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## R3.1 10. Proton transfer reactions: acid-base behaviour

## What are the mechanisms of chemical change?

#### The ionic theory

Acids were originally identified by their sour taste. Later, an acid was said to be the oxide of a non-metal combined with water, although hydrochloric acid does not fit into this definition. The ionic theory, which is still commonly used today, states that an **acid** is a substance which produces hydrogen ions, H<sup>+</sup>(aq), in aqueous solution, e.g.

 $HCl(aq) \rightarrow H^{+}(aq) + Cl^{-}(aq)$ 

In aqueous solution hydrogen ions are hydrated to form hydroxonium ions,  $H_3O^+(aq)$ . For the IB, it is correct to write either  $H^+(aq)$  or  $H_3O^+(aq)$  to represent the hydrogen ions in an aqueous solution. Strictly speaking, an acid gives a hydrogen ion concentration in aqueous solution greater than  $1.0 \times 10^{-7}$  mol dm<sup>-3</sup>. A base is a substance that can neutralize an acid. An alkali is a base that is soluble in water.

#### Brønsted-Lowry acids and bases

A Brønsted-Lowry acid is a substance that can *donate* a proton. A Brønsted-Lowry base is a substance that can *accept* a proton.

Consider the reaction between hydrogen chloride gas and water.

$$HCI(g) + H_2O(I) \rightleftharpoons H_3O^+(aq) + CI^-(aq)$$
  
acid base acid base

Under this definition, both HCl and  $H_3O^+$  are acids as both can donate a proton. Similarly, both  $H_2O$  and  $C\Gamma$  are bases as both can accept a proton.  $C\Gamma$  is said to be the **conjugate base** of HCl, and  $H_2O$  is the conjugate base of  $H_3O^+$ . The conjugate base of an acid is the species remaining after the acid has lost a proton. Every base also has a **conjugate acid**, which is the species formed after the base has accepted a proton.

Water is behaving as a base in the reaction with hydrogen chloride. Water can also behave as an acid.

$$NH_3(g) + H_2O(I) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$$
  
base acid acid base

Substances such as water, which can act both as an acid and as a base by donating or accepting a proton, are described as **amphiprotic**.

Many acids, particularly organic acids, contain one or more non-acidic hydrogen atoms. The location of the acidic hydrogen atom(s) should be clearly identified. For example, ethanoic acid should be written as  $C_3C_3C_3C_4$ , rather than  $C_2C_3C_4$ , so that the conjugate base can be identified as the carboxylate anion  $C_3C_3C_4$ .

#### Neutralization reactions with bases

Here are examples of the reactions of acids with bases:

• with metal hydroxides to form a salt and water, e.g.

$$CH_3COOH(aq) + NaOH(aq) \rightarrow NaCH_3COO(aq) + H_2O(I)$$

• with metal oxides to form a salt and water, e.g.

$$H_2SO_4(aq) + CuO(s) \rightarrow CuSO_4(aq) + H_2O(l)$$

• with ammonia and amines to form salts, e.g.

$$HCI(aq) + NH_3(aq) \rightarrow NH_4CI(aq)$$
  
 $HCI(aq) + C_2H_5NH_2 \rightarrow C_2H_5NH_3CI(aq)$ 

with reactive metals (those above copper in the activity series) to form a salt and hydrogen, e.g.

$$2HCl(aq) + Mg(s) \rightarrow MgCl_2(aq) + H_2(g)$$

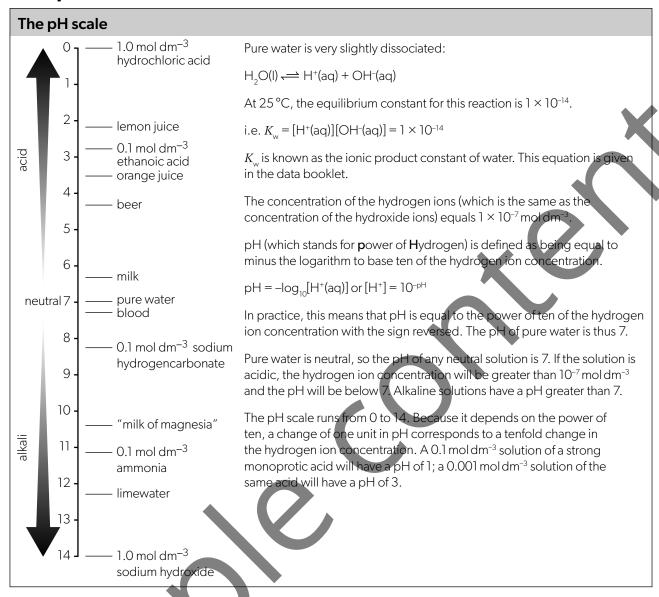
• with carbonates (soluble or insoluble) to form a salt, carbon dioxide, and water, e.g.

$$2HNO_3(aq) + Na_2CO_3(aq) \rightarrow 2NaNO_3(aq) + CO_2(g) + H_2O(l)$$
  
 $2HCl(aq) + CaCO_2(s) \rightarrow CaCl_2(aq) + CO_2(g) + H_2O(l)$ 

• with hydrogencarbonates to form a salt, carbon dioxide, and water, e.g.

$$HCI(aq) + NaHCO_3(aq) \rightarrow NaCI(aq) + CO_2(g) + H_2O(aq)$$

## The pH scale



#### Determination of pH

The pH of a solution can be determined in several ways.

#### 1. Using acid-base indicators

Indicators can be used to determine whether or not a solution is acidic. Common indicators include:

Indicator	Colour in acidic solution	Colour in alkaline solution
litmus	red	blue
phenolphthalein	colourless	pink
methyl orange	red	yellow

#### 2. Using a pH meter

A pH meter gives the most accurate and precise readings. The pH meter (or pH probe connected to a data logger) is calibrated using a buffer solution of known pH, then inserted into a solution to measure the pH.

#### 3. Using "universal" indicator

Universal indicator contains a mixture of indicators that give a range of colours at different pH values, as shown in the table below.

рН	[H <sup>+</sup> ] / mol dm <sup>-3</sup>	[OH <sup>-</sup> ] / mol dm <sup>-3</sup>	Description	Colour of universal indicator
0	1	$1 \times 10^{-14}$	very acidic	red
4	1 × 10 <sup>-4</sup>	1 × 10 <sup>-10</sup>	acidic	orange
7	1 × 10 <sup>-7</sup>	1 × 10 <sup>-7</sup>	neutral	green
10	1 × 10 <sup>-10</sup>	1 × 10 <sup>-4</sup>	basic	blue
14	1 × 10 <sup>-14</sup>	1	very basic	purple

#### The log<sub>10</sub> scale and p-scale

Normal scale: the distances between consecutive numbers are equal

-5 -4 -3 -2 -1 0 1 2 3 4 5

Log<sub>10</sub> scale: the distances between powers of ten are equal

This can be written as

 $10^{-5}$   $10^{-4}$   $10^{-3}$   $10^{-2}$   $10^{-1}$   $10^{0}$   $10^{1}$   $10^{2}$   $10^{3}$   $10^{4}$   $10^{5}$ 

p-scale: sometimes used by chemists to express equilibrium constants and concentration; it is equal to minus the power of ten in the logarithmic scale, so the scale becomes

5 4 3 2 1 0 -1 -2 -3 -4 -5

#### Strong, concentrated and corrosive

In English, the words "strong" and "concentrated" are often used interchangeably. However, in chemistry they have very precise meanings:

- strong: completely dissociated into ions
- concentrated: a high number of moles of solute per litre (dm³) of solution
- corrosive: chemically reactive.

