrations of carbonate and hydrogencarbonate ions. These act as a buffer, maintaining the pH of the sea within certain limits, and this allows marine life to exist:

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

Phosphate solutions can act as buffers because the second and third dissociations of phosphoric acid are weak:

$$H_3PO_4 \rightarrow H^+ + H_2PO_4^- \rightleftharpoons H^+ + HPO_4^{2-} \rightleftharpoons H^+ + PO_4^{3-}$$



Another useful buffer in the laboratory is potassium hydrogenphthalate, which is a *weak acid **and** its salt* all in one molecule:

Questions

Q1 The pH of 0·002 mol l^{-1} calcium hydroxide solution is

A 2.4
B 2.7
C 11.3
D 11.6

Q2 Which of the following statements is not always true for aqueous solutions at 298 K?

A $Kw = 10^{-14}$
B $pH = -\log_{10}[H^+]$
C $[H^+][OH^-] = 10^{-14}$
D $[H^+] = [OH^-] = 10^{-7}$ mol l^{-1}

Q3 500 cm^3 of 0·022 mol l^{-1} hydrochloric acid is added to 500 cm^3 of 0·020 mol l^{-1} sodium hydroxide solution. The pH of the resulting solution will be

A 2
B 3
C 4
D 5

Q4 Which of the following decreases when an aqueous solution of ethanoic acid is diluted?

A pH
B pK_a
C $[H^+]$
D the degree of dissociation

Q5 Which of the following indicators should be used in the titration of potassium hydroxide solution with ethanoic acid solution?

A Phenolphthalein, pH range 8·0 – 9·8
B Bromothymol blue, pH range 6·0 – 7·6
C Methyl red, pH range 4·2 – 6·2
D Methyl orange, pH range 3·1 – 4·4

Q6 Write the formula for the conjugate base of each of the following acids:

a) H_3O^+ 1

b) H_2O 1

c) NH_4^+ 1 ***(3)***

Q7 ***a)*** Calculate the pH of a solution of ethanoic acid with a concentration of 0.01 mol l^{-1}. (K_a ethanoic acid = 1.7×10^{-5}). **3**

b) A mixture of ethanoic acid and sodium ethanoate solution constitutes a buffer solution. Explain how this buffer solution is able to resist change in pH when small quantities of each of the following are added.

i) hydrochloric acid **2**

ii) sodium hydroxide solution **2**

c) The simplified equation for the pH of a buffer solution is:

$$pH = pK_a - \log\left(\frac{[acid]}{[salt]}\right)$$

A buffer solution was prepared from ethanoic acid (0.25 mol l^{-1}) and sodiumethanoate solution (0.15 mol l^{-1}).

Calculate the pH of the buffer solution. **2** ***(9)***

Q8 Propanoic acid is a weak acid. Sodium propanoate is a salt which can be formed from it. Both propanoic acid and sodium propanoate can be used as mould inhibitors.

a) Calculate the pH of 0·10 mol l^{-1} propanoic acid solution. **2**

b) 0·20 moles of sodium propanoate are added to 100 cm^3 of the 0·10 mol l^{-1} solution of propanoic acid.

Calculate the pH of the buffer solution formed. **2** ***(4)***

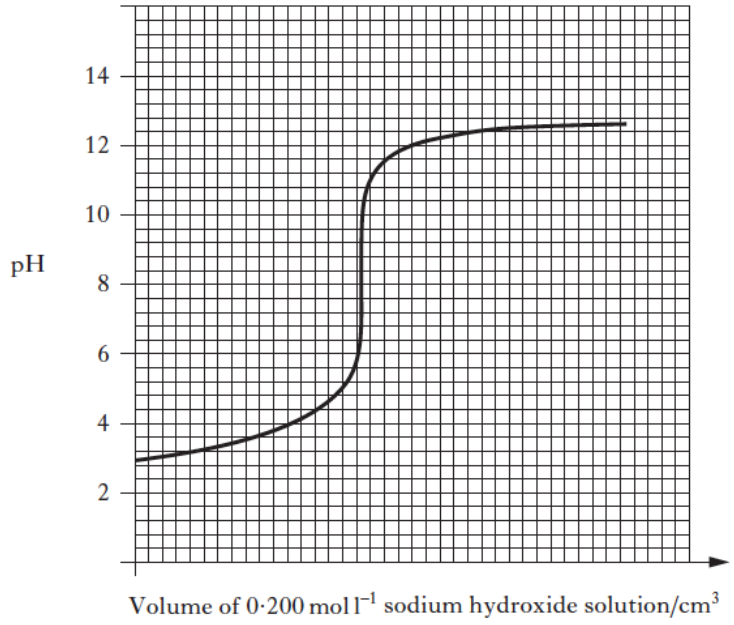
Q9 The salt sodium propanoate, $C_2H_5COO^-Na^+$, is produced when sodium hydroxide reacts with propanoic acid. When sodium propanoate is dissolved in water an alkaline solution is formed.

a) ***i)*** Write the formula for the conjugate base of propanoic acid. **1**

ii) Explain why a solution of sodium propanoate is alkaline. **2**

b) The titration of propanoic acid with sodium hydroxide can be followed using a pH meter.