Similarly, "weak" and "dilute" also have very different chemical meanings:

- weak: only slightly dissociated into ions
- **dilute:** a low number of moles of solute per litre of solution.

#### Strong and weak acids and bases

A strong acid is completely dissociated (ionized) into its ions in aqueous solution. Similarly, a strong base is completely dissociated into its ions in aqueous solution. Here are some examples of strong acids and bases.

#### Strong acids

#### Strong bases

hydrochloric acid, HCl sodium hydroxide, NaOH nitric acid, HNO $_3$  potassium hydroxide, KOH sulfuric acid, H $_3$ SO $_4$  barium hydroxide, Ba(OH) $_2$ 

Note: because one mole of HCl produces one mole of hydrogen ions it is known as a **monoprotic** acid. Sulfuric acid is known as a **diprotic** acid as one mole of sulfuric acid produces two moles of hydrogen ions.

Weak acids and bases are only slightly dissociated (ionized) into their ions in aqueous solution. Here are some examples of weak acids and bases.

#### Weak acids

#### Weak bases

ethanoic acid, CH<sub>3</sub>COOH "carbonic acid", H<sub>2</sub>CO<sub>3</sub> ammonia,  $NH_3$ aminoethane,  $C_2H_5NH_2$  The difference can be seen in their reactions with water.

• For a strong acid, the reaction goes to completion:

$$HCI(g) + H_2O(I) \rightarrow H_2O^+(ag) + CI^-(ag)$$

• For a weak acid, the equilibrium lies on the left, i.e. on the side with the weaker conjugate:

$$CH_3COOH(aq) + H_3O(I) \rightleftharpoons CH_3COO^-(aq) + H_3O^+(aq)$$

A solution of hydrochloric acid consists only of hydrogen ions and chloride ions in water, whereas a solution of ethanoic acid contains mainly undissociated ethanoic acid molecules with only a very few hydrogen ions and ethanoate ions.

• For a strong base, the reaction goes to completion:

$$KOH(s) \xrightarrow{H_2O(I)} K^+(aq) + OH^-(aq)$$

• For a weak base, the equilibrium lies on the left:

$$NH_2(g) + H_2O(I) \rightleftharpoons NH_4^+(ag) + OH^-(ag)$$

## Strong and weak acids and bases and simple pH calculations

#### Strong acid and base pH calculations

For pure water the pH must be 7 at 25 °C as the concentration of H+(aq) is equal to the concentration of  $OH^{-}(aq)$  and  $[H^{+}(aq)] \times [OH^{-}(aq)] = 1 \times 10^{-14}$ . Strong acids are completely dissociated so, for example, the hydrogen ion concentration of 0.100 mol dm<sup>-3</sup> hydrochloric acid, HCl(aq), will be 0.100 mol dm<sup>-3</sup> as each mole of acid produces one mole of hydrogen ions when it dissociates (ionizes). The pH of  $0.100\,mol\,dm^{-3}$ HCI(aq) will therefore be equal to  $-log_{10}(0.100) = 1$ .

If the acid is diluted ten times, then the new hydrogen ion concentration will be 0.0100 mol dm<sup>-3</sup> and the pH will be equal to  $-\log_{10}(0.0100)$  or  $-\log_{10}(1.00 \times 10^{-2}) = 2$ .

Sulfuric acid is assumed, for simplicity, to be a strong diprotic acid. The hydrogen ion concentration of

 $0.0100 \,\mathrm{mol}\,\mathrm{dm}^{-3}\,\mathrm{H}_2\mathrm{SO}_4(\mathrm{aq})$  is therefore  $2\times0.0100$  or  $2.00 \times 10^{-2}$  mol dm<sup>-3</sup> and the pH will equal  $-\log_{10}(2.00 \times 10^{-2}) = 1.7.$ 

Note that pH is a measure of concentration, so 10.0 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HCI(aq) has the same pH as 100 cm<sup>3</sup> of 0.100 mol dm<sup>-3</sup> HCl(aq). Also note that  $[H^{+}(aq)] \neq 10^{-pH}$ so if the pH of an acid is 3, then  $[H^{+}(aq)] = 10^{-3} = 1.0 \times 10^{-3} \,\text{mol dm}^{-3}$ 

To calculate the pH of a strong base, you need to work out the hydroxide concentration first and then calculate the hydrogen ion concentration using the expression  $[H^{+}(aq)] \times [OH^{-}(aq)] = 1 \times 10^{-3}$ 

#### Worked example 1

Calculate the pH of 0.100 mol dm<sup>-3</sup> NaOH(aq).

 $[OH^{-}(aq)] = 0.100 \, \text{mol dm}^{-3}$ 

$$[H^{+}(aq)] = \frac{1 \times 10^{-14}}{0.100} = 1 \times 10^{-13} \,\text{mol dm}^{-3}$$

$$pH = -log_{10}(1.00 \times 10^{-13}) = 13$$

#### Worked example 2

Calculate the pH of  $0.100 \,\mathrm{mol}\,\mathrm{dm}^{-3}\,\mathrm{Ba}(\mathrm{OH})_2(\mathrm{aq})$ .

 $OH^{-}(aq) = 0.200 \,\text{mol dm}^{-3}$ 

$$[H^{+}(aq)] = \frac{1 \times 10^{-14}}{0.200} = 5 \times 10^{-14} \,\text{mol dm}^{-3}$$

$$pH = -log_{10}(5.00 \times 10^{-14}) = 13.3$$

#### Experiments to distinguish between strong and weak acids and bases

#### 1. pH measurement

Because a strong acid produces a higher concentration of hydrogen ions in solution than a weak acid with the same concentration, the pH of a strong acid is lower than that of a weak acid. Similarly, a strong base has a higher pH in solution than a weak base with the same concentration

0.100 mol dm<sup>-3</sup> HCl(aq) 0.1 = Hq

0.100 moldm<sup>-3</sup> CH<sub>3</sub>COOH pH = 2.9

## 2. Conductivity measurement

Strong acids and strong bases in solution give much higher readings on a conductivity meter than equimolar (equal concentration) solutions of weak acids or bases, because they contain more ions in solution.

#### Concentration measurement

As the concentration of hydrogen ions is much greater, the rate of reaction of strong acids with metals, metal oxides, metal hydroxides, metal hydrogencarbonates, and metal carbonates is greater than that of weak acids with the same concentration.

#### **Acid** rain

#### Oxides of sulfur, SO

Sulfur dioxide occurs naturally from volcanoes. It is produced industrially from the combustion of sulfur-containing fossil fuels and the smelting of sulfide ores.

$$S(s) + O_2(g) \rightarrow SO_2(g)$$

In the presence of sunlight, sulfur dioxide is oxidized to sulfur trioxide.

$$SO_2(g) + \frac{1}{2}O_2(g) \rightarrow SO_3(g)$$

These oxides can react with water in the air to form sulfurous acid and sulfuric acid:

$$SO_2(g) + H_2O(I) \rightarrow H_2SO_3(aq)$$

sulfurous acid

$$SO_3(g) + H_2O(I) \rightarrow H_2SO_4(aq)$$

sulfuric acid

#### Oxides of nitrogen, NO

Nitrogen oxides occur naturally from electrical storms and bacterial action. Nitrogen monoxide, NO, is produced in the internal combustion engine and in jet engines.

$$N_2(g) + O_2(g) \rightarrow 2NO(g)$$

Oxidation to nitrogen dioxide occurs in the air.

$$2NO(g) + O_{g}(g) \rightarrow 2NO_{g}(g)$$

The nitrogen dioxide then reacts with water to form nitric acid and nitrous acid:

$$2NO_2(g) + H_2O(I) \rightarrow HNO_3(aq) + HNO_2(aq)$$
  
nitric acid nitrous acid

or is oxidized directly to nitric acid by oxygen in the presence of water:

$$4NO_{2}(g) + O_{2}(g) + 2H_{2}O(l) \rightarrow 4HNO_{3}(aq)$$

#### **Acid** rain

Pure rainwater is naturally acidic, with a pH of 5.65, due to the presence of dissolved carbon dioxide. Carbon dioxide itself is not responsible for acid rain since acid rain is defined as rain with a pH less than 5.6. It is the oxides of sulfur and nitrogen present in the atmosphere which are responsible for **acid deposition**—the process

by which acidic particles, gases, and precipitation leave the atmosphere. Wet deposition, due to the acidic oxides dissolving and reacting with water in the air, is known as "acid rain" and includes fog, snow, and dew as well as rain. Dry deposition includes acidic gases and particles.

#### Vegetation

Increased acidity in the soil leaches important nutrients, such as Ca<sup>2+</sup>, Mg<sup>2+</sup>, and K<sup>+</sup>. Reduced levels of Mg<sup>2+</sup> can cause a reduction in chlorophyll, lowering the ability of plants to photosynthesize. Many trees have been seriously affected by acid rain. Symptoms include stunted growth, thinning of tree tops, and yellowing and loss of leaves. The main cause is leaching of aluminium from rocks into the soil water. The Al<sup>3+</sup> ion damages the roots and prevents trees from taking up enough water and nutrients to survive.

#### Buildings

Stone that contains calcium carbonate, such as marble, is eroded by acid rain. Calcium carbonate reacts with sulfuric acid to form calcium sulfate, which is washed away by rainwater thus exposing more stone to corrosion. Salts can also form within the stone, causing the stone to crack and disintegrate.

$$CaCO_3(s) + H_2SO_4(aq) \rightarrow CaSO_4(aq) + CO_2(g) + H_2O(l)$$

#### Lakes and rivers

Increased levels of aluminium ions in water can kill fish. Aquatic life is also highly sensitive to pH. Below pH 6, numbers of sensitive fish, such as salmon and minnow, decline as do insect larvae and algae. Snails cannot survive a pH less than 5.2 and, below pH 5.0, many microscopic animal species disappear. Below pH 4.0 lakes are effectively dead. Nitrates present in acid rain can also lead to eutrophication.

#### **Human health**

The acids formed when  $NO_x$  and  $SO_x$  dissolve in water irritate the mucous membranes and increase the risk of respiratory illnesses, such as asthma, bronchitis, and emphysema. In acidic water, there is more probability of poisonous ions, such as  $Cu^{2+}$  and  $Pb^{2+}$ , leaching from pipes and high levels of aluminium in water may be linked to Alzheimer's disease.

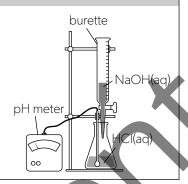
#### Methods to lower or counteract the effects of acid rain

- Reduce amounts of NO<sub>x</sub> and SO<sub>x</sub> formed, e.g. by improved engine design, using catalytic converters, and removing sulfur before, during, and after combustion of sulfur-containing fuels.
- 2. Switch to alternative methods of energy production (e.g. wind and solar power) and reduce the amount of fuel burned, e.g. by reducing private transport,
- increasing public transport, and designing more efficient power stations.
- 3. Liming of lakes: adding calcium oxide or calcium hydroxide (lime) neutralizes the acidity, increases the amount of calcium ions and precipitates aluminium from solution. This has been shown to be effective in many, but not all, lakes where it has been tried.

### pH curves

#### Data from strong acid-strong base titrations

The method of titration to determine an unknown concentration of either an acid or a base by reacting it with a known concentration of an alkali or an acid has already been discussed on page 20. Normally, for an acid-base titration, an indicator is added. Indicators change colour within certain pH ranges. For example, methyl orange changes colour (from red to yellow) between pH 4.4 and 6.2 whereas phenolphthalein changes colour (from colourless to pink) between pH 8.3 and 10.0. The difference between pH 4.4 and pH 10.0 is large, so indicators are not very accurate for determining the equivalence point. The titration can also be carried out using a pH meter and the change in pH can be monitored. By recording the pH after every cm³ has been added, enough data can be collected to plot a graph.



#### Calculating theoretical pH change

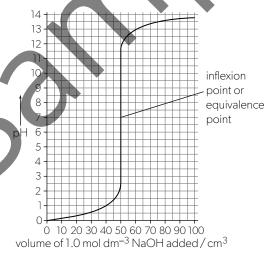
The pH change can also be determined theoretically. Consider starting with  $50 \, \text{cm}^3$  of  $1.00 \, \text{mol dm}^{-3}$  hydrochloric acid solution, HCl(aq). Since  $[H^+(aq)] = 1.00 \, \text{mol dm}^{-3}$  the initial pH will be 0. After  $49.0 \, \text{cm}^3$  of  $1.00 \, \text{mol dm}^{-3}$  sodium hydroxide solution, NaOH(aq), has been added there will be  $1.0 \, \text{cm}^3$  of the original  $1.0 \, \text{mol dm}^{-3}$  hydrochloric acid solution remaining

that has not been neutralized. 1.0 cm $^3$  of 1.00 mol dm $^{-3}$  hydrochloric acid contains  $1.0 \times 10^{-3}$  mol of H $^*$ (aq) ions. This is in  $99 \, \text{cm}^3$  of solution (which is almost  $100 \, \text{cm}^3$ ) so  $[H^+(aq)] = 1.00 \times 10^{-2}$  mol dm $^{-3}$  and the pH is 2. Similar calculations can be made for when further  $0.10 \, \text{cm}^3$  amounts of  $1.00 \, \text{mol dm}^{-3}$  sodium hydroxide solution are added, to give the following table.

Volume of NaOH added / cm³	49.0	49.1	49.2	49.3	49.4	49.5	49.6	49.7	49.8	49.9	50.0
рН	2.00	2.05	2.10	2.15	2.22	2.30	2.40	2.52	2.70	3.00	7.00
Volume of NaOH added / cm³	50.0	50.1	50.2	50.3	50.4	50.5	50.6	50.7	50.8	50.9	51.0
рН	7.00	11.00	11.30	11.48	11.60	11.70	11.78	11.85	11.90	11.95	12.00

#### Interpreting pH curves

By plotting the data calculated above, or data collected experimentally during a titration, you can interpret the data and determine several important points. This is called a pH curve. The general shape of a pH curve for the reaction between a monoprotic strong acid and a monoprotic strong base is always like the example below:

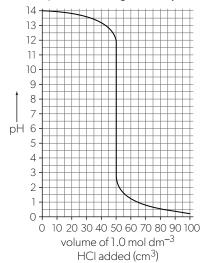


The area on the graph where the pH changes most rapidly and the line is almost vertical is called the inflexion point or equivalence point. It represents the

stoichiometric point when equal amounts of acid and base have reacted. The line is almost vertical as the change occurs within a very small change in volume of added NaOH(aq). Almost all acid-base indicators change colour within this region. This means that for a strong acid-strong base titration it does not really matter which indicator is used. The point where the indicator changes colour is known as the end point and is almost identical to the equivalence point. Reading vertically

downwards from the equivalence point gives the volume of acid or base needed to reach neutralization.