The graph below was obtained when 40·0 cm^3 of an aqueous solution of propanoic acid was titrated with 0·200 mol l^{-1} sodium hydroxide.



i) The initial pH was recorded as 2·93.
Calculate the initial concentration of the propanoic acid. **3**

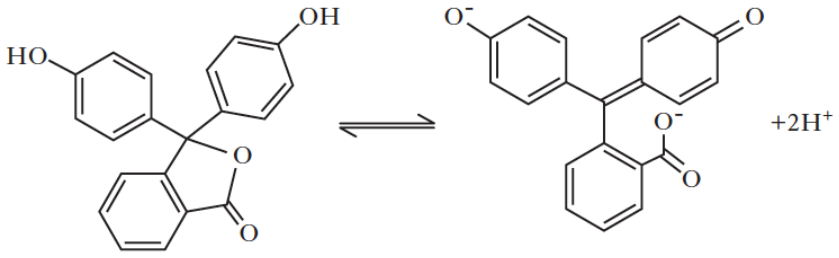
ii) The table shows four indicators which could be used to detect the end-point of a titration.

Indicator	pH range
Phenolphthalein	8·3 – 10·0
Bromophenol red	5·2 – 6·8
Methyl orange	3·1 – 4·4
Methyl red	4·2 – 6·3

Why is phenolphthalein the most suitable indicator for this titration? **1**

Q9 contd

c) Phenolphthalein is a weak acid. The equation shows how phenolphthalein dissociates.



unionised molecule (colourless) ion (pink)

With reference to the above equilibrium, explain why the colour changes from colourless to pink at the end-point. **1** ***(8)***

Q10 Phosphoric(V) acid, H_3PO_4, is triprotic. When neutralised by sodium hydroxide solution, it can form three different salts.

a) Give the formula for each of the three sodium salts of the acid. **2**

b) The first stage of the ionisation of phosphoric (V) acid has a dissociation constant of 7.08×10^{-3}.

Calculate the approximate pH of a 0.1 mol l^{-1} solution of phosphoric(V) acid.

(You can assume that the other two stages in the ionisation do not significantly affect the hydrogen ion concentration). **3** ***(5)***

Q11 Limewater is a saturated solution of calcium hydroxide. At 20°C, 100 cm^3 of a limewater solution conatined 0.126g of calcium hydroxide.

a) Calculate the concentration of of hydroxide ions, in mol l-1, in this solution. **2**

b) Using your answer to part a), calculate the pH of the solution **2** ***(4)***

Q12 250 cm^3 of sulphurous acid solution was prepared by dissolving 1.6g of sulphur dioxide in water at 298K.

a) Calculate the concentration of the acid in mol l^{-1}. **2**

b) Using your answer to ***a)*** and your Data Booklet, calculate the pH of the acid solution. **3**

c) Why is this acid unsuitable for use as a primary standard? **1**

d) If this acid is standardised using a strong alkali, what will be the approximate pH range of the indicator needed for the titration? **1** ***(7)***

Q13 Most Indicators are weak acids of general formula HIn. Their dissociation in aqueous solution can be represented as:

$$\underset{\text{colour A}}{HIn} \rightleftharpoons \underset{\text{colour B}}{H^+ + In^-}$$

$$K_{indicator} = \frac{[H^+]\,[In^-]}{[HIn]}$$

At the end point, [In-] = [HIn] and therefore Kindicator = $[H^+]$.

Use the above and the information in the table below to answer the questions that follow.

Indicator	$K_{indicator}$	Colour change (low pH → high pH)
Methyl yellow	5.1×10^{-4}	red → yellow
Bromothymol blue	1.0×10^{-7}	yellow → blue
Thymol Blue	1.3×10^{-9}	yellow→ blue

a) At what pH would the colour change be expected to take place in each of the indicators? **2**

b) A student is asked to carry out a titration of ethanoic acid and sodium hydroxide. Which indicator in the table is most suitable for the titration? Give a reason for your choice. **2** ***(4)***

Q14 An acidic buffer consists of a solution of a weak acid and one of its salts. This can be prepared by reacting a weak acid with an alkali.

20·0 cm^3 of 1·00 mol l^{-1} potassium hydroxide solution was added to 40·0 cm^3 of 1·00 mol l^{-1} aqueous ethanoic acid forming a buffer solution.

a) Calculate the concentration of

i) $K^+_{(aq)}$ **1**

ii) $H^+_{(aq)}$ in the buffer solution. **3**

b) Explain how this solution would resist change in pH if a few more drops of the potassium hydroxide solution were added. **2** ***(6)***