Similarly, a graph can be plotted when HCl is added to NaOH. The pH is initially around 14 and falls to around 0 after neutralization.



## AHL: Calculations involving pH, pOH and p $K_{_{\scriptscriptstyle{W}}}$

#### The ionic product of water

Pure water is very slightly ionized:

$$H_2O(I) \longleftrightarrow H^+(aq) + OH^-(aq)$$

$$\Delta H^{\Theta} = +57.3 \, \text{k/mol}^{-1}$$

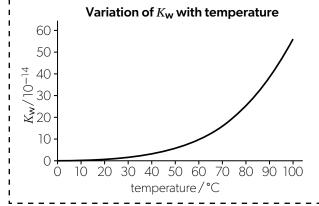
$$K_c = \frac{[H^+(aq) \times [OH^-(aq)]}{[H_2O(I)]}$$

Since the equilibrium lies far to the left, the concentration of water can be regarded as constant so:

$$K_{W} = [H^{+}(aq)] \times [OH^{-}(aq)] = 1.00 \times 10^{-14} \text{ at } 298 \text{ K}$$

where  $K_{w}$  is known as the ionic product of water.

The dissociation of water into its ions is an endothermic process, so the value of  $K_{\rm w}$  will increase as the temperature is increased.



For pure water:

 $[H^{+}(aq)] = [OH^{-}(aq)] = 1.00 \times 10^{-7} \text{ mol dm}^{-3} \text{ at } 298 \text{ K}$ 

From the graph:  $K = 1.00 \times 10^{-13}$  at 334 K (61 °C)

At this temperature:

 $[H^{+}(aq)] = \sqrt{1.00 \times 10^{-13}} = 3.16 \times 10^{-7} \,\text{mol dm}^{-3}$ 

#### pH, pOH and p $K_{\omega}$ for strong acids and bases

As stated earlier in this chapter, the pH of a solution depends only upon the hydrogen ion concentration and is independent of the volume of the solution.

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

i.e. 
$$[H^{+}(aq)] = 10^{-pH}$$

For strong monoprotic acids, the hydrogen ion concentration is equal to the concentration of the acid. For strong diprotic acids, the hydrogen ion concentration is twice the value of the acid, concentration.

The use of the logarithmic scale can be extended to other values, e.g. pOH and p $K_{\rm w}$ .

$$\mathrm{pOH} = -\mathrm{log_{10}}[\mathrm{OH}(\mathrm{aq})] \text{ and } \mathrm{p}K_{\mathrm{w}} = -\mathrm{log_{10}}K_{\mathrm{w}}$$

i.e. 
$$[OH^{-}(aq)] = 10^{-pOH}$$

Taking logarithms to base ten, the expression for the ionic product of water,  $K_{\rm w} = [{\rm H^+(aq)}] \times [{\rm OH^-(aq)}]$  becomes:

$$\log_{10} K_{\rm w} = \log_{10} [H^{+}(aq)] + \log_{10} [OH^{-}(aq)]$$

This can also be written as:

$$-\log_{10}K_{w} = -\log_{10}[H^{+}(aq)] - \log_{10}[OH^{-}(aq)]$$

$$-\log_{10}[H^{+}(aq)] = pH \text{ and } -\log_{10}[OH^{-}(aq)] = pOH$$

This leads to the useful expression:

$$pK_w = pH + pOH$$

At 25 °C, 
$$K_{W} = 10^{-14}$$
 and pH + pOH = 14

This expression gives another way of calculating the pH of a strong base since the pOH can be determined directly from the hydroxide ion concentration and then be subtracted from 14.

#### **Worked example**

Determine the pH of  $4.00 \times 10^{-3}$  mol dm<sup>-3</sup> Ba(OH)<sub>2</sub>.

$$[OH^{-}(aq)] = 2 \times 4.00 \times 10^{-3} = 8.00 \times 10^{-3} \text{ mol dm}^{-3}$$

$$pOH = -log_{10}(8.00 \times 10^{-3}) = 2.10$$

$$pH = 14 - 2.10 = 11.9$$

#### Calculations with weak acids and bases AHL ¦

#### Weak acids

The dissociation of a weak acid, HA, in water can be written as  $HA(aq) \rightleftharpoons H^{+}(aq) + A^{-}(aq)$ .

The equilibrium expression for this reaction is:  $K_a = \frac{[H^+] \times [A^-]}{[HA]}$  where  $K_a$  is known as the acid dissociation constant.

For example, to calculate the pH of 0.100 mol dm<sup>-3</sup> CH<sub>3</sub>COOH given that  $K_3 = 1.8 \times 10^{-5}$  mol dm<sup>-3</sup> at 298 K:

	$CH_3COOH(aq) \longleftrightarrow CH_3COO^-(aq) + H^+(aq)$			
Initial concentration / mol dm <sup>-3</sup>	0.100	-	_	
Equilibrium concentration / mol dm <sup>-3</sup>	(0.100 - x)	X	Х	

$$K_{\rm a} = \frac{[{\rm CH_3COO^-}] \times [{\rm H^+}]}{[{\rm CH_3COOH}]} = \frac{x^2}{(0.10-x)} = 1.8 \times 10^{-5} \, {\rm mol \, dm^{-3}} \\ \Rightarrow x^2 + (1.8 \times 10^{-5} x) - 1.8 \times 10^{-6} = 0$$
 Solving the quadratic equation gives  $x = 1.33 \times 10^{-3} \, {\rm mol \, dm^{-3}}$  pH =  $-\log_{10}(1.33 \times 10^{-3}) = 2.88$ 

$$pH = -log_{10}(1.33 \times 10^{-3}) = 2.88$$

If the acids are quite weak, the equilibrium concentration of the acid can be assumed to be the same as its initial concentration. Provided this assumption is stated, it is usual to simplify the expression in calculations to avoid a quadratic equation. In the above example:

$$K_{\rm a} = \frac{\rm [CH_3COO^-]\times[H^+]}{\rm [CH_3COOH]} = \frac{\rm [H^+]^2}{0.10} = 1.8\times10^{-5}\,\rm mol\,dm^{-3} \\ \Rightarrow \rm [H^+] = \sqrt{1.8\times10^{-6}} = 1.34\times10^{-3}\,\rm mol\,dm^{-3} \\ pH = 2.87$$

#### **Worked examples**

1. The pH of a 0.020 mol dm<sup>-3</sup> solution of a weak acid is 3.9. Find the  $K_3$  of the acid.

$$K_{\rm a} = \frac{[{\rm H}^+]^2}{(0.020 - [{\rm H}^+])} \approx \frac{10^{-3.9} \times 10^{-3.9}}{0.020}$$
$$= 7.92 \times 10^{-7} \,\text{mol dm}^{-3}$$

2. An acid whose  $K_3$  is  $4.1 \times 10^{-6}$  moldm<sup>-3</sup> has a pH of 4.5. Find the concentration of the acid.

[HA] = 
$$\frac{[H^+]^2}{K_a}$$
 =  $\frac{10^{-4.5} \times 10^{-4.5}}{4.1 \times 10^{-6}}$  = 2.44 × 10<sup>-4</sup> mol dm<sup>-3</sup>

Note that the weaker the weak acid the smaller the value of  $K_a$  and the larger the value of  $pK_a$ . Thus ethanoic acid (p $K_{\rm a}$  = 4.76) is a weaker acid than methanoic acid (p $K_{\rm a}$  = 3.75). The same is true with  $K_{\rm b}$ for weak bases

#### Weak bases

The reaction of a weak base can be written:

$$B(aq) + H_2O(I) \longleftrightarrow BH^+(aq) + OH^-(aq)$$

Since the concentration of water is constant:

$$K_{\rm b} = \frac{[{\rm BH^+}] \times [{\rm OH^-}]}{[{\rm B}]}$$
 where  $K_{\rm b}$  is the base dissociation

If one considers the reverse reaction of BH<sup>+</sup> acting as

an acid to give B and H<sup>+</sup>, then 
$$K_a = \frac{[B] \times [H^+]}{[BH^+]}$$

So 
$$K_a \times K_b = \frac{[B] \times [H^+]}{[BH^+]} \times \frac{[BH^+] \times [OH^-]}{[B]}$$
  
=  $[H^+] \times [OH^-] = K_w$ 

$$\begin{aligned} & pK_{\rm a} = -{\rm log_{10}}K_{\rm a}; \ pK_{\rm b} = -{\rm log_{10}}K_{\rm b}; \ {\rm and} \\ & pK_{\rm w} = -{\rm log_{10}}K_{\rm w} = 14, \ {\rm so} \ pK_{\rm a} + pK_{\rm b} = 14 \end{aligned}$$

#### Worked examples

1. The  $K_{\rm L}$  value for ammonia is  $1.8 \times 10^{-5}$  mol dm<sup>-3</sup>. Find the pH of a  $1.00 \times 10^{-2}$  mol dm<sup>-3</sup> solution.

Since 
$$[NH_4^+] = [OH^-]$$
 then:

$$K_{\rm b} = \frac{[{\rm OH}^-]^2}{[{\rm NH}_3]} \approx \frac{[{\rm OH}^-]^2}{1.00 \times 10^{-2}} = 1.8 \times 10^{-5}$$

$$[OH^{-}] = \sqrt{1.8 \times 10^{-7}} = 4.24 \times 10^{-4} \,\text{mol dm}^{-3}$$

$$\Rightarrow$$
 pOH =  $-\log_{10}(4.24 \times 10^{-4}) = 3.37$ 

$$\Rightarrow$$
 pH = 14 - 3.37 = 10.6

2. The pH of a  $3.00 \times 10^{-2}$  mol dm<sup>-3</sup> solution of weak base is 10.0. Calculate the  $pK_b$  value of the base.

$$pH = 10.0 \text{ so } pOH = 4.0$$

$$K_{\rm b} = \frac{10^{-4} \times 10^{-4}}{3.00 \times 10^{-2}} = 3.33 \times 10^{-7} \,\mathrm{mol}\,\mathrm{dm}^{-3}$$

$$\Rightarrow$$
 p $K_{\rm b}$  = 6.48

3. The value for the  $pK_3$  of methylamine (aminomethane) is 10.66. Calculate the concentration of an aqueous solution of methylamine with a pH of 10.8.

$$pK_b = 14 - 10.66 = 3.34$$
;  $pOH = 14 - 10.8 = 3.2$ 

$$[CH_3NH_2] = \frac{[OH^-]^2}{K_b} = \frac{10^{-3.2} \times 10^{-3.2}}{10^{-3.34}}$$

$$= 8.71 \times 10^{-4} \, \text{mol dm}^{-3}$$

## AHL | Salt hydrolysis, indicators and pH curves

#### Salt hydrolysis

Sodium chloride is neutral in aqueous solution. It is the salt of a strong acid and a strong base so its ions remain completely dissociated in solution.

Salts made from a weak acid and a strong base, such as sodium ethanoate, are alkaline in solution. This is because the ethanoate ions combine with hydrogen ions from water to form mainly undissociated ethanoic acid, leaving excess hydroxide ions in solution.

$$NaCH_{3}COO(aq) \longrightarrow Na^{+}(aq) + CH_{3}COO^{-}(aq) + H_{2}O(l) \longrightarrow OH^{-}(aq) + H^{+}(aq)$$
strong base so completely dissociated CH<sub>3</sub>COOH(aq)

Similarly, salts derived from a strong acid and a weak base will be acidic in solution.

$$\begin{array}{c} \mathrm{NH_4Cl(aq)} & \longrightarrow \mathrm{NH_4}^+(\mathrm{aq}) + \mathrm{Cl}^-(\mathrm{aq}) \\ & + \\ \mathrm{H_2O(l)} & \longrightarrow \mathrm{OH}^-(\mathrm{aq}) + \ \mathrm{H}^+(\mathrm{aq}) \end{array} \qquad \begin{array}{c} \mathrm{strong\ acid} \\ \mathrm{so\ completely} \\ \mathrm{dissociated} \\ \end{array}$$

#### **Indicators**

An indicator is a weak acid (or weak base) in which the dissociated form is a different colour to the undissociated form.

$$K_{\text{ind}} = [H^{+}] \times \frac{[\text{lnd}^{-}]}{[\text{Hlnd}]}$$

Assuming the colour changes when [Ind ]  $\approx$  [HInd] then the end point of the indicator will be when [H<sup>+</sup>]  $\approx K_{\rm ind}$ , i.e. when pH  $\approx$  p $K_{\rm ind}$ . Different indicators have different  $K_{\rm ind}$  values and so change colour within different pH ranges.

Indicator	$pK_{ind}$	pH range	Use
methyl orange	3.7	3.1–4.4	titrations with strong acids
phenolphthalein	9.6	8.3–10.0	titrations with strong bases

An appropriate indicator for a titration has an end point range that coincides with the pH at the equivalence point. Universal indicator is a mixture of many indicators with a wide pH range of colour change.

## pH curves for titrations involving weak acids and bases

Consider titrating 50.0 cm<sup>3</sup> of 1.00 mol dm<sup>-3</sup> CH<sub>3</sub>COOH with 1.00 mol dm<sup>-3</sup> NaOH. CH<sub>3</sub>COOH(aq) + NaOH(aq)  $\rightarrow$  NaCH<sub>3</sub>COO(aq) + H<sub>2</sub>O(I)

 $K_{\rm a}=1.8\times 10^{-5}$ . Making the usual assumptions, the initial [H<sup>+</sup>] =  $\sqrt{K_{\rm a}\times [{\rm CH_3COOH}]}$  and pH = 2.37. This means that the *y*-intercept will be higher than for a strong acid.

When  $49.0\,\mathrm{cm^3}$  of the  $1.00\,\mathrm{mol\,dm^3}$  NaOH has been added,  $[\mathrm{CH_3COO^-}] \approx 0.05\,\mathrm{mol\,dm^-^3}$  and  $[\mathrm{CH_3COOH}] \approx 1.0 \times 10^{-2}\,\mathrm{mol\,dm^{-3}}$ .

$$[H^{+}] = \frac{K_{3} \times [CH_{3}COOH]}{[CH_{3}COO]} = \frac{1.8 \times 10^{-5} \times 1 \times 10^{-3}}{0.05}$$

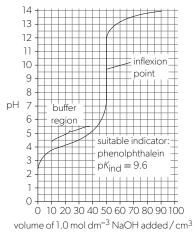
 $= 3.6 \times 10^{-7} \, \text{mol dm}^{-3} \, \text{and pH} = 6.44$ 

The pH changes more slowly in this region with a weak acid, as a buffer solution forms, so it is sometimes called the buffer region. See page 114.

When  $25 \text{ cm}^3$  of alkali have been added, half of the acid has been turned into salt, so  $pK_3 = pH$ .

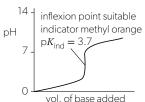
After the equivalence point, the graph will follow the same pattern as the strong acid-strong base curve as more sodium hydroxide is simply being added to the solution.

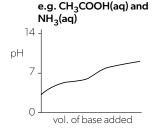
Similar arguments can be used to explain the shapes of pH curves for strong acid-weak base, and weak acid-weak base titrations. Titrations involving weak acids with weak bases should not be



used in analytical chemistry since there is no sharp inflexion point.

# Strong acid-weak base e.g. HCl(aq) and NH<sub>3</sub>(aq) 4 - inflexion point suitable indicator methyl grange





Weak acid-weak base

### **AHL** Buffer solutions

A buffer solution resists changes in pH when small amounts of acid or alkali are added to it.

#### **Acidic buffers**

An acidic buffer solution can be made by mixing a weak acid together with the salt of that acid and a strong base. An example is a solution of ethanoic acid and sodium ethanoate. The weak acid is only slightly dissociated in solution, but the salt is fully dissociated into its ions, so the concentration of ethanoate ions is high.

$$NaCH_3COO(aq) \rightarrow Na^+(aq) + CH_3COO^-(aq)$$
  
 $CH_3COOH(aq) \rightleftharpoons CH_3COO^-(aq) + H^+(aq)$ 

If some acid is added, the extra H<sup>+</sup> ions coming from the acid are removed as they combine with ethanoate ions to form undissociated ethanoic acid.

The concentration of H<sup>+</sup> ions remains unaltered.

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

If some alkali is added, the hydroxide ions from the alkali are removed by their reaction with the undissociated acid to form water, so again the H<sup>+</sup> ion concentration stays constant.

$$CH_3COOH(aq) + OH^-(aq) \rightarrow CH_3COO^-(aq) + H_2O(I)$$

In practice, acidic buffers are often made by taking a solution of a strong base and adding excess weak acid to it, so that the solution contains the salt and the unreacted weak acid.

$$\label{eq:NaOH(aq) + CH_3COOH(aq) - NaCH_3COO(aq) + H_2O(I) + CH_3COOH(aq) - Salt} \\ \text{limiting reagent} \\ \text{salt} \\ \text{excess weak acid}$$

buffer solution

#### Alkali buffers

An alkali buffer with a fixed pH greater than 7 can be made from a weak base together with the salt of that base with a strong acid. An example is ammonia with ammonium chloride.

$$\begin{aligned} \text{NH}_4\text{Cl(aq)} &\rightarrow \text{NH}_4^+\text{(aq)} + \text{Cl}^-\text{(aq)} \\ \text{NH}_3\text{(aq)} &+ \text{H}_2\text{O(I)} \rightleftharpoons \text{NH}_4^+\text{(aq)} + \text{OH}^-\text{(aq)} \end{aligned}$$

If  $H^+$  ions are added, they will combine with  $OH^-$  ions to form water and more of the ammonia will dissociate to replace them. If more  $OH^-$  ions are added, they will combine with ammonium ions to form undissociated ammonia. In both cases, the hydroxide ion concentration and the hydrogen ion concentration remain constant.

#### **Buffer calculations**

The equilibrium expression for weak acids also applies to acidic buffer solutions, e.g. ethanoic acid/sodium ethanoate solution.

$$K_{a} = \frac{[H^{+}] \times [CH_{3}COO^{-}]}{[CH_{3}COOH]}$$

The essential difference now is that the concentrations of the two ions from the acid will not be equal.

Since the sodium ethanoate is completely dissociated, the concentration of the ethanoate ions in solution will be the same as the concentration of the sodium ethanoate, only a very little will come from the acid.

If logarithms are taken and the equation is rearranged, then:

$$pH = pK_a + log_{10} \frac{[CH_3COO^-]}{[CH_3COOH]}$$

So, the pH of the buffer does not change on dilution, as the concentration of the ethanoate ions and the undissociated acid will be affected equally.

Also, the buffer will be most efficient when  $[CH_3COO^-]$  =  $[CH_3COOH]$ . At this point, which equates to the half-equivalence point when ethanoic acid is titrated with sodium hydroxide, the pH of the solution will equal the  $pK_3$  value of the acid. This is known as the buffer region.

#### Worked example 1

Calculate the pH of a buffer containing  $0.200 \, \text{mol}$  of sodium ethanoate in  $500 \, \text{cm}^3$  of  $0.100 \, \text{mol} \, \text{dm}^{-3}$  ethanoic acid, given that  $K_a$  for ethanoic acid =  $1.8 \times 10^{-5} \, \text{mol} \, \text{dm}^{-3}$ .

$$[CH_3COO^-] = 0.400 \text{ mol dm}^{-3};$$
  
 $[CH_3COOH] = 0.100 \text{ mol dm}^{-3}$ 

$$K_{\rm a} \approx \frac{[{\rm H}^+] \times 0.400}{0.100} = 1.8 \times 10^{-5} \,{\rm mol\,dm^{-3}}$$

$$[H^+] = 4.5 \times 10^{-6} \,\text{mol dm}^{-3} \,\text{so, pH} = 5.35$$

#### Worked example 2

Calculate what mass of sodium propanoate must be dissolved in  $1.00 \, \text{dm}^3$  of  $1.00 \, \text{mol dm}^{-3}$  propanoic acid (p $K_a = 4.87$ ) to give a buffer solution with a pH of 4.5.

$$[C_2H_5COO^-] = \frac{K_a \times [C_2H_5COOH]}{[H^+]} = \frac{10^{-4.87} \times 1.00}{10^{-4.5}}$$

 $= 0.427 \, \text{mol dm}^{-3}$ 

Mass of NaC<sub>2</sub>H<sub>5</sub>COO required =  $0.427 \times 96.07 = 41.0g$ 

## Multiple-choice questions—Proton transfer reactions: acid-base behaviour

- 1. Which statement about hydrochloric acid is false?
  - A. It can react with copper to give hydrogen.
  - **B.** It can react with sodium carbonate to give carbon dioxide.
  - **C.** It can react with ammonia to give ammonium chloride.
  - D. It can react with copper oxide to give water.
- 2. 1.00 cm<sup>3</sup> of a solution has a pH of 3. What is the pH of 100 cm<sup>3</sup> of the same solution?
  - **A**. 1
- **B.** 3
- **C**. 5
- **D.** Impossible to calculate from the data given.
- 3. Which statement(s) is/are true about separate solutions of a strong acid and a weak acid both with the same concentration?
  - I. They both have the same pH.
  - II. They both have the same electrical conductivity.
  - A. I and II
- C. II only
- B. I only
- D. Neither I nor II
- 4. Identify the correct statement about 25 cm<sup>3</sup> of a solution of 0.1 mol dm<sup>-3</sup> ethanoic acid, CH<sub>2</sub>COOH.
  - A. It will contain more hydrogen ions than 25 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> hydrochloric acid.
  - **B.** It will have a pH greater than 7.
  - C. It will react exactly with 25 cm<sup>3</sup> of 0.1 mol dm<sup>-3</sup> sodium hydroxide.
  - **D.** It is completely dissociated into ethanoate and hydrogen ions in solution.
- 5. What is the pH of  $1.0 \times 10^{-4}$  mol dm<sup>-3</sup> sulfuric acid,  $H_2SO_4(aq)$ ?
  - **A.** -4
- **C**. 4
- B. between 3 and 4
- D. between 4 and 5
- 6. NH<sub>3</sub>(aq), HCl(aq), NaOH(aq), CH<sub>3</sub>COOH(aq)

When 1.0 mol dm<sup>-3</sup> solutions of the substances above are arranged in order of decreasing pH, what is the order?

- A. NaOH(aq), NH<sub>3</sub>(aq), CH<sub>3</sub>COOH(aq), HCI(aq)
- **B.** NH<sub>3</sub>(aq), NaOH(aq), HCl(aq), CH<sub>3</sub>COOH(aq)
- C. CH<sub>2</sub>COOH(aq), HCl(aq), NaOH(aq), NH<sub>2</sub>(aq)
- D. HCl(aq), CH<sub>3</sub>COOH(aq), NH<sub>3</sub>(aq), NaOH(aq)
- 7. Which statement is true about two solutions, one with a pH of 3 and the other with a pH of 6?
  - **A.** The solution with a pH of 3 is twice as acidic as the solution with a pH of 6.
  - **B.** The solution with a pH of 6 is twice as acidic as the solution with a pH of 3.
  - **C.** The hydrogen ion concentration in the solution with a pH of 6 is one thousand times greater than that in the solution with a pH of 3.

- **D.** The hydrogen ion concentration in the solution with a pH of 3 is one thousand times greater than that in the solution with a pH of 6.
- **8.** Which of the following is **not** a conjugate acid-base pair?
  - A.  $HNO_3/NO_3^-$
- C. NH<sub>3</sub>/NH<sub>2</sub>
- B. H<sub>2</sub>SO<sub>4</sub>/HSO<sub>4</sub>-
- **D.** H<sub>2</sub>O<sup>+</sup>/OH<sup>-</sup>
- 9. Which gas cannot lead to acid rain?
  - A. CO<sub>2</sub>

C.NO

- **B.** SO<sub>2</sub>
- D. NO.
- 10. Which statement is true during the titration of a known volume of a strong acid with a strong base?
  - A. There is a steady increase in pH.
  - **B.** There is a sharp increase in pH around the end point.
  - C. There is a steady decrease in pH.
  - **D.** There is a sharp decrease in pH around the end point.
- 11. What is the pH of 0.001 mol dm<sup>-3</sup> potassium hydroxide solution, KOH(aq)?
  - **A.** 1
- **B**. 3
- **C**. 11
- **D.** 13
- 12. Which statement is correct?
  - A. A weak acid is highly dissociated and has a strong conjugate base.
  - **B.** A weak acid is slightly dissociated and has a weak conjugate base.
  - **C.** A weak base is a proton donor and has a strong conjugate acid.
  - **D.** A weak base is a proton acceptor and has a strong conjugate acid.
- **13.** Which will react with hydrochloric acid to give water as one of the products?
  - I. magnesium oxide
  - II. sodium carbonate
  - III. potassium hydrogencarbonate
  - A. I and II only
- C. II and III only
- B. I and III only
- D. I, II, and III
- **14.** Which solution will have the highest electroconductivity?
  - **A.**  $1.00 \,\text{mol dm}^{-3} \,\text{H}_2 \,\text{SO}_4 \,\text{(aq)}$
  - **B.** 1.00 mol dm<sup>-3</sup> NaOH(aq)
  - C. 2.00 mol dm<sup>-3</sup> CH<sub>3</sub>COOH(aq)
  - **D.** 2.00 mol dm<sup>-3</sup> NH<sub>3</sub>(aq)
- **15.** 5.0 cm<sup>3</sup> of aqueous solution of sodium hydroxide with a pH of 11 is mixed with 445.0 cm<sup>3</sup> of distilled water. What is the pH of the resulting solution?
  - **A.** 7

**C**.9

**B.** 8

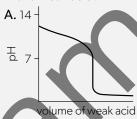
**D.** 10

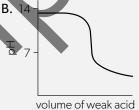
#### AHL

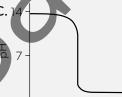
16. Three acids, HA, HB, and HC, have the following

 $K_a(HA) = 1 \times 10^{-5}$   $K_a(HB) = 2 \times 10^{-5}$   $K_a(HC) = 1 \times 10^{-6}$ What is the correct order of increasing acid strength (weakest first)?

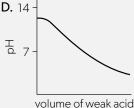
- A. HA, HB, HC
- C. HC, HA, HB
- B. HC, HB, HA
- D. HB. HA. HC
- 17. Which of the following reagents could not be added together to make a buffer solution?
  - A. NaOH(aq) and CH<sub>3</sub>COOH(aq)
  - **B.** NaCH<sub>3</sub>COO(aq) and CH<sub>3</sub>COOH(aq)
  - C. NaOH(aq) and NaCH<sub>2</sub>COO(aq)
  - D. NH<sub>4</sub>Cl(aq) and NH<sub>3</sub>(aq)
- 18. Which statement is true when 1.0 cm<sup>3</sup> of a weak acid solution is added to 100 cm<sup>3</sup> of a buffer solution?
  - A. The volume of the resulting mixture is 100 cm<sup>3</sup>.
  - B. There is almost no change in the pH of the solution.
  - C. The pH of the solution increases noticeably.
  - D. The pH of the solution decreases noticeably.
- 19. Which salt forms an acidic solution in water?
  - A. CH<sub>3</sub>COONa
- C. KHCO.
- B. Na<sub>2</sub>CO<sub>2</sub>
- D. NH<sub>4</sub>NO<sub>2</sub>
- 20. An indicator changes colour in the pH range 8.3–10.0. This indicator should be used when titrating a known volume of:
  - A. a strong acid with a weak base
  - B. a weak acid with a weak base
  - C. a weak base with a strong acid
  - D. a weak acid with a strong base
- 21. Which curve represents the titration of a strong base with a weak acid?







volume of weak acid

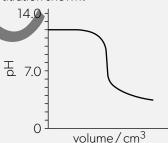


- 22. What is the pH of the resulting solution when 50.0 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> NaOH is added to 100 cm<sup>3</sup> of 1.0 mol dm<sup>-3</sup> ethanoic acid?  $(pK_3 \text{ of CH}_3 \text{COOH} = 4.76)$ 
  - **A.** 4.76
- C. between 2 and 3
- **B.** between 5 and 7
- D > 7

- 23. Which combination of reactants is likely to have a pH in the region of 8.5 at the equivalence point?
  - A. HCl(ag) + NaOH(ag)
  - B. CH<sub>3</sub>COOH(aq) + NaOH(aq)
  - C.  $CH_3COOH(aq) + NH_3(aq)$
  - **D.**  $HCl(aq) + NH_{3}(aq)$
- 24. What is the order of increasing acid strength?

Acid	$K_{a}$	$pK_{a}$
C <sub>6</sub> H <sub>5</sub> OH	1.02 × 10 <sup>-10</sup>	
C <sub>2</sub> H <sub>5</sub> OH		15.50
CH <sub>2</sub> CICOOH	1.35 × 10 <sup>-3</sup>	
C <sub>6</sub> H <sub>5</sub> COOH		4.20

- A. CH\_CICOOH < C\_H\_COOH < C2H5OH
- B.  $C_2H_2OH < C_2H_2OH < C_3H_3OH < C_3H_3$ CH<sub>2</sub>CICOOI
- **C.** C<sub>2</sub>H<sub>2</sub>COOH < CH<sub>2</sub>CICOOH < C<sub>2</sub>H<sub>2</sub>OH <  $C_2H_5OH$
- D. C.H.OH < C.H COOH < CH\_CICOOH <  $C_cH_cOH$
- Which is the best indicator to use for the acid-base titration shown?



- **A.** methyl red (p $K_3 = 5.1$ )
- **B.** methyl orange (p $K_a = 3.7$ )
- **C.** phenolphthalein (p $K_3 = 9.6$ )
- **D.** bromophenol blue (p $K_2 = 4.2$ )
- **26.** The p $K_1$  values for ethylamine,  $C_2H_5NH_2$ , diethylamine, (C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>NH, and triethylamine,  $(C_2H_5)_3N$ , are 3.35, 3.16, and 3.25, respectively.

Which statements are correct?

- **I.** Diethylamine is the strongest of the three bases.
- II.  $(C_2H_5)_2NH_2^+ + H_2O \Longrightarrow (C_2H_5)_2NH + H_3O^+$  $pK_a = 10.84$
- III.  $C_2H_5NH_2 + H_2O \rightleftharpoons C_2H_5NH_2^+ + OH^ K_{\rm b} = 10^{-3.35}$
- A. I and II only
- C. II and III only
- B. I and III only
- D. I, II, and III

## Short-answer questions—Proton transfer reactions: acid-base behaviour

[1]

[2]

[2]

[1]

[4]

[2]

[1]

[2]

[2]

- 1. a) (i) Define a Brønsted–Lowry base.
  - (ii) Deduce the two acids and their conjugate bases in the following reaction:

 $H_2O(I) + HCI(aq) \rightleftharpoons H_3O^+(aq) + CI^-(aq)$ 

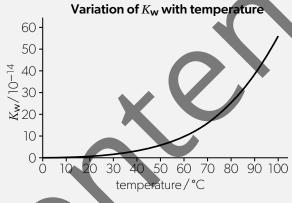
- **b)** Ethanoic acid, CH<sub>3</sub>COOH, is a weak acid.
  - (i) Explain the difference between a strong acid and a weak acid.
  - (ii) State the equation for the reaction of ethanoic acid with aqueous ammonia.
  - (iii) Compare and contrast the reactions of 1.00 mol dm<sup>-3</sup> hydrochloric acid and 1.00 mol dm<sup>-3</sup> ethanoic acid with excess magnesium metal.
- 2. a)  $1.00 \, \text{cm}^3$  of  $5.00 \times 10^{-3} \, \text{mol dm}^{-3}$  sulfuric acid,  $H_2 \, \text{SO}_4(\text{aq})$ , is added to an empty volumetric flask.
  - (i) Calculate the pH of the sulfuric acid solution.

    Assume that it is a strong diprotic acid. [2]
  - (ii) Determine the pH of the diluted solution if the total volume is made up to 100 cm<sup>3</sup> with distilled water. [2]
  - **b)** State the equation for the reaction of sulfuric acid with sodium hydroxide solution. [1]
  - c) The diluted solution in a)(ii) is used to titrate  $25.0 \,\mathrm{cm}^3$  of  $1.00 \times 10^{-4} \,\mathrm{mol}\,\mathrm{dm}^{-3}$  sodium hydroxide solution.
    - (i) Describe what will be observed when the end point is reached if phenolphthalein is used as the indicator for this titration.
    - (ii) Determine the volume of acid needed to reach the equivalence point of this titration [2]
- 3. When hydrochloric acid is added to a solution of sodium hydrogencarbonate, NaHCO<sub>3</sub>(aq), carbon dioxide is evolved.
  - a) State the equation for this reaction.
  - **b)** The hydrogencarbonate ion can act either as an acid or a base according to Brønsted–Lowry theory.
    - (i) Deduce the formula of the conjugate base if it is behaving as an acid.
    - (ii) Deduce the formula of the acid if it is behaving as a conjugate base. [1]
    - c) State the equations for the reaction of hydrochloric acid with:
    - (i) copper(II) oxide, CuO
    - (ii) sodium carbonate, Na<sub>2</sub>CO<sub>2</sub>.
- 4. a) Explain why rain water with a pH of 6 is not classified as "acid rain" even though its pH is less than 7?
  - b) State the equation for the formation of nitrogen(II) oxide, NO(g), in an internal combustion engine and describe, with equations, how it is converted into nitric acid in the atmosphere.

- c) Explain why marble statues become corroded by acid rain. [2]
- d) Outline why adding calcium hydroxide (lime) to lakes can reduce the effects of acid deposition. [2]

#### AHL -----

5. The graph below shows how the ionic product of water,  $K_{w'}$  varies with temperature.



- a) State the equation for the dissociation of water and deduce from the graph whether the reaction is exothermic or endothermic. [2]
- b) Determine the hydrogen ion concentration and the hydroxide ion concentration in pure water at 90 °C and hence deduce the pH of pure water at this temperature. [3]
- **6.** The acid dissociation constant,  $K_a$ , for lactic acid, CH(CH<sub>2</sub>)(OH)COOH, is  $1.38 \times 10^{-4}$  at 298 K.
  - a) Explain why lactic acid can exist in two different enantiomeric forms.
  - **b)** Calculate the pH of 0.100 mol dm<sup>-3</sup> lactic acid solution at 298 K.
  - c) Determine the mass of lactic acid that must be added together with 2.00 g of sodium hydroxide to make 500 cm<sup>3</sup> of a buffer solution at 298 K with a pH of 4.00.
- 7. a) (i) State the equation for the reaction between propanoic acid, C<sub>2</sub>H<sub>5</sub>COOH(aq), and water and deduce the equilibrium expression.
  - (ii) Calculate the pH of a  $2.00 \times 10^{-3}$  mol dm<sup>-3</sup> solution of propanoic acid (p $K_3 = 4.87$ ).
  - (iii) State any assumptions you have made in arriving at your answer to a)(ii).
  - **b)** 25.0 cm³ of 2.00 × 10<sup>-3</sup> mol dm<sup>-3</sup> sodium hydroxide solution, NaOH(aq), was added to 50 cm³ of 2.00 × 10<sup>-3</sup> mol dm<sup>-3</sup> propanoic acid.
    - (i) Identify all the chemical species present in the resulting solution.
    - (ii) Explain how the resulting solution can function as a buffer solution if a small amount of alkali is added. [2]

[3]

[4]

[2]

[3]

[2]

[2]